On the System: Sodium Sulphate—Sodium Chromate—Water. II.

By

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In our laboratory, I. Takeuchi[1] studied, on the suggestion of one of the authors, the heterogeneous equilibria in the system of sodium sulphate, sodium chromate and water at 15° and 25°. This article is a continuation of that work.

The transition points of the hydrates of sodium sulphate and chromate are as follows, as given in the literature:

$$Na_2SO_4 \cdot 10H_2O \underset{32.383^\circ}{\rightleftarrows} Na_2SO_4 + 10H_2O,^2$$

$$Na_2CrO_4 \cdot 10H_2O \underset{19.52^\circ}{\rightleftarrows} Na_2CrO_4 \cdot 6H_2O + 4H_2O,^3$$

$$Na_2CrO_4 \cdot 6H_2O \underset{26.6^\circ}{\rightleftarrows} Na_2CrO_4 \cdot 4H_2O + 2H_2O,^3$$

$$Na_2CrO_4 \cdot 4H_2O \underset{62.8^\circ}{\rightleftarrows} Na_2CrO_4 + 4H_2O.^3$$

Takeuchi has shown that the two salts have complete miscibilty as a solid solution at 15°, at which they are both decahydrate and isomorphous, but that at 25°, at which the sulphate is still decahydrate, while the chromate hexahydrate, the sulphate dissolves the chromate as a decahydrated solid solution to the extent of the molar fraction of 0·34, but the chromate hexahydrate can not take up the sulphate at all. He showed also that when the amount of the chromate in the solution exceeds a 77 molar percentage of the total salts, the sulphate separates

[1] Mem. Col. Sci. Kyoto Imp. Univ., **1**, 249 (1915).

[2] Richards and Wells, Zeitschr. physik. Chem., **43**, 471 (1903).

[3] Richards and Kelly, J. Amer. Chem. Soc., **33**, 847 (1911).

out as the anhydrous salt. The present authors took up the further study of the equilibria in the same system at 28°, 31° and 33°.

Sodium sulphate, Jap. Pharm., was thrice recrystallised and used in fine crystals of the decahydrate. As to the chromate, the pure preparation of C. Merck was recrystallised and it was also prepared from the bichromate after Richards.[1] The limits of the temperature of the existence of the hexahydrate are narrow, and as it was found difficult to obtain it from its supersaturated solution when there was no sample of the hexahydrate to be used as the crystallisation nucleus, the following method was devised: The decahydrate is heated above 21° and some water is driven off from the fused mass by evaporation. It is then cooled below 19° and the solidified mass is heated again above 21°. The decahydrate fuses and the hexahydrate remains as crystals.

The experimental methods were the same as those of Takeuchi in the essential points.

The results of the experiments are given in Tables 1, 2, and 3 and Figures 1, 2, and 3, where the compositions of the solutions and residues (in some cases somewhat moist with the mother liquor) are represented by the formula:

$$100mH_2O\ xNa_2CrO_4\ (100-x)\ Na_2SO_4.$$

TABLE I.

Temperature: 28·0°.

No.	Solution.		Residue.	
	x	m	x	m
1	0·00	22·10	0·00	10·00
2	8·15	21·47	0·84	10·58
3	25·15	20·32	4·96	9·98
4	26·18	19·66	4·94	10·60
5	33·39	18·29	5·48	9·81
6	40·51	17·37	—	—
7	44·09	16·87	14·35	10·14
8	47·87	16·51	12·17	9·80
9	54·88	14·68	12·32	7·79
10	55·55	14·76	12·76	7·78
11	54·70	14·64	10·63	7·00
12	55·91	14·88	6·69	1·88
13	56·40	15·03	8·05	2·23

[1] Richards and Kelly, *Loc. cit.*

No.	Solution.		Residue.	
	x	m	x	m
14	56·72	15·37	9·41	2·33
15	60·89	14·96	6·12	1·56
16	62·35	14·47	9·36	2·22
17	63·03	14·53	5·89	1·09
18	64·31	14·32	10·36	2·39
19	69·98	14·12	8·53	1·66
20	79·38	13·35	11·60	1·85
21	91·35	11·34	7·71	0·84
22	95·64	10·37	63·22	2·91
23	94·78	10·52	87·63	4·28
24	94·36	10·47	85·14	4·09
25	98·19	10·20	100·00	4·39
26	100·00	10·51	100·00	4·32

Fig. 1.

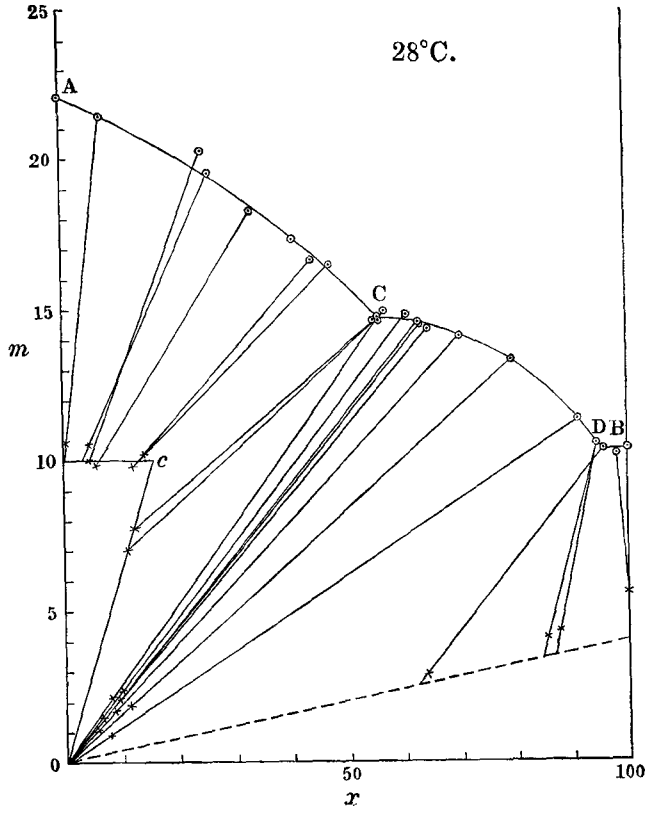


TABLE II.

Temperature : 31·0°.

No.	Solution.		Residue.	
	x	m	x'	m'
1	0 00	17·88	0·00	10·00
2	3·81	17·51	0·49	10·43
3	8·46	16·98	1·23	10·48
4	10.39	16·72	1·59	10·22
5	13·67	16·33	2·89	10·14
6	17·12	16·07	3·34	10·30
7	17·46	15·99	—	—
8	18·60	15·90	3·87	9·54
9	21.31	15·70	4·11	9·51
10	27 02	15 64	3·16	1·83
11	29·18	15·77	3·57	1·82
12	37·99	15·90	4·85	1·96
13	51·05	15·19	3·90	0·90
14	76.90	13·66	10·77	1·91
15	88·14	12·24	9·28	1·22
16	95·51	9·85	89·29	4·16
17	96 35	9·86	99·02	4·47
18	93·55	9·80	95·83	4·30
19	100·00	10·24	100·00	4·22

Fig. 2.

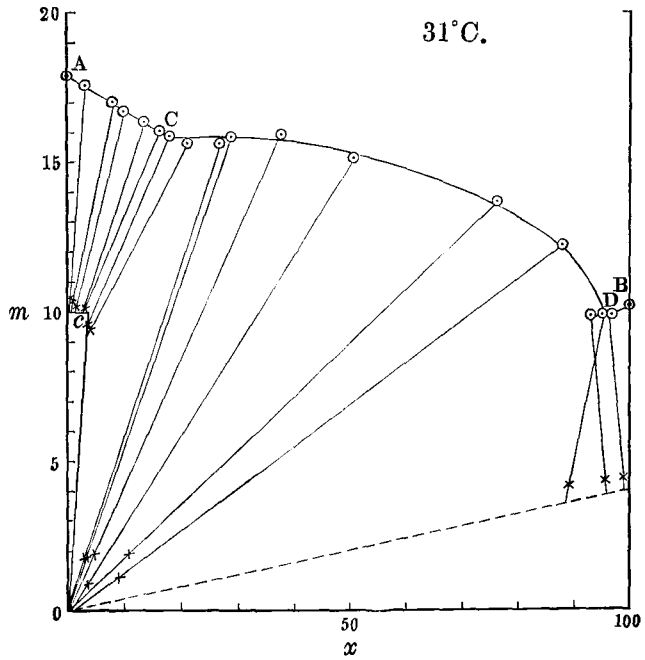
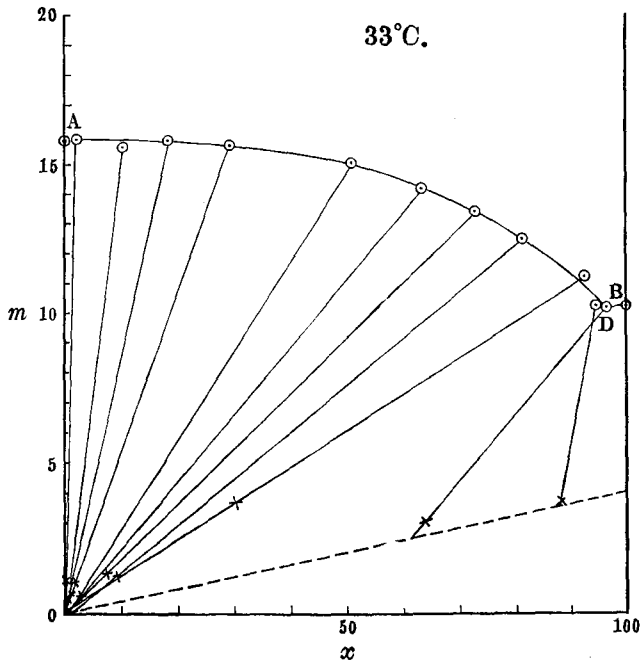


TABLE III.

Temperature: 33·0°.

No.	Solution.		Residue.	
	x	m	x	m
1	0.00	15.83	0.00	0.00
2	2.55	15.92	0.19	1.08
3	10.70	15.59	0.22	0.10
4	18.64	15.77	0.67	0.52
5	29.40	15.59	1.28	0.63
6	51.53	15.04	2.71	0.64
7	63.64	14.14	3.06	0.61
8	73.55	13.48	7.29	1.42
9	83.38	12.47	9.18	1.32
10	92.42	11.24	30.69	3.16
11	94.28	10.23	87.94	3.71
12	96.37	10.20	63.61	3.10
13	100.00	10.25	100.00	4.52

Fig. 3.



At 28° and 31°, the chromate is tetrahydrated and the solubility of the chromate in the sulphate as the decahydrate decreases as the temperature rises. It is estimated from the diagrams that the molar fractions of the chromate in the saturated solid solutions are 0·16 at 28° and 0·04 at 31°. Takeuchi noticed that the corresponding number at 25° is about 0·34 and it agrees approximately with the formula $2Na_2SO_4 \cdot Na_2CrO_4 \cdot 30H_2O$. It is certain, however that this is a mere accident and the saturated solid solution is no compound, as it may be seen from the above data at 28° and 31° and also from the experimental data, not published, that the molar fraction of the chromate in the saturated solid solution at 22° is ca. 0·8.

According to Th. W. Richards and W. B. Meldrum,[1] the tetrahydrate of sodium chromate takes up to a small extent the sulphate as tetrahydrate. Unfortunately, this interesting paper came to the notice of the authors when their work was ended, and as our results were insufficient to show the existence of those solid solutions, this fact was not taken into consideration in the diagrams and dotted lines were used for the unascertained parts.

The point, D, representing the solution saturated with the anhydrous sulphate and the tetrahydrated chromate (or that saturated with the sulphate), moves slightly to the right as the temperature rises.

At 33°, the sulphate is already anhydrous and no solid solution of the decahydrate exists, and as to the tetrahydrated chromate, what stated above applies in this case.

Summary.

The heterogeneous equilibria in the system of sodium sulphate, sodium chromate and water at 28°, 31° and 33° have been described and illustrated by diagrams.

[1] J. Amer. Chem. Soc., **43**, 1542 (1921).