CXXXII.—*Sodium Sulphite and its Equilibrium with Water.**

By HAROLD HARTLEY and WILLIAM HENRY BARRETT.

IN the course of an investigation of the products of crystallisation of mixed solutions of sodium and potassium sulphites, it was found necessary to determine the properties of the end members of the series as little information was available concerning them.

Sodium sulphite has been studied previously by Fourcroy (Comey, *Dictionary of Solubilities*, 1896, p. 464), Mitscherlich (*Pogg. Annalen*, 1827, **12**, 140), Rammelsberg (*Pogg. Annalen*, 1846, **67**, 246; 1855, **94**, 507), Muspratt (*Phil. Mag.*, 1847, [iii], **30**, 414), Marignac (*Ann. des Mines*, 1857, [v], **12**, 32), Kremers (*Pogg. Annalen*, 1856, **99**, 50), Des Cloizeaux (*Ann. des Mines*, 1857, [v], **11**, 347; 1858, [v], **14**, 391), Schultz-Sellack (*J. pr. Chem.*, 1870, [ii], **2**, 459), de Forcrand (*Ann. Chim. Phys.*, 1884, [vi], **3**, 243), Röhrig (*J. pr. Chem.*, 1888, [ii], **37**, 222), Hartog (*Compt. rend.*, 1889, **109**, 179, 221, 436), Traube (*Zeitsch. f. Kryst. Min.*, 1894, **22**, 143), and Barth (*Zeitsch. physikal. Chem.*, 1892, **9**, 176).

Three forms have been described by one or other of the above authors, namely, Na_2SO_3 , $\text{Na}_2\text{SO}_3 \cdot 7\text{H}_2\text{O}$, and $\text{Na}_2\text{SO}_3 \cdot 10\text{H}_2\text{O}$. Of these the heptahydrate is stable at low temperatures, and the anhydrous salt at high. The decahydrate, first described by Muspratt, is a labile modification; its existence has been questioned by Schultz-Sellack and Röhrig, and we have failed to isolate it in spite of a large number of attempts under different conditions; however, the formation of mixed crystals of $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ and $\text{Na}_2\text{SO}_3 \cdot 10\text{H}_2\text{O}$, observed by Traube

* This title is substituted for that given in the abstract (*Proc.*, 1909, **25**, 164).

(*loc. cit.*), makes it probable that the decahydrate might [View Online](#) crystallise under exceptional circumstances. The present paper deals with the preparation of pure sodium sulphite, the properties of the anhydrous salt, the solubility of sodium sulphite in water, and the spontaneous crystallisation of its supersaturated solutions.

Preparation of Materials.

As the hydrated salt oxidises very readily in air, whilst the anhydrous modification is stable so long as it is kept dry, a quantity of pure anhydrous salt was prepared for use in the determinations. For this purpose, 40 grams of Merck's pure sodium carbonate were dissolved in 120 grams of air-free water, and a current of sulphur dioxide passed into the solution until the gain in weight showed that it was converted into sodium hydrogen sulphite; an equal quantity of sodium carbonate solution was then added, and the solution was quickly transferred to the vessel, *A* (Fig. 1), containing hydrogen, whence it was filtered through glass wool into the vessel *B*, which was surrounded by a bath of brine kept at a temperature of over 100° by blowing in steam. As the anhydrous salt is less soluble than the hydrated form above 22° , it crystallises when the temperature of the solution is raised, and the yield is increased by evaporating the solution in a stream of hydrogen. After some hours, the solution was drawn off by the tube *D*, the crystals being stopped by a small glass plug. The crystals were first washed with a mixture of alcohol and water, then with alcohol, and finally dried, all the operations being carried on in an atmosphere of hydrogen. The yield varied from 11 to 24 grams. The salt prepared by this method was free from sulphate. It was analysed by oxidising a known weight with bromine water and determining the sulphate by precipitation with barium chloride. The specimen used in the solubility determinations gave the following results :

0.6674 gave 1.2334 BaSO_4 . $\text{SO}_3 = 63.34$.

Na_2SO_3 requires $\text{SO}_3 = 63.47$ per cent.

FIG. 1.

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The salt therefore contained 99·87 per cent. of pure sodium sulphite. The results of two other analyses gave $\text{SO}_3 = 63\cdot23$ and $63\cdot37$ respectively. For experiments where the hydrated salt was required, a specimen recrystallised in hydrogen was used, but this never contained less than one per cent. of sulphate as an impurity.

FIG. 2.

Crystalline Form.

The crystalline form of hydrated sodium sulphite has been investigated by Rammelsberg (*loc. cit.*), Marignac (*loc. cit.*), and Des Cloizeaux (*loc. cit.*), who showed it to belong to the prismatic class of the monoclinic system with the axial ratios :

$$a : b : c = 1\cdot5728 : 1 : 1\cdot1694 ; \beta = 93^\circ 36'.$$

The anhydrous salt had not been investigated before. It crystallises in short, hexagonal prisms terminated by a basal plane and pyramid faces as shown in Fig. 2. The crystals were small, and the faces gave poor reflections.

System : Hexagonal (probably holohedral).

Axial ratios : $a : c = 1 : 1\cdot1246$.

Forms observed : $c\{0001\}$, $m\{10\bar{1}0\}$, $x\{10\bar{1}1\}$, $p\{10\bar{1}2\}$, $s\{11\bar{2}1\}$.

Angle measured.	Readings.	Limits.	Mean.	Calculated.
$c : x = 0001 : 10\bar{1}1$	13	$52^\circ 36' - 52^\circ 4'$	$52^\circ 24'$	—
$c : p = 0001 : 10\bar{1}2$	6	$32^\circ 54' - 31^\circ 48'$	$32^\circ 16'$	$32^\circ 59'$
$c : s = 0001 : 11\bar{2}1$	6	$66^\circ 30' - 65^\circ 0'$	$65^\circ 40'$	$66^\circ 2'$

The crystals possess a perfect cleavage parallel to the basal plane, they are strongly birefringent, cleavage fragments showing a uniaxial figure of negative character in convergent light.

The densities of both hydrated and anhydrous crystals were determined by the method of flotation in a mixture of xylene and acetylene tetrabromide with the following results :

$\text{Na}_2\text{SO}_3 \cdot 7\text{H}_2\text{O}.$		$\text{Na}_2\text{SO}_3.$	
Temperature of observation.	$\Delta_4^{15}.$	Temperature of observation.	$\Delta_4^{15}.$
15·2°	1·5934	15·4°	2·6327
15·2	1·5944	15·0	2·6352
15·2	1·5944	15·4	2·6319
14·8	1·5934	15·4	2·6336
13·8	1·5945	15·4	2·6341
Mean.....	1·5939	Mean.....	2·6334

Buignet (*J. Pharm.*, 1861, [iii], 40, 161, 337) gives a value for the specific gravity of the hydrated salt of 1.561. [View Online](#)

Solubility Relations.

Freezing Points.—The freezing points of dilute solutions of sodium sulphite were found by the ordinary Beckmann method, the determinations being carried out in an atmosphere of hydrogen. The results are given in the following table, and are plotted in Fig. 3. The salt was added in the anhydrous condition, and owing to the sluggish transformation of the anhydrous salt into the less soluble hydrated modification, it was possible to prolong the freezing-point curve into the metastable region.

Na ₂ SO ₃ in grams.	Water in grams.	Parts of Na ₂ SO ₃ per 100 of water.	Temperature.
0.6888	32.3310	2.15	-0.76°
1.3623	32.3310	4.21	1.37
2.0330	32.3310	6.29	1.96
3.0350	32.3310	9.44	2.77
4.0355	32.3310	12.48	3.51
2.2980	13.3786	17.91	4.50

Na₂SO₃·7H₂O.—The solubility of the hydrated salt was determined by the sealed tube method, as described by Hartley and Thomas (*Trans.*, 1906, 89, 1016). Weighed amounts of salt and water were sealed up in small tubes, and two temperatures were found differing by about 0.4°, at the higher of which one or two small crystals were seen to dissolve, and at the lower to grow. The mean of these temperatures was taken as that of equilibrium of a solution of this concentration with the solid phase. The method gave satisfactory results, owing to the steep slope of the solubility curve, and was particularly convenient, as it avoided all difficulties arising from the oxidation of the solution. The results are given in the following table, and are plotted in Fig. 3.

Na ₂ SO ₃ in grams.	Water in grams.	Parts of Na ₂ SO ₃ per 100 parts of water.	Temperature.
0.4519	1.0252	44.08	37.2°
0.4270	1.0772	39.64	33.5
0.4394	1.2557	34.99	29.0
0.2991	0.9997	29.92	23.5
0.3258	1.2870	25.31	18.2
0.2423	1.2970	20.01	10.6
0.1300	0.7379	17.61	5.9
0.2626	1.7723	14.82	2.0
0.1440	1.1000	13.09	-1.9

It will be seen that the solubility curve cuts the ice curve at -3.5°, this being the cryohydric temperature.

Anhydrous Salt.—The tube method could not be used in this case owing to the small temperature-coefficient of the solubility and the

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slowness with which equilibrium is attained. Excess of the anhydrous salt was therefore stirred with water in a bottle containing hydrogen, air being excluded as far as possible by mercury traps. Portions of the solution were withdrawn and analysed from time to time. In the earlier determinations a weighed amount of solution was oxidised by means of bromine water, and the sulphite determined as sulphate. By this method the true solubility was increased by any sulphate formed

FIG. 3.

by leakage of air into the solubility bottle, and the results were found to be untrustworthy.

In order to obtain a direct estimation of the sulphite, a portion of the solution was drawn off through a glass wool filter into a weighed flask containing a known quantity of iodine solution, the flask was again weighed, and the excess of iodine determined by means of standard thiosulphate. Giles and Shearer (*J. Soc. Chem. Ind.*, 1884,

3, 187) have shown that under these conditions oxidation takes place according to the equation :

(compare also Volhard, *Annalen*, 1887, **242**, 94).

The results of two series of experiments are given in the following table :

Time stirred in hours.	Iodine solution in grams.	Na_2SO_3 solution in grams.	Excess of iodine solution in grams.	Parts of Na_2SO_3 per 100 of water.	Temperature.
<i>Series I.</i>					
11	99·81	5·933	28·56	28·29	60·4°
13	102·64	6·543	22·69	28·89	59·8
25	107·84	6·349	30·83	28·65	59·8
27	104·56	6·424	26·37	28·75	59·8
<i>Series II.</i>					
96	110·09	9·479	24·53	28·01	37·0
96	109·48	10·800	11·87	28·07	37·0
48	108·71	9·993	17·92	28·19	47·0
100	108·33	10·960	9·27	28·07	47·0
19	110·69	9·242	26·82	28·21	55·6
7	111·04	9·934	20·76	28·26	84·0

These numbers indicate that the solubility of the anhydrous salt is almost independent of the temperature, and that the transition point of the two modifications lies in the neighbourhood of 21·6°. This point was determined independently by means of a dilatometer. The volume of one gram-molecule of the hydrated salt is 158 c.c., while the volume occupied by the same weight of anhydrous salt and water is 178 c.c., the decomposition of the hydrated salt being thus accompanied by an increase of volume. A finely powdered mixture of anhydrous and hydrated salts was placed in the bulb of a dilatometer, which was then sealed off and filled with turpentine. It was placed in a thermostat with an electric regulator, and the readings of the level of the turpentine in the neighbourhood of the transition point were as follows :

Bath temp. = 21·89°.		Bath temp. = 22·09°.		Bath temp. = 22·69°.	
Hours in bath.	Scale reading.	Hours in bath.	Scale reading.	Hours in bath.	Scale reading.
0	146·6	0	146·1	0	145·7
5	145·4	1	146·1	3	145·8
6	145·3	6	146·1	18	146·5
8	145·2	9	146·1	20	146·6
20	144·5	20	146·1	23	146·9

These numbers indicate a transition temperature in the neighbourhood of 22·1°. The transition is extremely sluggish, less than 0·1 per cent.

of the hydrated salt being transformed to the anhydrous variety in twenty hours, when it is 0.6° above the transition temperature. The agreement between the transition temperatures determined by these two methods (21.6° and 22.1°) is as close as was expected in view of the difficulty of determining the solubility of the anhydrous salt.

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Spontaneous Crystallisation of Supersaturated Solutions.

The conditions under which ice and salt separate spontaneously from supersaturated solutions of sodium sulphite were investigated in exactly the same manner as in the similar case of sodium sulphate (Hartley, Jones and Hutchinson, Trans., 1907, 93, 825). Sealed tubes containing solutions freed from crystalline nuclei were cooled down, while they were constantly shaken until crystallisation occurred. One set of experiments was made with tubes containing solid matter and another without, in every case tubes containing solid which produced friction during shaking crystallised at a slightly higher temperature than those which did not. The occurrence of crystallisation was definite in both cases, in spite of the fact that sodium sulphite has the largest metastable region (approximately 30°) that has yet been recorded for a salt solution.

The results are given in the following tables, and the supersolubility curves in presence of solid matter are plotted with the solubility curves in Fig. 3. A comparison of the numbers in the two tables will show that the supersolubility curves in the absence of solid matter lie just outside those drawn in the figure.

Tubes Containing only Solution.

Na_2SO_3 in grams.	Water in grams.	Parts of Na_2SO_3 per 100 parts of water.	Temperature at which spontaneous crys- tallisation occurred.
0.4519	1.0252	44.08	10.6° S.
0.4270	1.0772	39.84	4.3° S.
0.3977	1.0790	36.86	-0.1° S.
0.4394	1.2557	34.99	-3.1° S.
0.4325	1.2215	34.67	-3.5° S.
0.2991	0.9997	29.92	-10.55° S.
0.3528	1.2870	25.32	-9.7° I.
0.2423	1.2070	20.02	-8.05° I.
0.2626	1.7723	14.82	-6.15° I.
0.2315	2.3380	9.92	-4.5° I.
0.1025	2.0325	5.04	-2.8° I.

Tubes with Solid Matter.

Na_2SO_3 in grams.	Water in grams.		Parts of Na_2SO_3 per 100 parts of water.	Temperature at which spontaneous crys- tallisation occurred.
0.2393	0.5870	Glass	40.75	7.9 S.
0.2360	0.6884	"	34.28	-1.6 S.
0.1698	0.5516	"	30.80	-7.3 S.
0.8197	2.7750	Garnets	29.54	-9.2 IS.
0.2187	0.8407	Glass	26.01	-8.9 I.
0.6393	2.5317	"	25.25	-8.7 I.
0.4770	2.3674	Garnets	20.15	-7.6 I.
0.2735	1.1414	"	19.34	-7.4 I.
0.1322	0.8943	Glass	16.43	-6.4 I.
0.1911	1.4778	"	12.93	-5.2 I.
0.1664	1.6623	"	10.00	-4.3 I.
0.1178	1.9381	"	6.10	-3.0 I.
0.0569	1.4204	"	4.06	-2.4 I.
0.0426	2.2516	"	1.89	-1.3 I.

S indicates that $\text{Na}_2\text{SO}_3 \cdot 7\text{H}_2\text{O}$ was produced.

I " " ice " "

In one case indicated by IS both phases were observed, this being the hypertectic point.

Water was found to crystallise at -1.0° in absence of solid, and at -0.6° when shaken with fragments of glass.

In no case was there any evidence of the spontaneous crystallisation of a hydrate other than $\text{Na}_2\text{SO}_3 \cdot 7\text{H}_2\text{O}$.

Summary.

1. Sodium sulphite exists in two stable modifications, $\text{Na}_2\text{SO}_3 \cdot 7\text{H}_2\text{O}$ and Na_2SO_3 , with a transition point in the neighbourhood of 22° .

2. The hydrated salt crystallises in the monoclinic system, the anhydrous in the hexagonal system.

3. Solubility curves have been traced for both modifications, also the freezing-point curve of dilute solutions.

4. The conditions under which spontaneous crystallisation of solutions of this salt takes place have been investigated, and super-solubility curves have been plotted for ice and $\text{Na}_2\text{SO}_3 \cdot 7\text{H}_2\text{O}$; the extent of the metastable region in the latter case corresponds with about 30° .

PHYSICAL CHEMISTRY LABORATORY,
BALLIOL AND TRINITY COLLEGE,
OXFORD.