1. Barium sulfite; BaSO$_3$; [7787-39-5]
2. Water; H$_2$O; [7732-18-5]

**CRITICAL EVALUATION:**

Barium sulfite crystallizes from aqueous solutions in the form of the anhydrous salt, BaSO$_3$. The solubility of BaSO$_3$ in water has not yet been thoroughly investigated. Numerical data have been reported by Autenrieth et al. (1), Rogowicz (2), Parsons (3), Mareček et al. (4), Rodin et al. (5), and Cohen et al. (6), yet not under directly comparable experimental conditions. In 1898, Autenrieth et al. (1) reported the value of 0.022 g/kg H$_2$O (m(BaSO$_3$) = 1.0 x 10$^{-4}$ mol kg$^{-1}$) at 289 K. Rogowicz (2) gave the values 0.1974 and 0.0177 g/dm$^3$ (c(BaSO$_3$) = 9.080 x 10$^{-4}$ and 8.14 x 10$^{-5}$ mol dm$^{-3}$) at 293 and 353 K, respectively. Parsons (3) reported the solubility product of BaSO$_3$ ($K_{sp}$) as 9.5 x 10$^{-10}$ mol$^2$ dm$^{-6}$ at 298.2 K from a source which is not given nor could be traced. This value is equivalent to a solubility of 6.7 mg/dm$^3$ (c(BaSO$_3$) = 3.08 x 10$^{-5}$ mol dm$^{-3}$). In 1983 Rodin et al. (5) determined some values from 1.23 x 10$^{-3}$ g/dm$^3$ (c(BaSO$_3$) = 5.7 x 10$^{-6}$ mol dm$^{-3}$) at 293 K to 3.5 x 10$^{-3}$ g/dm$^3$ (1.61 x 10$^{-5}$ mol dm$^{-3}$) at 353 K. Cohen et al. (6) reported that the amount of dissolved barium sulfite in solutions containing 0.7 mol dm$^{-3}$ NaCl and rapidly precipitated BaSO$_3$ at 298 K decreases from 3.0 x 10$^{-4}$ to 2.3 x 10$^{-4}$ mol kg$^{-1}$ (molality) within 24 hr. The change in the solubility is attributed to a phase transition of the precipitated barium sulfite. In 1970, Mareček et al. (4) determined the activity solubility product from equilibrium studies of the reaction BaSO$_3$(s) + CO$_3$$^2-$ ⇌ BaCO$_3$(s) + SO$_3$$^2-$ as 4.9 x 10$^{-10}$ mol$^2$ kg$^{-2}$ (molality scale) at 298.2 K.

The value of Mareček et al. (4) appears to be the most reliable solubility value with respect to the activity of Ba$^{2+}$ (aq) and SO$_3$$^2-$ (aq) at the present time. The total amount of dissolved barium sulfite including the undissociated BaSO$_3$ seems to be greater than that of Mareček et al. (4) and is probably approximately the same as the values given by Autenrieth et al. (1) and Parsons (3). The scarce information on the temperature shift in the solubility of BaSO$_3$ is contradictory. A negative temperature coefficient of the solubility is reported by Rogowicz (2), a positive temperature coefficient by Rodin et al. (5).

**TENTATIVE VALUES**

The solubility of BaSO$_3$ in water at room temperature is approximately 5 x 10$^{-5}$ mol kg$^{-1}$ (0.01 g/kg H$_2$O). The solubility product, based on the activities, is 5 x 10$^{-10}$ mol$^2$ kg$^{-2}$ (molality scale). The temperature coefficient of solubility is positive.

The solubility of barium sulfite in water is affected by the presence of a third component. This becomes evident by fragmentary experimental data on the ternary systems BaSO$_3$-SO$_2$-H$_2$O (7,8), BaSO$_3$-sucrose-H$_2$O (2,9), and BaSO$_3$-ethanol-H$_2$O (10). The solubility of BaSO$_3$ increases by about 10$^3$ with increasing SO$_2$ content (7,8) and decreases with increasing sucrose (2,9) and ethanol (10) content. In acids BaSO$_3$ is readily dissolved, but undergoes decomposition.
COMPONENTS:
1. Barium sulfite; BaSO₃; [7787-39-5]
2. Water; H₂O; [7732-18-5]

EVALUATOR:
H.D. Lutz,
Dept. of Chemistry,
University of Siegen,
FR Germany.
August 1983.

CRITICAL EVALUATION: (continued)

REFERENCES
## COMPONENTS:
1. Barium sulfite; BaSO₃; [7787-39-5]
2. Water; H₂O; [7732-18-5]

## ORIGINAL MEASUREMENTS:
Autenrieth, W.; Windaus, A.
*Z. Anal. Chem.* 1898, 37, 290-300.

## VARIABLES:
One temperature: 289 K

## PREPARED BY:
H.D. Lutz

## EXPERIMENTAL VALUES:
The solubility of barium sulfite in water at 16°C is
1 part of BaSO₃ per 46 000 parts of water.
This value is equal to (compiler)

\[ 2.2 \times 10^{-2} \text{ g BaSO₃/kg H₂O or } m(\text{BaSO₃}) = 1.0 \times 10^{-4} \text{ mol kg}^{-1}. \]

## AUXILIARY INFORMATION

### METHOD APPARATUS/PROCEDURE:
Saturation method. Equilibrium was established, with frequent shaking, after several days. The sulfite content of the saturated solution was determined iodometrically.

### SOURCE AND PURITY OF MATERIALS:
BaSO₃ was precipitated from a solution of barium chloride with Na₂SO₃ and washed carefully with distilled water.

### ESTIMATED ERROR:

### REFERENCES:
COMPONENTS:

1. Barium sulfite; BaSO₃; [7787-39-5]
2. Water; H₂O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Rodin, I.V.; Margulis, E.V.

VARIABLES:

Four temperatures: 293 - 363 K

EXPERIMENTAL VALUES:

The solubilities of barium sulfite in water at various temperatures are reported. The solubility products are defined as $K_{sp}(\text{BaSO}_3) = [\text{Ba}^{2+}]^2$.

<table>
<thead>
<tr>
<th>t/°C</th>
<th>Ba</th>
<th>BaSO₃</th>
<th>$10^{5c}$/mol dm⁻³</th>
<th>$10^{11}K_{sp}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>0.78</td>
<td>1.23</td>
<td>0.57</td>
<td>3.25</td>
</tr>
<tr>
<td>50</td>
<td>1.19</td>
<td>1.88</td>
<td>0.87</td>
<td>7.57</td>
</tr>
<tr>
<td>70</td>
<td>1.62</td>
<td>2.56</td>
<td>1.18</td>
<td>13.9</td>
</tr>
<tr>
<td>80</td>
<td>2.21</td>
<td>3.50</td>
<td>1.61</td>
<td>25.9</td>
</tr>
</tbody>
</table>

* Calculated by the compiler.

METHOD APPARATUS/PROCEDURE:

Saturation method. Equilibrium was established by stirring the saturated solution in thermostatically controlled glass tubes. Equilibrium was tested for analytically - 3 hr is reported to be sufficient. Barium was determined gravimetrically.

SOURCE AND PURITY OF MATERIALS:

Barium sulfite was precipitated from BaCl₂ solutions with Na₂SO₃.

ESTIMATED ERROR:

Temperature: ±0.5 K.

REFERENCES:
COMPONENTS:
1. Barium sulfite; BaSO₃; [7787-39-5]
2. Sucrose; C₆H₁₂O₆; [50-99-7]
3. Water; H₂O; [7732-18-5]

ORIGINAL MEASUREMENTS:
Rogowicz, J.

VARIABLES:
Two temperatures: 293 and 353 K

PREPARED BY:
H.D. Lutz

EXPERIMENTAL VALUES:

<table>
<thead>
<tr>
<th>Sucrose mass %</th>
<th>Composition of saturated solution</th>
<th>( g \text{ BaSO}_3/100 \text{ cm}^3 )</th>
<th>( 10^3 \text{c(BaSO}_3)/\text{mol dm}^{-3} \text{a} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td></td>
<td>20°C</td>
<td>80°C</td>
</tr>
<tr>
<td>0</td>
<td>0.01974</td>
<td>0.00177</td>
<td>0.9080</td>
</tr>
<tr>
<td>10</td>
<td>0.01040</td>
<td>0.00335</td>
<td>0.4784</td>
</tr>
<tr>
<td>20</td>
<td>0.00968</td>
<td>0.00289</td>
<td>0.4453</td>
</tr>
<tr>
<td>30</td>
<td>0.00782</td>
<td>0.00223</td>
<td>0.3597</td>
</tr>
<tr>
<td>40</td>
<td>0.00484</td>
<td>0.00158</td>
<td>0.2226</td>
</tr>
<tr>
<td>50</td>
<td>0.00298</td>
<td>0.00149</td>
<td>0.1371</td>
</tr>
<tr>
<td>66 (saturated soln.)</td>
<td>0.00223</td>
<td></td>
<td>0.1026</td>
</tr>
</tbody>
</table>

\( \text{a Calculated by the compiler.} \)

AUXILIARY INFORMATION

METHOD APPARATUS/PROCEDURE:
Saturation method. Sulfite was determined iodometrically, barium gravimetrically as \( \text{BaSO}_4 \).

SOURCE AND PURITY OF MATERIALS:
Barium sulfite was precipitated by mixing freshly prepared solutions of barium hydroxide and sulfurous acid. Sucrose was recrystallized from alcohol.

ESTIMATED ERROR:

REFERENCES:
COMPONENTS:
1. Barium sulfite; BaSO₃; [7787-39-5]
2. Sulfur dioxide; SO₂; [7446-09-5]
3. Water; H₂O; [7732-18-5]

ORIGINAL MEASUREMENTS:
Conrad, F.H.; Beuschlein, W.L.

VARIABLES:
One temperature: 298 K
Pressure of SO₂

PREPARED BY:
B. Engelen

EXPERIMENTAL VALUES:

<table>
<thead>
<tr>
<th>t/°C</th>
<th>Ptotal</th>
<th>PSO₂ᵃ</th>
<th>g SO₂/100 g H₂O</th>
<th>BaSO₃ᵇ</th>
<th>m(BaSO₃)ᶜ</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>659</td>
<td>847</td>
<td>7.23</td>
<td>0.25</td>
<td>8.48</td>
</tr>
</tbody>
</table>

ᵃ Corrected for P_H₂O and converted to bar by the compiler.
ᵇ SO₂ required to form the monosulfite.
ᶜ Calculated from combined SO₂ by the compiler.

METHOD APPARATUS/PROCEDURE:
Equilibrium, which was established after more than 12 hr, was studied in a special flask with connections to a weighing pipette for analysing the saturated solution, and to a mercury monometer to measure the pressure of the gas over the solution.

Total, free and combined SO₂ were determined by acidimetric and iodometric titration, respectively (1).

SOURCE AND PURITY OF MATERIALS:
Preparation of BaSO₃ was not given. The SO₂ used was SO₃-free. The amount of inert or non-absorbable gases was about 0.15%.

REFERENCES:
### COMPONENTS:
1. Barium sulfite; BaSO$_3$; [7787-39-5]
2. Sodium chloride; NaCl; [7647-14-5]
3. Water; H$_2$O; [7732-18-5]

### ORIGINAL MEASUREMENTS:
Cohen, A.; Zangen, M.; Goldschmidt, J.M.E.

### VARIABLES:
- One temperature: 298 K
- One concentration of NaCl: 0.7 mol dm$^{-3}$
- Time of stirring

### EXPERIMENTAL VALUES:
The solubility of rapidly precipitated BaSO$_3$ at 25°C decreases from $3.0 \times 10^{-4}$ to $2.3 \times 10^{-4}$ mol kg$^{-1}$ (molality) within 24 hr. The change in the solubility is attributed to phase transition of the obtained barium sulfite.

### AUXILIARY INFORMATION

**METHOD APPARATUS/PROCEDURE:**
The solubility of BaSO$_3$ was determined in a stirred solution of aqueous NaCl (concentration 0.7 mol dm$^{-3}$). Method of analysis not given.

**SOURCE AND PURITY OF MATERIALS:**
Barium sulfite was precipitated by mixing equivalent amounts of aqueous solutions of BaCl$_2$ and Na$_2$SO$_3$.

**ESTIMATED ERROR:**

**REFERENCES:**
**COMPONENTS:**
1. Barium sulfate; BaSO₃; [7787-39-5]
2. Sodium carbonate; Na₂CO₃; [497-19-8]
3. Sodium sulfite; Na₂SₐO₃; [7757-83-7]
4. Water; H₂O; [7732-18-5]

**ORIGINAL MEASUREMENTS:**
Mareček, J.; Erdös, E.

**PREPARED BY:**
H.D. Lutz

**VARIABLES:**
One temperature: 298 K
Concentration of Na₂CO₃ and Na₂SO₃

**EXPERIMENTAL VALUES:**
The authors studied the equilibrium of the reaction

\[
\text{BaSO}_3(s) + \text{CO}_3^{2-} \rightleftharpoons \text{BaCO}_3(s) + \text{SO}_3^{2-}
\]

in aqueous solutions of Na₂CO₃ and Na₂SO₃. From the equilibrium constant found at 25°C

\[
K = \frac{[\text{SO}_3^{2-}]/[\text{CO}_3^{2-}]} = 0.243
\]

and the activity solubility product of BaCO₃ [513-77-9] reported by Townley et al. (1) and Hogge et al. (2)

\[
K_{SO}(\text{BaCO}_3) = 2.03 \times 10^{-9} \text{ [mol}^2 \text{ kg}^{-2}\text{]}
\]

the activity solubility product of barium sulfite at 25°C

\[
K_{SO}(\text{BaSO}_3) = 4.9 \times 10^{-10} \text{ [mol}^2 \text{ kg}^{-2}\text{]}^{a}
\]

was calculated by the authors.

\[^{a}\text{ Molality scale.}\]

**METHOD APPARATUS/PROCEDURE:**
Equilibrium was studied under nitrogen in a special apparatus with connections to a weighing pipette, to analyse the solutions saturated with barium sulfate and barium carbonate. The solutions were made by adding an excess of solid BaSO₃, BaCO₃, or mixtures of BaSO₃ and BaCO₃ to solutions containing various amounts of Na₂SO₃ and Na₂CO₃ (mNa⁺ = 0.1 to 1 mol kg⁻¹). Equilibrium was established after 20 hr. Sulfite was determined iodometrically and carbonate acidimetrically after oxidizing the sulfite with H₂O₂. Furthermore, the content of sodium was determined gravimetrically as sulfate to check the amount of sulfite oxidized to sulfate in the saturated solution.

**SOURCE AND PURITY OF MATERIALS:**
BaSO₃ was prepared from BaCO₃ and gaseous SO₂. BaCO₃ was precipitated from saturated Ba(OH)₂ solution with gaseous CO₂. Sodium carbonate was prepared by thermal decomposition of NaHCO₃. Water was redistilled, boiled and saturated with N₂. The other chemicals used were commercial products of p.a. purity.

**ESTIMATED ERROR:**
Temperature: ±0.05 K;
K (equilibrium): ±0.7% (estimated by authors).

**REFERENCES:**