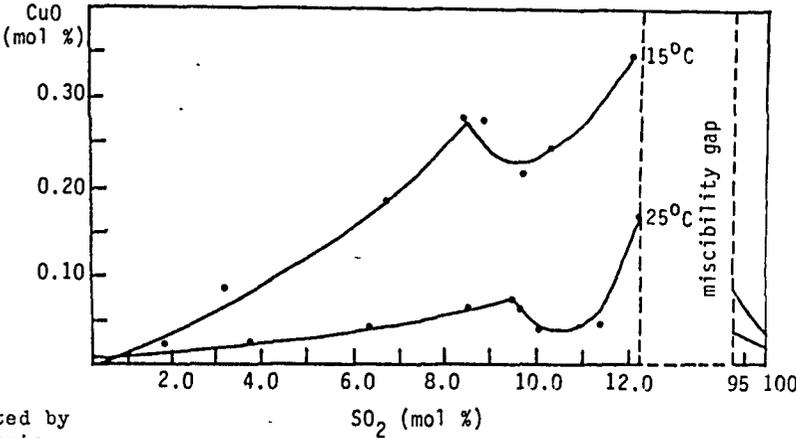


<p>COMPONENTS:</p> <ol style="list-style-type: none"> <li>Copper(I,II) sulfite; <math>\text{Cu}_2\text{SO}_3 \cdot \text{CuSO}_3</math>; [15293-86-4]</li> <li>Water; <math>\text{H}_2\text{O}</math>; [7732-18-5]</li> </ol>	<p>EVALUATOR:</p> <p>H.D. Lutz, Dept. of Chemistry, University of Siegen, FR Germany.</p> <p>June 1983.</p>
<p>CRITICAL EVALUATION:</p> <p>Copper(I,II) sulfite crystallizes from aqueous solution in the form of the hydrate <math>\text{Cu}_2\text{SO}_3 \cdot \text{CuSO}_3 \cdot 2\text{H}_2\text{O}</math> (Chevreul's salt) (1) [13814-81-8]. The formation of other hydrates, e.g. Pean's salt (2), could not be confirmed (3). Copper(I,II) sulfite has been claimed to be insoluble in water (4,5), slightly soluble in sulfurous acid (4,5) and in other acids (4,6), soluble in aqueous <math>\text{NH}_3</math> solutions (4,7), and insoluble in <math>\text{CuSO}_4</math> solutions (8). Numerical data have been given by Terres <i>et al.</i> (9), Pesin <i>et al.</i> (10), and Margulis <i>et al.</i> (11). Pesin <i>et al.</i> (10) report that the solubility of <math>\text{Cu}_2\text{SO}_3 \cdot \text{CuSO}_3 \cdot 2\text{H}_2\text{O}</math> in pure water is <math>1.09 \times 10^{-3} \text{ mol kg}^{-1}</math> (molality) (0.042 mass %) at 298.2 K and <math>3.62 \times 10^{-3} \text{ mol kg}^{-1}</math> (0.140 mass %) at 333.2 K. Margulis <i>et al.</i> (11) determined <math>c(\text{Cu}_2\text{SO}_3 \cdot \text{CuSO}_3) = 8.71 \times 10^{-5} \text{ mol dm}^{-3}</math> at 293 K and <math>1.9 \times 10^{-6} \text{ mol dm}^{-3}</math> at 363K. The data given by Terres <i>et al.</i> (9) may be extrapolated to pure water to be in the range <math>1 \times 10^{-3}</math> to <math>1 \times 10^{-2} \text{ mol kg}^{-1}</math>. Thus the solubility given by Pesin <i>et al.</i> (10) may be of the right order of magnitude. The same seems to be true for the positive temperature coefficient of solubility reported by Pesin <i>et al.</i> (10). Pesin <i>et al.</i> (10) also report that the solubility of copper(I,II) sulfite increases to <math>3.20 \times 10^{-3}</math> and <math>1.22 \times 10^{-2} \text{ mol kg}^{-1}</math> at 298.2 K and 333.2 K, respectively, with concentration of <math>\text{CuSO}_4 \cdot 5\text{H}_2\text{O}</math> increasing to 30 mass %. The solubility of copper(I,II) sulfite increases to <math>m(\text{CuO}) = 0.170</math> and <math>0.043 \text{ mol kg}^{-1}</math> with increasing <math>\text{SO}_2</math> content at 288.2 and 298.2 K, respectively, as reported by Terres <i>et al.</i> (9). Normal copper(II) sulfite or hydrates of it are not known.</p> <p>REFERENCES</p> <ol style="list-style-type: none"> <li>Chevreul <i>Ann. Chim. (Paris)</i> <u>1812</u>, 83, 181.</li> <li>Péan de St. Gilles, L. <i>Ann. Chim. Phys.</i> <u>1854</u>, 42, 23.</li> <li>Brauer, G.; Eichner, M. Z. <i>Anorg. Allg. Chem.</i> <u>1956</u>, 287, 95.</li> <li>Berthier, P. <i>Ann. Chim. Phys.</i> <u>1843</u>, 7, 74.</li> <li>Omori, K.; Okuwaki, A.; Suzuki, T.; Ito, H.; Okabe, T. <i>Bull. Chem. Soc. Japan</i> <u>1966</u>, 39, 78.</li> <li>Doeppling, O. <i>Bull. Acad. Imp. Sci. St.-Petersbourg</i> <u>1851</u>, 9, 179.</li> <li>Rogojski, J.-B. <i>C.R. Trav. Chim.</i> <u>1851</u>, 7, 156.</li> <li>Gin, G. <i>Chem. News J. Phys. Sci.</i> <u>1903</u>, 88, 5.</li> <li>Terres, E.; Ruhl, G. <i>Angew. Chem.</i> <u>1934</u>, 47, 332.</li> <li>Pesin, Ya.M.; Shabashova, M.L. <i>Zh. Prikl. Khim.</i> <u>1950</u>, 23, 350; <i>J. Appl. Chem. USSR (Eng. Transl.)</i> <u>1950</u>, 23, 365.</li> <li>Margulis, E.V.; Rodin, I.V. <i>Zh. Neorg. Khim.</i> <u>1982</u>, 27, 374; <i>Russ. J. Inorg. Chem. (Eng. Transl.)</i> <u>1982</u>, 27, 211.</li> </ol>	

<b>COMPONENTS:</b> 1. Copper(I,II) sulfite; $\text{Cu}_2\text{SO}_3 \cdot \text{CuSO}_3$ ; [15293-86-4] 2. Sulfur dioxide; $\text{SO}_2$ ; [7446-09-5] 3. Water; $\text{H}_2\text{O}$ ; [7732-18-5]	<b>ORIGINAL MEASUREMENTS:</b> 1. Terres, E.; Ruhl, G. <i>Angew. Chem.</i> 1934, 47, 332-4. 2. Terres, E.; Ruhl, G. <i>Beitrage zur Chemie der schwefligen Saure, Beiheft zu den Zeitschriften des Vereinsdeutscher Chemiker No 8, 1934.</i>
<b>VARIABLES:</b> Two temperatures: 288 and 298 K Concentration of $\text{SO}_2$	<b>PREPARED BY:</b> H.D. Lutz, B. Engelen
<b>EXPERIMENTAL VALUES:</b> The authors report the solubility of $\text{Cu}_2\text{SO}_3 \cdot \text{CuSO}_3 \cdot 2\text{H}_2\text{O}$ (Chevreul's salt) [13814-81-8] in aqueous sulfurous acid solutions at 15 and 25°C. The experimental data are given in a graph, in the first paper. Numerical data are reported in the second paper. <div style="text-align: center;">  </div> <p>Reprinted by permission</p> <p style="text-align: right;">(continued on next page)</p>	
<b>AUXILIARY INFORMATION</b>	
<b>METHOD APPARATUS/PROCEDURE:</b> $\text{SO}_2$ - $\text{H}_2\text{O}$ mixtures were treated together with solid copper(I,II) sulfite in closed glass ampoules at the stated temperatures. The solutions obtained were filtered through a fine glass frit, and after oxidation of the sulfite were analysed for sulfate and copper content.	<b>SOURCE AND PURITY OF MATERIALS:</b> Chevreul's salt was obtained from copper sulfate and sodium sulfite.  <b>ESTIMATED ERROR:</b>   <b>REFERENCES:</b>

## COMPONENTS:

1. Copper(I,II) sulfite;  $\text{Cu}_2\text{SO}_3 \cdot \text{CuSO}_3$ ; [15293-86-4]
2. Sulfur dioxide;  $\text{SO}_2$ ; [7446-09-5]
3. Water;  $\text{H}_2\text{O}$ ; [7732-18-5]

## ORIGINAL MEASUREMENTS:

1. Terres, E.; Ruhl, G. *Angew. Chem.* 1934, 47, 332-4.
2. Terres, E.; Ruhl, G. *Beitrage zur Chemie der schwefligen Saure, Beiheft zu den Zeitschriften des Vereinsdeutscher Chemiker No 8, 1934.*

## EXPERIMENTAL VALUES (continued):

Composition of the saturated solutions<sup>a</sup>

$\text{SO}_2$ mol %	$\text{CuO}$ mol %	$m(\text{CuO})^b$ $10^{-2} \text{ mol kg}^{-1}$	Solid phase
<u>Temperature = 15°C</u>			
1.84	0.02	1.13	$\text{Cu}_2\text{SO}_3 \cdot \text{CuSO}_3 \cdot 2\text{H}_2\text{O}$
3.18	0.08	4.59	"
6.72	0.18	10.7	"
8.26	0.28	17.0	"
8.73	0.27	16.5	$\text{Cu}(\text{HSO}_3)_2^?$
9.65	0.21	12.9	"
10.25	0.24	14.9	"
<u>Temperature = 25°C</u>			
0.05	0.01	0.56	$\text{Cu}_2\text{SO}_3 \cdot \text{CuSO}_3 \cdot 2\text{H}_2\text{O}$
3.72	0.02	1.15	"
6.32	0.04	2.37	"
8.47	0.06	3.64	"
9.45	0.07	4.29	"
9.54	0.06	3.68	$\text{Cu}(\text{HSO}_3)_2^?$
10.05	0.04	2.47	"
11.32	0.09	5.64	"
12.18	0.17	10.8	"

<sup>a</sup> The mixtures separate into two liquid layers at concentrations of  $\text{SO}_2$  between 12.2 and 93 mol %.

<sup>b</sup> Compilers.

COMPONENTS:	ORIGINAL MEASUREMENTS:						
1. Copper(I,II) sulfite; $\text{Cu}_2\text{SO}_3 \cdot \text{CuSO}_3$ ; [15293-86-4] 2. Copper(II) sulfate; $\text{CuSO}_4$ ; [7758-98-7] 3. Water; $\text{H}_2\text{O}$ ; [7732-18-5]	Pesin, Ya.M.; Shabashova, M.L.  <i>Zh. Prikl. Khim.</i> <u>1950</u> , 23, 350-6; *J. <i>Appl. Chem. USSR (Eng. Transl.)</i> <u>1950</u> , 23, 365-72.						
VARIABLES:	PREPARED BY:						
Two temperatures: 298 and 333 K Concentration of $\text{CuSO}_4$	H.D. Lutz						
EXPERIMENTAL VALUES:							
The authors report the solubility of $\text{Cu}_2\text{SO}_3 \cdot \text{CuSO}_3 \cdot 2\text{H}_2\text{O}$ (Chevreul's salt) [13814-81-8] in water and in solutions of various $\text{CuSO}_4$ concentration at 25 and 60°C.							
Concentration of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ mass %	Composition of saturated solutions						
	25°C			60°C			
	mass %		$10^3 m$	mass %		$10^3 m$	
	Determination Copper	Sulfur	Mean value $\text{mol kg}^{-1}$ (compiler)	Determination Copper	Sulfur	Mean value $\text{mol kg}^{-1}$ (compiler)	
0	0.042	0.042	0.042	1.09	0.141 0.139	0.140	3.62
10	0.086	0.090	0.088	2.43	0.309 0.315	0.312	8.64
20	0.090	0.102	0.096	2.85	0.331 0.337	0.334	9.94
30	0.098	0.102	0.100	3.20	0.380 0.378	0.379	12.18
AUXILIARY INFORMATION							
METHOD APPARATUS/PROCEDURE:				SOURCE AND PURITY OF MATERIALS:			
Saturation method. The water and the solutions of $\text{CuSO}_4$ were boiled to drive off the oxygen. Equilibrium was established after 24 hr. The solutions were analysed for copper and sulfur (methods not given, but are assumed to be the same as in a previous paper by the authors (1), i.e. copper was determined iodometrically and sulfur as $\text{BaSO}_4$ ).				$\text{Cu}_2\text{SO}_3 \cdot \text{CuSO}_3 \cdot 2\text{H}_2\text{O}$ was prepared (as described in a previous paper by the authors (1)) by adding a 10% solution of $\text{CuSO}_4$ to a solution of sodium sulfite at 70-80°C. The crystalline precipitate that formed (after standing for 2-3 hr) was washed with water until the reaction for the $\text{SO}_4^{2-}$ ion disappeared, and then dried at 90-100°C.			
ESTIMATED ERROR:							
REFERENCES:				1. Pesin, Ya.M.; Shabashova, M.L. <i>Zh. Prikl. Khim.</i> <u>1950</u> , 23, 278.			

<b>COMPONENTS:</b> 1. Copper(I,II) sulfite; $\text{Cu}_2\text{SO}_3 \cdot \text{CuSO}_3$ ; [15293-86-4] 2. Water; $\text{H}_2\text{O}$ ; [7732-18-5]	<b>ORIGINAL MEASUREMENTS:</b> Margulis, E.V.; Rodin, I.V. <i>Zh. Neorg. Khim.</i> <u>1982</u> , 27, 374-7; * <i>Russ. J. Inorg. Chem. (Eng. Transl.)</i> <u>1982</u> , 27, 211-3.																																							
<b>VARIABLES:</b> Six temperatures: 293 - 363 K	<b>PREPARED BY:</b> H.D. Lutz																																							
<b>EXPERIMENTAL VALUES:</b> The authors report the solubility of $\text{Cu}_2\text{SO}_3 \cdot \text{CuSO}_3 \cdot 2\text{H}_2\text{O}$ (Chevreul's salt) [13814-81-8] in water at various temperatures, and the solubility product of this compound, defined as $K_{\text{SO}}(\text{Cu}_2\text{SO}_3 \cdot \text{CuSO}_3 \cdot 2\text{H}_2\text{O}) = [\text{Cu}^{2+}][\text{Cu}^+]^2[\text{SO}_3^{2-}]^2$ .  <div style="text-align: center;">Composition of the saturated solutions</div> <table border="1" style="margin-left: auto; margin-right: auto;"> <thead> <tr> <th rowspan="2">t/°C</th> <th colspan="2">Cu</th> <th colspan="2"><math>\text{Cu}_2\text{SO}_3 \cdot \text{CuSO}_3</math></th> </tr> <tr> <th>mg/dm<sup>3</sup></th> <th><math>10^5 c(\text{Cu})</math> mol dm<sup>-3</sup></th> <th><math>K_{\text{SO}}/\text{mol}^5</math> dm<sup>-15</sup></th> <th><math>10^5 c^a/\text{mol}</math> dm<sup>-3</sup></th> </tr> </thead> <tbody> <tr> <td>20</td> <td>16.6</td> <td>26.1</td> <td><math>1.21 \times 10^{-18}</math></td> <td>8.71</td> </tr> <tr> <td>30</td> <td>12.4<sup>b</sup></td> <td>22.1<sup>b</sup></td> <td><math>5.27 \times 10^{-19\text{b}}</math></td> <td>6.50</td> </tr> <tr> <td>40</td> <td>2.7</td> <td>4.25</td> <td><math>1.39 \times 10^{-22}</math></td> <td>1.42</td> </tr> <tr> <td>50</td> <td>1.8</td> <td>2.84</td> <td><math>1.84 \times 10^{-23}</math></td> <td>0.94</td> </tr> <tr> <td>70</td> <td>0.94</td> <td>1.48</td> <td><math>7.10 \times 10^{-25}</math></td> <td>0.49</td> </tr> <tr> <td>90</td> <td>0.37</td> <td>0.58</td> <td><math>6.56 \times 10^{-27}</math></td> <td>0.19</td> </tr> </tbody> </table> a Calculated by the compiler from mg Cu/dm <sup>3</sup> . b Inconsistent data ( $12.4 \text{ mg Cu/dm}^3 \neq 22.1 \times 10^{-5} \text{ mol dm}^{-3}$ ).		t/°C	Cu		$\text{Cu}_2\text{SO}_3 \cdot \text{CuSO}_3$		mg/dm <sup>3</sup>	$10^5 c(\text{Cu})$ mol dm <sup>-3</sup>	$K_{\text{SO}}/\text{mol}^5$ dm <sup>-15</sup>	$10^5 c^a/\text{mol}$ dm <sup>-3</sup>	20	16.6	26.1	$1.21 \times 10^{-18}$	8.71	30	12.4 <sup>b</sup>	22.1 <sup>b</sup>	$5.27 \times 10^{-19\text{b}}$	6.50	40	2.7	4.25	$1.39 \times 10^{-22}$	1.42	50	1.8	2.84	$1.84 \times 10^{-23}$	0.94	70	0.94	1.48	$7.10 \times 10^{-25}$	0.49	90	0.37	0.58	$6.56 \times 10^{-27}$	0.19
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<b>METHOD APPARATUS/PROCEDURE:</b> The solubility of copper(I,II)sulfite was studied by the isothermal method. The experiments were carried out in a water thermostat with mechanical stirring in closed flasks. The time required for saturation was 2.5 hr. The solutions were analysed for sulfite (method not given).	<b>SOURCE AND PURITY OF MATERIALS:</b> Copper(I,II)sulfite was precipitated from $\text{CuSO}_4$ solutions with $\text{Na}_2\text{SO}_3$ (molar ratio $\text{Na}_2\text{SO}_3/\text{CuSO}_4 = 1:1$ ) at temperatures > 40°C. After stirring for 2 hr, the precipitate was filtered off, washed with water and acetone, and dried in air at room temperature.  <b>ESTIMATED ERROR:</b> Temperature: $\pm 0.5 \text{ K}$ .  <b>REFERENCES:</b>																																							