

<p>COMPONENTS:</p> <ol style="list-style-type: none"> 1. Calcium sulfite; CaSO_3; [10257-55-3] 2. Water; H_2O; [7732-18-5] 	<p>EVALUATOR</p> <p>H.D. Lutz, Dept. of Chemistry, University of Siegen, FR Germany. December 1983.</p>
<p>CRITICAL EVALUATION:</p> <p>Calcium sulfite crystallizes from aqueous solutions in the form of the hemihydrate, $\text{CaSO}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$ [29501-28-8] (1-3). A dihydrate, $\text{CaSO}_3 \cdot 2\text{H}_2\text{O}$ [10035-03-7], claimed in the older literature (4), could not be confirmed (1-3,5). Very recently a tetrahydrate, $\text{CaSO}_3 \cdot 4\text{H}_2\text{O}$ [72878-03-6], has been reported (6,7). This crystallizes in the presence of sodium citrate (6) or nitrilotri(methylene phosphonic acid) (7).</p> <p>Numerical data on the solubility of calcium sulfite, i.e. $\text{CaSO}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$, have been given by many authors (7-42). The published figures, however, differ to a great extent. This is probably caused by the very great tendency of calcium sulfite to form supersaturated solutions (7) and by the existence of several different modifications of $\text{CaSO}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$ (8,9,43). The difficulty in preparing sulfate-free samples of calcium sulfite and the tendency of $\text{CaSO}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$ to form solid solutions with calcium sulfate (44,45) must further be taken into account.</p> <p>SOLUBILITY OF CALCIUM SULFITE HEMIHYDRATE IN PURE WATER</p> <p>The values of the solubility of calcium sulfite in pure water at ambient temperature (288 - 303 K) given in the literature (7-20,42) vary from 8.7×10^{-5} (14) to 3.3×10^{-3} (7) mol dm^{-3} (molarity scale). The data reported by Farnell (15), 2.0×10^{-4} mol dm^{-3} at 303 K, Weisberg (10), 3.58×10^{-4} mol dm^{-3} at 291 K, Sano (20), 5.21×10^{-4} mol dm^{-3} at 298 K, Cohen <i>et al.</i> (8-9), 7.0×10^{-4} mol dm^{-3} at 298 K, Rengemo <i>et al.</i> (17), 7.6×10^{-4} mol dm^{-3} at 298.2 K, Marusawa (13), 7.91×10^{-4} mol dm^{-3} at 291 K, all on the molarity scale, and by Van der Linden (12), 4.10×10^{-4} mol kg^{-1} (molality scale) at 303 K, seem to be nearest to the true value.</p> <p>The solubility product of calcium sulfite was first determined by Marusawa (13,21) to be 4.4×10^{-7} $\text{mol}^2 \text{dm}^{-6}$ (molarity scale) at 291.2 K, on the assumption of incomplete dissociation of the dissolved calcium sulfite. From Debye-Hückel theory, a value of $3.66(2) \times 10^{-7}$ $\text{mol}^2 \text{dm}^{-6}$ can be obtained from the original data given by Marusawa (13). In 1958, the activity solubility product was calculated by Rengemo <i>et al.</i> (17) from equilibrium studies of the reaction, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}(\text{s}) + \text{SO}_3^{2-} \rightleftharpoons \text{CaSO}_3 \cdot \frac{1}{2}\text{H}_2\text{O}(\text{s}) + \text{SO}_4^{2-} + 1\frac{1}{2}\text{H}_2\text{O}$, at 298.2 K in aqueous NaClO_4 solutions of various ionic strengths to be $3.1 (\pm 1.5) \times 10^{-7}$ $\text{mol}^2 \text{dm}^{-6}$ (molarity scale).</p> <p>RECOMMENDED VALUES</p> <p>The solubility of $\text{CaSO}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$ in water at 298.2 K (25°C), on the molarity scale, is $4.5 (\pm 1.0) \times 10^{-4}$ mol dm^{-3} (0.054 ± 0.012 g $\text{CaSO}_3/\text{dm}^3$).</p> <p>The solubility product, based on the activities, is $3.1 (\pm 1.5) \times 10^{-7}$ $\text{mol}^2 \text{dm}^{-6}$ (molarity scale).</p>	

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CRITICAL EVALUATION: (continued)

The solubility of $\text{CaSO}_3 \cdot 1/2\text{H}_2\text{O}$ decreases slightly with increasing temperature (12-13,16,19,22). The following equation, fitted (by evaluator) from data given by Van der Linden (12) and Bobrovnik *et al.* (22), who are in relatively good agreement, is recommended.

$$\log S = -15.367 + 1155.67/T + 3.290 \log T \quad (1)$$

with S = solubility of $\text{CaSO}_3 \cdot 1/2\text{H}_2\text{O}$ on the molality scale (mol kg^{-1}) and T = temperature (K). The equation is valid for the range 293 - 373 K. A graph derived from this equation is shown in Fig. 1.

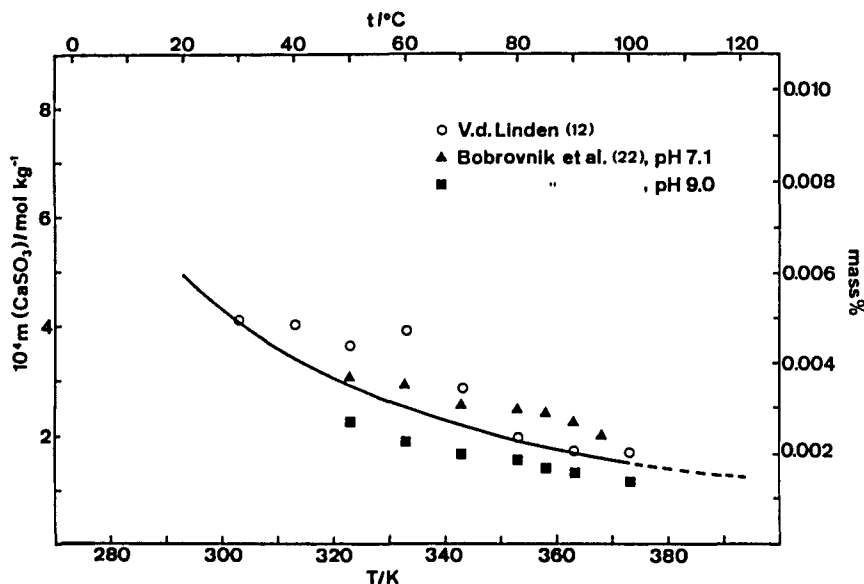


Fig 1. Solubility of calcium sulfite, $\text{CaSO}_3 \cdot 1/2\text{H}_2\text{O}$, in pure water (equation 1)

SOLUBILITY IN THE SYSTEM $\text{CaSO}_3\text{-SO}_2\text{-H}_2\text{O}$

The solubility of calcium sulfite increases very much with increasing SO_2 content of the solution (13,23-26). The numerical data given for ambient temperature and low SO_2 concentrations (up to 2.0 mol kg^{-1}), e.g. the results reported by Mebane *et al.* (25), Conrad *et al.* (27), and Kuz'minykh *et al.* (30), all on the molality scale, and by Marusawa (13) and Engelhardt (34), both on the molarity scale, are in good agreement. The following equation, fitted (by evaluator) with values given by Conrad *et al.* (27) and Kuz'minykh *et al.* (30), is recommended for the solubility of calcium sulfite in aqueous sulfurous acid solutions at 298 K (molality scale, mol kg^{-1}),

$$S = 0.460 \times m(\text{SO}_2 \text{ tot}) - 0.026 \times m^2(\text{SO}_2 \text{ tot}) \quad (2)$$

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CRITICAL EVALUATION: (continued)

This means that the ratio of dissolved calcium sulfite to total SO_2 concentration is nearly constant. A graph derived from this equation is shown in Fig. 2. The equation is valid for SO_2 concentrations up to $2.0 \text{ mol kg}^{-1} \text{ SO}_2$ at equilibrium pressure.

At higher SO_2 concentrations (up to 5.5 mol kg^{-1}) the data reported in the literature, e.g. by Conrad *et al.* (27), Simon *et al.* (33), and Humm (26), differ, as shown in Fig. 2. Data obtained by extrapolation of the graph (Fig. 2) seem to be more reliable.

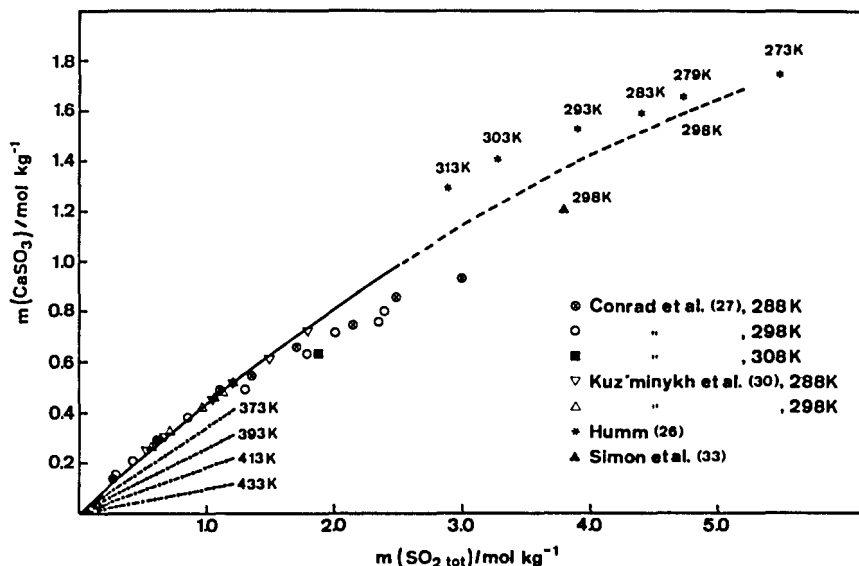


Fig. 2 Solubility of calcium sulfite in aqueous sulfurous acid solutions
 ----- recommended for 288 - 308 K, see equation (2),
 - · - · - from data given by Marusawa (23), Otuka (29), and Engelhardt (34)

The solubility of calcium sulfite at an equilibrium partial pressure of sulfur dioxide equal to 1 bar ($= 10^5 \text{ Pa}$) at ambient temperature has been determined by several authors, but the values obtained differ greatly, e.g. 1.45 (26), 1.22 (33), and 0.76 (27) mol kg^{-1} (molality scale) at concentrations of total SO_2 of 3.6, 3.79, and 2.4 mol kg^{-1} , respectively. Extrapolation of the data reported by Kuz'minykh *et al.* (30) to $P_{\text{SO}_2} = 1$ bar leads to the values $m(\text{CaSO}_3) = 0.98 \text{ mol kg}^{-1}$ and $m(\text{SO}_2 \text{ tot}) = 2.46 \text{ mol kg}^{-1}$, which are recommended.

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CRITICAL EVALUATION: (continued)

Numerical data on the solubility of calcium sulfite in aqueous sulfurous acid solutions below and above ambient temperature (23-32) indicate that the solubility of calcium sulfite decreases with increasing temperature at a given SO_2 concentration, but the temperature coefficient is relatively small. Therefore the equation given above is approximately valid, too, for temperatures other than 298 K, especially in the range from 273 to 333 K. Data at temperatures above 373 K have also been reported (23,28,29,34). Isotherms derived from these values (by evaluator) are included in Fig. 2. There are some indications that the ratio $m(\text{CaSO}_3)/m(\text{SO}_2 \text{ tot})$ of aqueous sulfurous acid solutions saturated with CaSO_3 increases from 273 to 313 K and decreases from 313 to 433 K.

Data on the partial pressure of sulfur dioxide over saturated solutions of calcium sulfite are given by Humm (26), Conrad *et al.* (27), Gishler *et al.* (28), and Kuz'minykh *et al.* (30), but only the values given by Conrad *et al.* (27) and Kuz'minykh *et al.* (30) agree to some extent. For a given partial pressure of SO_2 the solubility of calcium sulfite decreases with increasing temperature due to the decreasing solubility of sulfur dioxide. The data given by Kuz'minykh *et al.* (30) are recommended (Fig. 3).

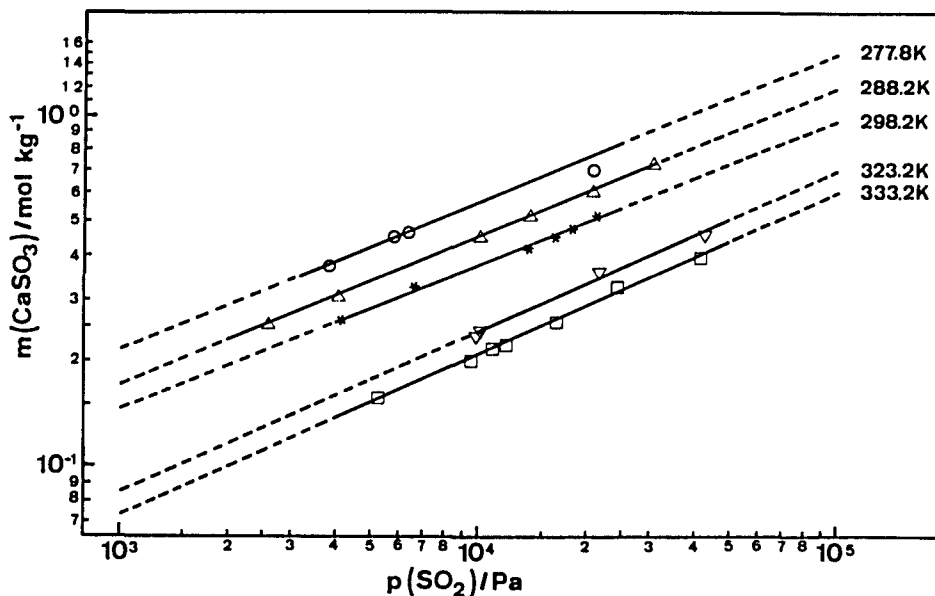


Fig. 3 Solubility of calcium sulfite in aqueous sulfurous acid solutions and partial pressure of sulfur dioxide (30)

The solubility products, $K_1 = [\text{Ca}^{2+}] \times [\text{HSO}_3^-]^2 / p\text{SO}_2$ and $K_2 = [\text{Ca}^{2+}] \times [\text{HSO}_3^-]^2 / [\text{H}_2\text{SO}_3]$, of $\text{CaSO}_3 \cdot 1/2\text{H}_2\text{O}$ in the presence of gaseous SO_2 at 298.2, 308.2, and 348.2 K have been

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CRITICAL EVALUATION: (continued)

determined by Nilsson *et al.* (31,32) from equilibrium studies of the reactions $\text{SO}_2(\text{g}) + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{SO}_3$ and $\text{CaSO}_3 \cdot 1/2\text{H}_2\text{O} + \text{SO}_2(\text{g}) + 1/2\text{H}_2\text{O} \rightleftharpoons \text{Ca}^{2+} + 2\text{HSO}_3^-$ at different concentrations of NaClO_4 as ionic medium. The data obtained are:

$m(\text{NaClO}_4)/\text{mol kg}^{-1}$	1			3.5		
T/K	298.2	308.2	348.2	298.2	308.2	348.2
$K_1/\text{mol}^3\text{kg}^{-3}\text{bar}^{-1}$	1.208	0.543	0.048	0.294	0.121	0.013
$K_2/\text{mol}^2\text{kg}^{-2}$	0.871	0.741	0.170	0.263	0.151	0.041

SOLUBILITY OF CALCIUM SULFITE IN THE PRESENCE OF CaSO_4 , NH_4NO_3 , NaCl , SODIUM PHOSPHATE, NaClO_4 , HCl , H_3PO_4 , NaOH , SUCROSE, GLUCOSE, XYLOSE, ACETIC ACID, CITRIC ACID, LIGNOSULFONIC ACID, SODIUM FORMATE, SODIUM ACETATE, SODIUM CITRATE, ALCOHOL, AND SEA-WATER.

In the system $\text{CaSO}_3\text{-CaSO}_4\text{-H}_2\text{O}$ (12-14,16,37) the solubility of $\text{CaSO}_3 \cdot 1/2\text{H}_2\text{O}$ decreases with increasing CaSO_4 content to approximately half the amount soluble in pure water for solutions saturated with gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, (12,14,16). This behaviour has been observed for all temperatures studied, *viz.* 293.2 K (16), 298.2 K (14), 303.2 K (12), 313.2 K (12,14), 323.2 K (12), 333.2 K (12,14), 343.2 K (12), 353.2 K (12,14), 363.2 K (12), and 373.2 K (12). The solubility of calcium sulfite in solutions saturated with gypsum decreases with increasing temperature (12), as found for pure water.

Experimental data on the solubility of $\text{CaSO}_3 \cdot 1/2\text{H}_2\text{O}$ in the presence of ammonium nitrate at 303 K are given by Dubovaya *et al.* (38). The figures indicate that the solubility at first increases and then decreases with increasing NH_4NO_3 content due to ionic strength effects. The same is obviously true in solutions containing sodium chloride (39). A relatively large increase in the solubility of calcium sulfite has been found (by Wurz *et al.* (16)) in the presence of Na_3PO_4 , but the reported numerical data given for one concentration, $c(\text{Na}_3\text{PO}_4) = 0.033 \text{ mol dm}^{-3}$, and four temperatures (293, 313, 333, and 353 K) cannot be directly compared with the solubility in pure water because of the altered pH. Data on the solubility in aqueous sulfurous acid solutions containing 1 and 3.5 mol kg^{-1} (molality) sodium perchlorate as ionic medium have been reported by Nilsson *et al.* (32) for 298.2, 308.2, and 348.2 K. The solubility of calcium sulfite in sea-water has been studied by Kurota *et al.* (37), but the figures seem to be too high.

The solubility of calcium sulfite increases greatly in the presence of acids. Numerical data are given for HCl (39), H_3PO_4 (25), acetic acid (16,20), and citric and lignosulfonic acid (16). The sodium salts of the organic acids under consideration also increase the solubility of calcium sulfite (16). The same has been found in the presence of sodium hydroxide (20).

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<p>CRITICAL EVALUATION: (continued)</p> <p>Numerical data on the solubility of calcium sulfite at different pH values have been given by several authors (16,18-20,22,39). The solubility increases with both increasing and decreasing pH (20). The minimum value of the solubility at pH 8.5 is found to be smaller than that of pure water (20,22).</p> <p>The solubility of calcium sulfite is also affected by the presence of sugar (10-12,15,16,18,19,22,40). Numerical data have been reported on sucrose, glucose (12,16), and xylose (16). The solubility of $\text{CaSO}_3 \cdot 1/2\text{H}_2\text{O}$ at first increases and then decreases with increasing sucrose content of the solution (10,22). The values obtained by Bobrovnik <i>et al.</i> (22) are recommended.</p> <p>Arnal <i>et al.</i> (41) reported on the solubility of calcium sulfite in aqueous ethanol solutions. The value of $8 \times 10^{-4} \text{ mol dm}^{-3}$ (molarity scale) in a solution with 67.2 mass % ethanol seems to be too high.</p> <p>REFERENCES</p> <ol style="list-style-type: none"> 1. Matthews, F.W.; McIntosh, A.O. <i>Can. J. Res., Sect. B</i> <u>1948</u>, 26, 747. 2. Setoyama, K.; Takahashi, S.; Sekiya, M. <i>Sekko to Sekkai</i> <u>1976</u>, 141, 57. 3. Lutz, H.D.; El-Suradi, S. <i>Z. Anorg. Allg. Chem.</i> <u>1976</u>, 425, 134. 4. <i>Gmelins Handbuch der Anorganischen Chemie</i>, 8. Auflage, Springer Verlag, Heidelberg, <u>1974</u>, Vol. 28, Part B 3, p 664. 5. Tsuyuki, N.; Kasai, J. <i>Nippon Kagaku Kaishi</i> <u>1976</u>, (1), 59. 6. Matsuno, T.; Koishi, M. <i>Nippon Kagaku Kaishi</i> <u>1979</u>, 1687. 7. McCall, M.T.; Tadros, M.E. <i>Colloids and Surfaces</i> <u>1980</u>, 1, 161. 8. Cohen, A.; Zangen, M.; Goldschmidt, J.M.E. <i>Inorg. Nucl. Chem. Lett.</i> <u>1980</u>, 16, 165. 9. Cohen, A.; Zangen, M.; Koenisbuch, M.; Goldschmidt, J.M.E. <i>Desalination</i> <u>1982</u>, 41, 215. 10. Weisberg, J. <i>Bull. Soc. Chim. Fr.</i> <u>1896</u>, 15, 1247. 11. Robart, J. <i>Bull. Assoc. Chim. Sucr. Distill. Fr. Colon.</i> <u>1913</u>, 31, 108. 12. Van der Linden, T. <i>Arch. Suikerind. Ned.-Indie</i> <u>1916</u>, 24, 1113; <i>Dtsch. Zuckerind.</i> <u>1916</u>, 41, 815; <i>J. Soc. Chem. Ind., London</i> <u>1917</u>, 36, 96. 13. Marusawa, T. <i>Kogyo Kagaku Zasshi</i> <u>1917</u>, 20, 287. 14. Bichowsky, F.R. <i>J. Am. Chem. Soc.</i> <u>1923</u>, 45, 2225. 15. Farnell, R.G.W. <i>J. Soc. Chem. Ind. London, Trans. Commun.</i> <u>1925</u>, 44, 530. 16. Wurz, O.; Swoboda, O. <i>Text.-Rundsch.</i> <u>1948</u>, 3, 201. 	

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