

<p>COMPONENTS:</p> <ol style="list-style-type: none"> 1. Sodium sulfite; Na_2SO_3; [7757-83-7] 2. Water; H_2O; [7732-18-5] 	<p>EVALUATOR:</p> <p>Mary R. Masson, Dept. of Chemistry, University of Aberdeen, Meston Walk, Old Aberdeen, AB9 2UE, Scotland, UK. June 1984</p>
<p>CRITICAL EVALUATION:</p> <p>There have been 5 studies of the binary system sodium sulfite - water (1 - 5). However, the data given by Efanov <i>et al.</i> (5) are expressed in units of g-equivalents per litre, and therefore cannot be compared with the other data. Data are also available from ternary systems (6 - 24). The data show a good deal of scatter, probably because of the difficulty of preventing oxidation of sulfite to sulfate at all stages from preparation to determination.</p> <p>Data for the equilibrium with ice (269-273 K) come from (1) and (2). Two points from (1) had to be rejected, but otherwise the data are in reasonable agreement. The regression equation is</p> $(T - 273.15) = -0.0137 - 0.347y + 0.0026y^2 \quad s = 0.027 \quad (15 \text{ pts})$ <p>or alternatively</p> $y = -0.0317 - 2.85(T - 273.2) + 0.0809(T - 273.2)^2 \quad s = 0.088 \quad (15 \text{ pts})$ <p>where $y = 100w$ is the solubility in mass % of Na_2SO_3, T is the temperature in K, and s is the estimated standard deviation of the dependent variable about the regression line.</p> <p>For the temperature range 273 - 309 K, the solid phase in equilibrium with the saturated solution is $\text{Na}_2\text{SO}_3 \cdot 7\text{H}_2\text{O}$ [10102-15-5]. Data were available from (1 - 4, 6 - 9, 11, 12, 14 - 16, 19, 21 - 23); there were 79 points in all. All 10 data points from (7) were rejected, because they were totally inconsistent with the other data. Other data points were rejected when regression analysis showed them to lie outwith $\pm 2s$ of the regression line. The process was repeated until a line was obtained with all points lying inside $\pm 2s$. The rejected points came from the following reference: (1) - 1 out of 8 total, (2) - 2/24, (3) - 2/5, (4) - 1/3, (11) - 1/1, (23) - 2/2. The final regression equation is</p> $y = 12.03 + 0.377(T - 273.2) + 0.00325(T - 273.2)^2 \quad s = 0.207 \quad (60 \text{ pts})$ <p>For the temperature range 307 - 373 K, where the solid phase is the anhydrous salt Na_2SO_3, data were available in (1 - 4, 8, 10, 13, 17 - 20, 22, 23); there were 52 points. All but 1 of the 11 points from (1) were rejected because they were completely lacking in agreement with the other data. Other points rejected because they lay outside $\pm 2s$ came from (2) - 3/19, (3) - 4/5, (4) - 2/4, (8) - 1/1, (13) - 2/3, (18) - 1/1, (19) - 1/2, (23) - 1/1. The final regression equation is</p> $y = 34.2 - 0.2024(T - 273.2) + 0.000760(T - 273.2)^2 \quad s = 0.135 \quad (27 \text{ pts})$ <p>The temperature of the transition point between the 7-hydrate and the anhydrous salt has</p>	

Sodium Sulfite

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2. Water; H_2O ; [7732-18-5]	Dept. of Chemistry, University of Aberdeen, Meston Walk, Old Aberdeen, AB9 2UE, Scotland, UK. June 1984

CRITICAL EVALUATION: (continued)

been variously reported to be 295.2 K (22°C) (1), 306.6 K (33.4°C) (2), 298.2 - 305.2 K (6), 304.7 K (31.5°C) (12) and 306.7 (36.5°C) (31). The point of intersection of the relevant regression equations is 306.57 K (33.41°C). The solubility at that point is 28.25 mass % of Na_2SO_3 .

The ice curve intersects the 7-hydrate line at a eutectic temperature of 269.70 K (-3.46°C); the solubility there is 10.8 mass % of Na_2SO_3 .

Rodnyanskii and Galinker (4) actually report solubilities up to 633 K (360°C), but their data were reported only in graphical form, and precision of reading the graph was not good.

With as much data as are available for this system, it would have been hoped to be able to give recommended values. However, because there is such a lot of scatter in the data, it was felt that the values derived from the regression equations should be designated merely as Tentative.

TENTATIVE SOLUBILITIES

T/K	Solubility	
	mass %	molality mol/kg
	$\text{Na}_2\text{SO}_3 \cdot 7\text{H}_2\text{O}$	
273.2	12.03	1.085
278.2	14.0	1.29
283.2	16.1	1.52
288.2	18.4	1.79
293.2	20.9	2.10
298.2	23.5	2.44
303.2	26.3	2.83
308.2	29.2	3.27
	Na_2SO_3	
308.2	28.0	3.09
313.2	27.3	2.98
318.2	26.6	2.88
323.2	25.95	2.78
328.2	25.3	2.69
333.2	24.8	2.62
338.2	24.2	2.53
343.2	23.7	2.46
348.2	23.3	2.41
353.2	22.8	2.34
358.2	22.5	2.30
363.2	22.1	2.25
368.2	21.8	2.21
373.2	21.5	2.17

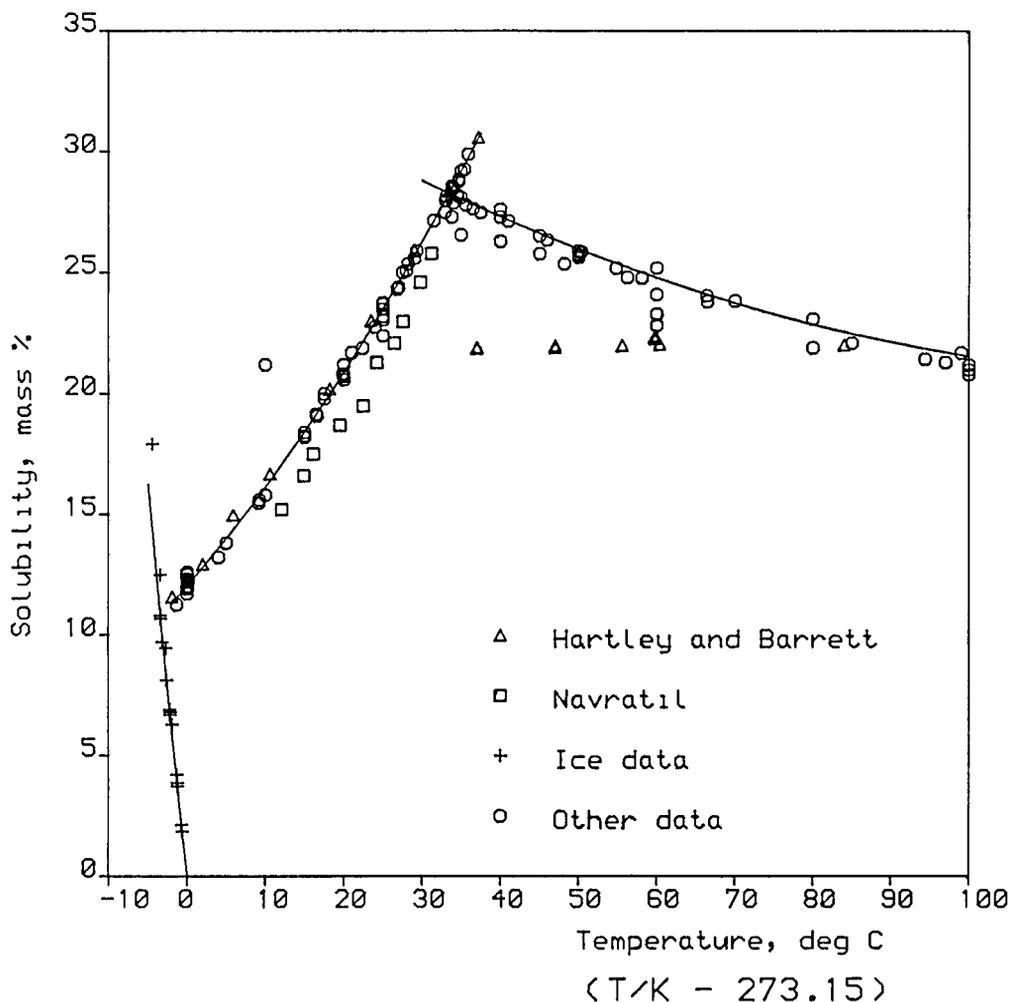
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CRITICAL EVALUATION: (continued)



TERNARY SYSTEMS

Sodium sulfite - sodium sulfate - water. This system has been studied by a number of workers (10 - 18), at a number of temperatures. At 273.2 and 273.3 K, the data of Rivett and Lewis (14) and Palkina (15) are in good agreement. The data of Sotova *et al.* (16) are also in agreement, apart from one or two points. Palkina gives no information about the solid phases, and the others differ in their conclusions about the solid phases. A first glance at the phase diagrams would suggest that there were two solid phases, viz. anhydrous Na_2SO_3 and Na_2SO_4 . Sotova merely states that the two solid phases are $\text{Na}_2\text{SO}_3 \cdot 7\text{H}_2\text{O}$ and $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$. Rivett and Lewis say that there are two series of mixed crystals, one between the heptahydrates and the other between the decahydrates. In neither case is convincing evidence presented. It seems certain that some sort of

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CRITICAL EVALUATION: (continued)

mixed crystals are indeed formed, because almost certainly it is not the anhydrous salts that are formed.

The data given by Palkina (15) for 278.2, 283.2, 288.2 and 293.2 K appear to be in accord with the data of Rivett and Lewis (14) for 290.7 K and Lewis and Rivett (12) for 294.2 K. The phase diagram for 290.7 K appears to suggest that there are two solid phases, $\text{Na}_2\text{SO}_3 \cdot 7\text{H}_2\text{O}$, and $\text{Na}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$, forming a simple eutonic system, and this does appear to be possible, although perhaps it would have been expected to find $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ rather than the 7-hydrate. Kuznetsova and Sedova (32) report finding $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ from sulfate-rich solutions, and solid solutions from sulfite-rich solutions, but their solubility data is not in good agreement with the rest. However, the authors again believed that two series of mixed crystals were formed (14). At 298.2 K, the data of Palkina (15) are in agreement with those of Rivett and Lewis (14), and the data of Kuznetsova and Yaroshenko (11) are also essentially in agreement, although they show rather more scatter. The phase diagram for (11) shows a simple eutonic system, with solids $\text{Na}_2\text{SO}_3 \cdot 7\text{H}_2\text{O}$ and $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, but there is not much data. The one for (14) suggests that one solid is $\text{Na}_2\text{SO}_3 \cdot 7\text{H}_2\text{O}$, but the tie-lines at the sulfate side of the diagram meet between the positions for the 7-hydrate and 10-hydrate, which suggests the possibility again of mixed crystals. The authors (14) again propose that there are two series of mixed crystals, one between the heptahydrates and the other between the decahydrates. Palkina (15) also believed this, but did not provide any supporting data. Rivett and Lewis (14) report also a metastable system at 298.2 K; here the solid phases are the anhydrous salts, and mixed crystals are formed extensively.

The data of Sotova *et al.* (18) and Lewis and Rivett (13) for 333.2 K, are in reasonable agreement, apart from a bit of scatter in Sotova's results. Lewis and Rivett also report a short metastable region. The phase diagrams for this temperature show no eutonic, but that a range of solid solutions of the two anhydrous salts are formed. Lewis and Rivett report finding 5 series of such solid solutions. The same sort of phase diagram is seen at 313.2 K (13), 318.2 K (13), 310.7 K (14), and at 373.2 K, where the agreement between Durymanova and Telepneva (10) and Sotova *et al.* (17) is reasonable. Small amounts of data for several other temperatures given by Lewis and Rivett (12) seem in accord with other data. Data given by Wöhler and Dierksen (26) are not in particularly good agreement with the rest.

Sodium sulfite - sodium chloride - water. At 298.2 K, the data of Durymanova and Telepneva (9) are in reasonable agreement with those of Kobe and Hellwig (3), apart from at a part of the curve where Kobe and Hellwig appear to have reported a metastable region. The reported solid phases are NaCl and $\text{Na}_2\text{SO}_3 \cdot 7\text{H}_2\text{O}$, but the phase diagram in (9) suggests that there may be a region where mixed crystals are formed. The data given by Labash and Lusby (8) for 293.2 K seem to be reasonably in accord with (9). At 333.2 K the data of Labash and Lusby (8) agree reasonably with those of Kobe and Hellwig (3),

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<p>CRITICAL EVALUATION: (continued)</p> <p>apart from at one or two points. At this temperature, the phase diagram does appear to show a simple eutonic system, with NaCl and Na_2SO_3 being the solid phases.</p> <p><u>Sodium sulfite - sodium pyrosulfite - water.</u> Data for this system are available at 273.2 K (16), 288.2 K (19), 298.2 K (19, 23), 308.2 K (19, 23), 318.2 K (19), 333.2 K (18) and 273.2 K (17). For 298.2 K, the data are in good but not perfect agreement. At 308.2 K, the data show the same trends, but differ by about 1 - 2%. At all temperatures, a simple eutonic system is observed; at 298.2 K and below, the solid phases are $\text{Na}_2\text{SO}_3 \cdot 7\text{H}_2\text{O}$ and $\text{Na}_2\text{S}_2\text{O}_5$, and at 308.2 K and above, they are Na_2SO_3 and $\text{Na}_2\text{S}_2\text{O}_5$.</p> <p><u>Sodium sulfite - ammonium sulfite - water.</u> Data are reported by Labash and Lusby (8) for 293.2 and 333.2 K, and by Zil'berman and Ivanov (20) for 333.2 and 358.2 K. The data at 333.2 K are in reasonable agreement.</p> <p><u>Sodium sulfite - sodium thiosulfate - water.</u> Data are given by Palkina (15) for 273.2 - 298.2 K, by Mochalov and Monina (21) for 288.2 K, and by Wöhler and Dierksen (26) for 296.2 - 353.2 K. At 288.2 K, the data for the sulfite branch of the solubility curve are in good agreement, but Mochalov and Monina found about 1% more thiosulfate in the thiosulfate branch.</p> <p><u>Other ternary systems.</u> The system sodium sulfite - ethanol - water has been studied by Navrátil and Nývlt (7) and Klebanov and Ostapkevich (22), but the data are not directly comparable. The data in (7) are suspect, because the binary data extracted were found to be unreliable. The system sodium sulfite - sodium hydroxide - water was studied by Hammick and Currie (6) at temperatures from 273.3 K to 305.2 K. The system sodium sulfite - sodium 2-naphtholate - water was studied by Teslo et al. (25) at temperatures between 313.2 and 375.2 K.</p> <p>MORE COMPLEX SYSTEMS</p> <p>Systems involving sodium sulfite, water, with sodium sulfate and sodium chloride (9, 10); with sodium pyrosulfite and sodium sulfate (11, 27, 33), with ammonium sulfite, ammonium chloride and sodium chloride (20, 30); and with 2-naphthol and sodium hydroxide (29) have been studied. No comparisons were possible, however.</p> <p>REFERENCES</p> <ol style="list-style-type: none"> 1. Hartley, H.; Barrett, W.H. <i>J. Chem. Soc.</i> <u>1909</u>, 95, 1178. 2. Foerster, F.; Brosche, A.; Norberg-Schutz, Chr. <i>Z. Phys. Chem.</i> <u>1924</u>, 10, 435. 3. Kobe, K.A.; Hellwig, K.C. <i>Ind. Eng. Chem.</i> <u>1955</u>, 47, 1116. 4. Rodnyanskii, I.M.; Galinker, I.S. <i>Tf. Khar'kovsk Sel'skokhoz. Inst.</i> <u>1961</u>, 35, 69. 	

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CRITICAL EVALUATION: (continued)	
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<p>CRITICAL EVALUATION: (continued)</p> <ol style="list-style-type: none">30. Labash, J.A.; Lusby, G.R. <i>Can. J. Chem.</i> <u>1955</u>, 33, 787.31. Arii, K. <i>Sci. Rep. Tohoku Imp. Univ.</i> <u>1932</u>, 21, 772.32. Kuznetsova, A.G.; Sedova, V.A. <i>VINITI Deposited Document</i> <u>1981</u>, 5710-81.33. Kuznetsova, A.G.; Sedova, V.A. <i>VINITI Deposited Document</i> <u>1981</u>, 5711-81.	