

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

By

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It is a familiar fact that there exist mixed crystals between sodium sulphate and sodium chromate; but no systematic study from the stand point of the phase rule has yet been published.

Sodium chromate forms three hydrates, namely, deca-, hexa- and tetrahydrates, of which the first is isomorphous with the decahydrate of sodium sulphate. A few data given by T. W. Richards¹ refer to the relative composition of mixed crystals of decahydrates and mother liquor. The present article is an account of the result of a study on the equilibriums of the system at 15.0° and 25.0°.

Materials: Pure crystallised sodium sulphate, of E. Merck, was recrystallised as $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$. Sodium chromate neutral, of the same factory, was three times recrystallised as decahydrate $\text{Na}_2\text{CrO}_4 \cdot 10\text{H}_2\text{O}$, which was found to contain no other impurities than sodium sulphate. On standing its supersaturated solution at about 20° for crystallisation, hexahydrate $\text{Na}_2\text{CrO}_4 \cdot 6\text{H}_2\text{O}$ was prepared. As the crystals thus obtained contained a small quantity of sodium sulphate, pure salt, prepared by neutralizing sodium bichromate with pure sodium hydroxide after the method proposed by Richards², was used whereat the content of sodium chromate amounted to 95 per cent or more. Ordinary distilled water was used.

Method of Experiment: Mixtures of the three substances in different proportions were put each in an Erlenmeyer flask of capacity of about 30 cc. which was made to rotate in a thermostat. After one or two days when the equilibrium would have been attained, the content was filtered through cotton wool or filter paper to separate the saturated solution from the residue, filtration being carried out by means

¹ J. Am. Chem. Soc., 33, 855 (1911).

² *loc. cit.*, 849.

of a funnel and a receiver which had been immersed in the same thermostat. In order to remove the adhering mother liquor from the residue, the latter was pressed between folded filter paper previously warmed to about the same temperature as that of the thermostat.

Method of Analysis: Chromate was estimated by the ordinary method of iodimetry. Sulphate was determined as barium sulphate after reducing the chromate to the chromic salt with hydrochloric acid and alcohol. The precipitation of barium sulphate produced in this way was not always quite free from chromic salt, but the latter did not considerably affect the result. The residue was heated in a hard glass tube drawn out upward at both ends¹ at 150°–200° and the water, which might be contained as water of crystallisation, driven off. The amounts of water in the residue and in the solution were both found by subtraction. It was impossible to remove perfectly the adhering mother liquor from the residue, and consequently it had sometimes to be determined graphically by extrapolation.

The results were as follows :

TABLE I.
Temperature: 15.0°

No.	Composition of solution in gram percentage.			Composition of residue in gram percentage.		
	Na ₂ CrO ₄	Na ₂ SO ₄	H ₂ O	Na ₂ CrO ₄	Na ₂ SO ₄	H ₂ O
1	0	11.70	88.30	0	44.08	55.92
2	2.42	10.58	87.00	0.66	42.29	57.05
3	3.92	10.08	86.00	1.25	41.90	56.85
4	6.72	9.24	84.04	1.95	40.89	57.16
5	8.91	8.35	82.74	2.68	40.97	56.35
6	11.51	7.57	80.92	3.96	39.41	56.63
7	14.90	6.41	78.69	6.12	37.71	56.17
8	15.14	6.43	78.43	6.63	37.15	56.22
9	20.03	5.05	74.92	10.96	33.15	55.89
10	22.83	4.33	72.84	13.60	30.72	55.68
11	24.21	4.23	71.56	15.94	29.04	55.02
12	26.06	3.78	70.16	18.78	25.77	55.45

¹ See Ostwald-Luther, *Physiko-Chemische Messungen.*, 3 Aufl., 264.

No.	Composing of solution in gram percentage.			Composition of residue in gram percentage.		
	Na ₂ CrO ₄	Na ₂ SO ₄	H ₂ O	Na ₂ CrO ₄	Na ₂ SO ₄	H ₂ O
13	28.49	3.18	69.33	22.89	22.37	54.74
14	31.34	2.32	66.34	29.03	16.39	54.58
15	33.34	1.55	65.11	35.48	10.71	53.81
16	33.90	1.31	64.79	38.62	7.49	53.89
17	36.44	0.47	63.09	43.66	2.96	53.38
18	37.17	0.24	62.59	46.06	1.06	52.88
19	37.45	0	62.55	47.35	0	52.65

If we take the formula $100m \text{ H}_2\text{O} \cdot x\text{Na}_2\text{CrO}_4 \cdot (100-x)\text{Na}_2\text{SO}_4$ to represent the compositions of the solution and of the residue, the last table gives the following :

TABLE II.

No.	Solution		Residue.	
	x	m	x	m
1	0	59.5	0	100
2	16.69	54.0	1.35	10.5
3	25.42	50.2	2.54	10.4
	38.94	43.8	4.03	10.6
5	48.32	40.4	5.41	10.2
6	57.18	36.1	8.11	10.4
7	67.07	31.9	12.46	10.3
8	67.36	31.4	13.55	10.3
9	77.66	26.1	22.48	10.3
10	82.22	23.6	27.96	10.3
11	83.37	22.2	32.48	10.1
12	85.81	20.8	39.52	10.5
13	88.71	19.1	47.28	10.2
14	92.22	17.6	60.84	10.3
15	94.98	16.7	74.40	10.2
16	95.80	16.5	81.90	10.3
17	98.56	15.4	92.83	10.2
18	19.27	15.0	97.44	10.1
19	100.00	15.0	100.00	10.0

The corresponding tables for the other temperature are as follows :

TABLE III.

Temperature : 25.0°.

No.	Composition of solution in gram percentage.			Composition of residue in gram percentage.		
	Na ₂ CrO ₄	Na ₂ SO ₄	H ₂ O	Na ₂ CrO ₄	Na ₂ SO ₄	H ₂ O
1	0	21.90	78.10	0	44.08	55.92
2	1.56	20.76	77.68	0.55	42.85	56.60
3	2.53	20.12	77.35	0.82	43.48	55.70
4	4.02	18.96	77.02	1.22	42.03	56.75
5	4.95	18.62	76.43	1.29	43.09	55.62
6	9.66	16.49	73.85	2.91	41.02	56.07
7	14.19	14.71	71.10	4.49	39.56	55.95
8	14.85	13.87	71.28	4.18	39.36	56.46
9	16.22	13.91	69.87	5.72	38.46	55.82
10	23.72	10.69	65.59	9.22	37.00	53.78
11	26.13	10.02	63.85	12.51	32.35	55.14
12	31.70	8.32	59.98	16.11	30.01	53.88
13	31.43	8.49	60.08	15.59	34.08	50.33
14	31.84	8.63	59.53	12.86	54.14	33.00
15	32.34	8.03	59.63	5.71	85.81	8.48
16	34.75	6.75	58.50	5.94	84.35	9.71
17	38.59	4.44	56.97	5.70	86.94	7.36
18	39.22	4.38	56.40	8.83	79.22	11.95
19	42.48	2.79	54.73	13.27	72.66	14.07
20	43.80	2.20	54.00	25.50	56.72	17.78
21	43.83	2.29	53.88	48.54	18.21	33.25
22	43.26	2.44	54.30	58.18	3.45	38.37
23	43.57	2.18	54.25	53.85	10.59	35.56
24	43.69	2.12	54.19	53.89	8.78	37.33
25	43.49	2.24	54.27	57.93	2.10	39.97
26	43.53	2.20	54.27	58.50	1.47	40.03
27	44.61	1.08	54.31	59.17	0.38	40.45
28	45.76	0	54.24	59.75	0	40.25

TABLE IV.

No.	Solution.		Residue.	
	x	m	x	m
1	0	28.1	0	100
2	6.19	27.7	1.11	103
3	9.94	27.3	1.62	99
4	15.68	27.0	2.48	104
5	18.93	26.2	2.55	99
6	33.93	23.3	5.85	102
7	45.70	21.3	9.06	100
8	48.43	20.9	8.53	104
9	50.57	19.6	11.56	101
10	66.12	16.4	17.92	94.1
11	69.57	15.3	25.33	100
12	76.97	13.1	32.00	96.4
13	76.44	13.2	28.63	83.1
14	76.39	12.8	17.23	40.0
15	77.95	12.9	5.52	0.74
16	81.87	12.4	5.82	0.86
17	88.40	11.7	5.44	0.62
18	88.71	11.5	8.90	1.08
19	93.06	10.8	13.81	1.32
20	94.57	10.5	28.27	1.77
21	94.41	10.4	70.03	4.31
22	93.96	10.6	93.67	5.55
23	94.60	10.6	81.67	4.85
24	94.76	10.6	84.32	5.25
25	94.46	10.6	96.03	5.96
26	94.55	10.6	97.23	5.98
27	97.30	10.7	99.29	6.14
28	100.00	10.6	100.00	6.00

The data in Tables II and IV are diagrammatically shown in Fig. 1 and Fig. 2 respectively, taking m as ordinates and x as abscissas.

From Fig. 1, it is seen that decahydrates of sodium chromate and sodium sulphate are mutually miscible in all proportions at 15.0°. The solubility curve, however, has a point of inflection from which we can suspect some discontinuity in the residue, probably at the point,

$x = \text{ca. } 33$, and this becomes conspicuous in the results at the other temperature.

From Fig. 2 it is clear that the solubility curve at 25.0° consists of three branches. The solutions represented by the first branch AB are in equilibrium with decahydrated mixed crystals which are represented by the points in the horizontal ab , b denoting the limiting composition of the mixed crystals. Thus the range of existence of mixed crystals at 25.0° is from 0 to about 34 mol. per cent of the chromate. When more chromate is added to the system, the mixed crystals are decomposed and give rise to the anhydrous sulphate, the composition of the solution remaining constant at B so long as the mixed crystals still remain. The solutions represented by the second branch BC are in equilibrium with anhydrous sulphate as the residue. In these cases the residue was a very fine powder and revealed its crystalline state only under a microscope, so that the adhering mother liquor could not be completely removed and this fact caused a somewhat remarkable error in the result. But in Fig. 2 the tie lines which connect the points in BC and their corresponding points representing the residues pass almost through the origin which represents anhydrous sodium sulphate, and, consequently, this salt must form the residue in those solutions.

The third branch of the solubility curve intersects with the second at C . One of the two solid phases with which the solution C is in equilibrium is obviously anhydrous sodium sulphate, the other is very likely pure hexahydrated chromate, since the straight line connecting the points representing anhydrous sulphate and pure hexahydrate passes through almost all the points which represent the residues with which the solution C is in equilibrium. Thus it seems that the hexahydrated sodium chromate does not form mixed crystals with the sulphate at 25.0° .

The point b which represents the limit of miscibility in the crystals is determined in Fig. 2 by the intersection of the straight line representing the residues which are in equilibrium with the solution B and the horizontal line representing ten mols of water. Within the limit of the error of the extrapolation, the composition of b is in good coincidence with that of a double salt $2\text{Na}_2\text{SO}_4 \cdot \text{Na}_2\text{CrO}_4 \cdot 30\text{H}_2\text{O}$. But further investigations are required for the conclusion of the existence of the double salt and to my regret, time has not allowed me the solution of the question.

To Prof. Y. Osaka, at whose suggestion this work was undertaken, the author wishes to express sincere thanks for his interest and advice.



Fig. 1.
Temperature : 15.°0

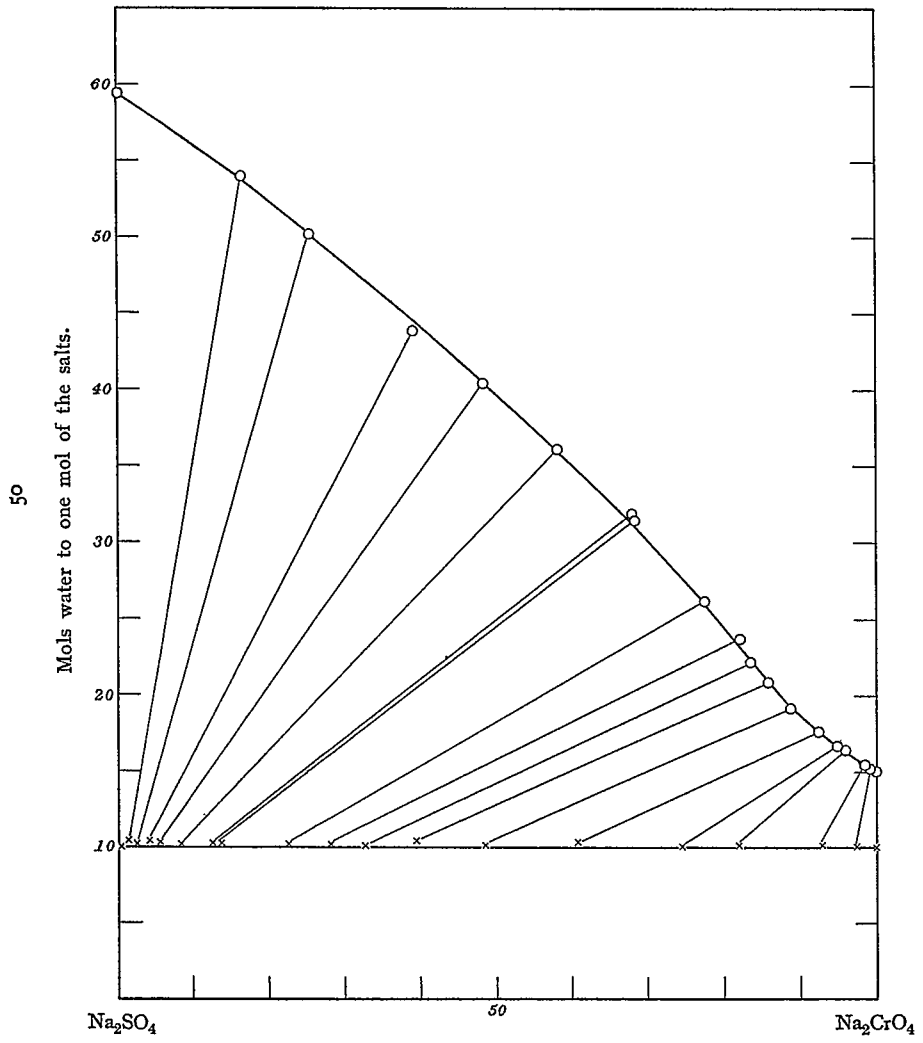


Fig. 2.
Temperature : 25.°0

