

# On the Equilibria in the Systems consisting of Ammonium Chromate, Ammonium Sulphate and Water, and Ammonium Chromate, Potassium Chromate and Water at 25° C.

By

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The solubilities of each of the compounds, ammonium chromate, ammonium sulphate, potassium chromate and potassium sulphate have been studied by several authors.<sup>1</sup> These four salts give four pairs of two salts with a common ion. The equilibrium in the system of ammonium sulphate, potassium sulphate and water, and that in the system of potassium chromate, potassium sulphate and water at 25° C., have been also investigated by Amadori<sup>2</sup> and by Fock<sup>3</sup> respectively. The writer has taken up, at the suggestion of Prof. Osaka, the study of the equilibria in the other two cases, namely the systems consisting of ammonium sulphate, ammonium chromate and water, and of ammonium chromate, potassium chromate and water, at 25° C.

At first the writer intended, after completing the study of the equilibria in the above-named systems of two salts with a common ion and water, to investigate the equilibrium in the system of the reciprocal salt pairs composed of the four salts in question, but to his great regret, he was prevented from continuing this work beyond the study of those two three-component systems which remained to be investigated.

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<sup>1</sup> Cf. Seidell's Solubilities of Inorganic and Organic Compounds, 2nd ed. (1921); Comey's A Dictionary of Solubilities of Inorganic Compounds, 2nd ed. (1921); Landolt, Bernstein, Roth, Schell, Tabellen 1 (1923).

<sup>2</sup> Amadori, Tables annuelles internationales de Constantes et Données numériques, vol. 3, 341.

<sup>3</sup> Fock, Seidell's Solubilities of Inorganic and Organic Compounds, p. 559.

**PART I.**

On the Equilibrium in the System:  
Ammonium Chromate, Ammonium Sulphate and Water at 25° C.

## MATERIALS.

Pure crystallised ammonium sulphate of Pharm. Jp. was twice recrystallised. During the recrystallisation, the amount of ammonia lost by evaporation was replaced by pouring a small quantity of aqueous ammonia into the solution from time to time. The crystals were used in the moist state, as the presence of the moisture is unobjectionable in this work.

As ammonium chromate could not be got commercially in a pure state, it was prepared, after the method of von Max Gröger<sup>1</sup> by adding an equivalent amount of 10 percent aqueous ammonia to a chromic oxide solution. The ammonium chromate thus prepared contained a little excess of ammonia, which was removed by repeated washing with water.

## EXPERIMENTAL PROCEDURE.

The experimental procedure was the usual one, as practised in this laboratory. The rotation of a mixed solution in an Erlenmeyer flask in a thermostat at 25° C., had to be continued four or five days before the equilibrium was attained.

## METHOD OF ANALYSIS.

The *chromate* was estimated by the ordinary method of iodimetry. The *ammonia* was determined by distillation of the sample with an addition of caustic soda to a known weight of 6.29 percent sulphuric acid and titrating back the excess of the acid with a standard solution of sodium hydroxide. At first, methyl orange was used as the indicator, but as it was difficult to ascertain exactly the final point of neutralization, alizarin red was used throughout the most part of this work. The amount of *sulphate* radical and of *water* were found by calculation. As the complete removal of some adhering mother liquor from the residue was impossible, its composition was determined by Schreinemakers' residue method.

<sup>1</sup> Zs. analyt. Chem., **58**, 412 (1908).

RESULTS.

The results are represented in Table I:

Table I.

No.	Composition of solution in gram percentages.			Composition of residue in gram percentages.		
	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	(NH <sub>4</sub> ) <sub>2</sub> CrO <sub>4</sub>	H <sub>2</sub> O	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	(NH <sub>4</sub> ) <sub>2</sub> CrO <sub>4</sub>	H <sub>2</sub> O
1	43.41	0.00	56.59	98.97	0.00	1.03
2	39.73	3.67	56.60	95.91	3.03	1.06
3	39.13	4.22	56.65	95.53	5.44	1.03
4	39.11	4.23	56.66	89.43	9.53	1.04
5	39.96	4.36	56.78	78.08	20.89	1.03
6	37.72	4.51	57.77	70.57	28.42	1.01
7	38.06	4.88	57.05	55.74	43.22	1.04
8	34.82	6.98	58.20	36.15	62.82	1.03
9	30.81	9.04	60.15	12.82	86.14	1.04
10	26.81	11.73	62.46	6.47	92.48	1.05
11	17.13	16.76	66.11	2.72	96.20	1.08
12	14.97	17.76	67.36	0.94	98.05	1.01
13	2.78	23.22	74.00	0.16	98.76	1.08
14	0.00	25.16	74.84	0.00	98.94	1.06

If we take the formula,  $100m\text{H}_2\text{O} \cdot x(\text{NH}_4)_2\text{CrO}_4 \cdot (100-x)(\text{NH}_4)_2\text{SO}_4$ , to represent the composition of the solution and the residue, the data in the last table lead to the following results:

Table II.

No.	Solution.		Residue.	
	<i>m</i>	<i>x</i>	<i>m</i>	<i>x</i>
1	9.56	0.00	0.09	0.00
2	9.71	7.46	0.08	2.68
3	9.71	8.56	0.08	5.98
4	9.71	8.59	0.08	8.47

5	9.74	8.85	0.08	18.86
6	10.17	9.41	0.08	25.88
7	9.89	10.02	0.08	40.25
8	10.45	14.84	0.08	60.25
9	11.41	20.31	0.08	82.26
10	12.38	27.54	0.09	92.57
11	15.30	45.95	0.09	96.91
12	16.29	50.63	0.09	98.91
13	23.71	88.12	0.09	99.81
14	25.11	100.00	0.09	100.00

The equilibrium relation of this system can be plotted, the data in Table II being taken as the coordinates, as shown in Fig. I.

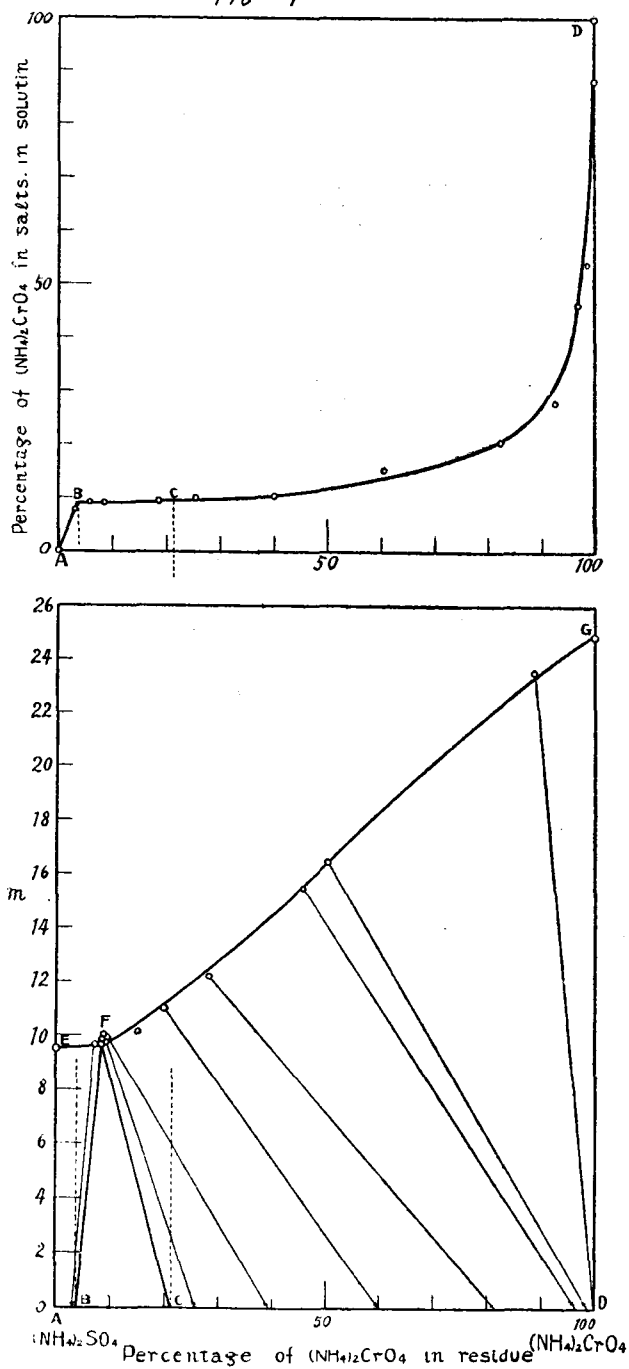
In the upper part of the figure, the relations between the molal percentages of the two salts in the liquid solutions and in the solid solutions are represented by a square diagram, the vertical side referring to the former and the horizontal side to the latter, the amounts of water in both phases not being taken into consideration.

The curve, AB, represents a series of solid solutions of ammonium chromate in ammonium sulphate and at B the solid solution becomes saturated. This point corresponds to 8.56 molal percentage of ammonium chromate in the liquid solution and 2.90 in the solid solution. When more ammonium chromate is added to the liquid solution, another kind of solid solution is produced, which is to be considered as the saturated solid solution of ammonium sulphate in ammonium chromate. When more ammonium chromate is added, the first solid solution gradually decreases and the second one increases. So long as they are both present, the liquid solution, as the theory demands, does not change its composition at all. As may be seen from the figure the position of the point C is difficult to determine exactly, but the composition of the residue which corresponds to it is estimated to be 21.50 in molal percentage. Thus, at 25° C., no solid solution of ammonium chromate and ammonium sulphate, which contains the former in a molal percentage between 2.90 and 21.50, exists.

The curve, CD, represents the second series of solid solutions.

In the lower part of the figure, the data in Table II are plotted referring to a rectangle, measuring  $m$  along the vertical side and  $x$  along the horizontal side. It is clear that the solubility curve of the two ammonium salts at 25° C. consists of two branches. The liquid solutions, represented by the first branch EF, are in equilibrium with the first

Fig 1



series of solid solutions, denoted by the points on the horizontal line AB. The compositions of these liquid solutions represented by the branch EF change gradually from  $[(\text{NH}_4)_2(\text{SO}_4, \text{CrO}_4)] \cdot 9.56\text{H}_2\text{O}$  to  $[(\text{NH}_4)_2(\text{SO}_4, \text{CrO}_4)] \cdot 9.71\text{H}_2\text{O}$ .

The other branch, FG, represents the liquid solutions in equilibrium with the second series of solid solutions, denoted by the points on the line CD. The compositions of these liquid solutions change from  $[(\text{NH}_4)_2(\text{SO}_4, \text{CrO}_4)] \cdot 9.71\text{H}_2\text{O}$  to  $[(\text{NH}_4)_2(\text{SO}_4, \text{CrO}_4)] \cdot 25.11\text{H}_2\text{O}$ .

## PART II.

On the Equilibrium in the System:

Potassium Chromate, Ammonium Chromate and Water at 25° C.

### MATERIALS.

Potassium chromate from C. Merck was twice recrystallised. The ammonium chromate was the same as that used in Part I.

### EXPERIMENTAL PROCEDURE.

The experimental procedure was similar to that practised in Part I.

### THE METHOD OF ANALYSIS.

The *ammonium* and *chromate* were estimated by the same method as in Part I. The amounts of *potassium* and of *water* were found by calculation.

### RESULTS.

The results of the experiments were as follows:

Table III.

No.	Composition of solution in gram percentages.			Composition of residue in gram percentages.		
	K <sub>2</sub> CrO <sub>4</sub>	(NH <sub>4</sub> ) <sub>2</sub> CrO <sub>4</sub>	H <sub>2</sub> O	K <sub>2</sub> CrO <sub>4</sub>	(NH <sub>4</sub> ) <sub>2</sub> CrO <sub>4</sub>	H <sub>2</sub> O
1	39.35	0.00	60.65	89.23	0.00	10.77
2	36.77	1.41	61.82	88.71	0.35	10.96
3	34.38	3.25	62.10	88.48	0.75	10.73
4	29.36	6.75	63.89	88.02	1.30	10.80
5	25.89	10.01	64.10	87.66	2.01	10.33

6	25.34	10.29	64.37	87.66	2.02	10.32
7	22.35	12.85	64.80	87.65	2.18	10.17
8	21.34	13.70	64.96	86.28	3.45	10.27
9	18.64	16.51	64.95	85.22	4.64	10.14
10	16.07	19.10	64.83	77.89	8.46	13.65
11	15.88	19.65	64.47	70.41	16.37	13.22
12	15.84	19.95	64.21	62.35	24.43	13.21
13	15.82	19.98	64.20	48.58	35.35	16.07
14	15.60	20.01	64.39	45.25	36.77	17.98
15	15.36	20.10	64.54	43.13	38.86	18.01
16	15.20	20.18	64.62	36.94	42.78	20.28
17	14.88	20.28	64.83	30.85	52.10	17.05
18	14.66	20.30	65.04	17.94	62.99	19.07
19	14.55	20.36	65.09	11.13	69.90	18.97
20	14.47	20.40	65.13	8.51	74.17	17.32
21	14.40	20.45	65.15	7.34	74.83	17.83
22	14.14	20.70	65.16	6.17	75.36	18.47
23	11.69	21.30	67.01	5.15	76.51	18.34
24	10.63	21.94	67.45	3.68	76.92	19.40
25	7.08	22.88	70.04	1.87	77.70	18.43
26	4.53	23.43	72.04	1.18	78.47	20.35
27	0.00	25.21	74.79	0.00	80.79	19.21

The data in Table III lead to those of Table IV, recalculating for the formula,  $100mH_2O \cdot x(NH_4)_2CrO_4 \cdot (100-x)K_2CrO_4$ .

Table IV.

No.	Solution.		Residue.	
	<i>m</i>	<i>x</i>	<i>m</i>	<i>x</i>
1	16.62	0.00	1.30	0.00
2	17.28	4.67	1.27	0.45
3	17.64	11.84	1.30	1.07
4	17.77	22.24	1.35	2.77
5	17.87	33.95	1.22	2.84

6	18.03	35.01	1.25	2.85
7	18.02	42.33	1.23	3.08
8	18.00	45.04	1.22	4.86
9	17.67	53.20	1.20	6.50
10	17.26	60.25	1.66	12.18
11	16.96	61.24	1.56	21.36
12	16.82	61.66	1.52	33.35
13	16.75	61.72	1.85	48.16
14	16.87	62.09	2.10	50.92
15	16.96	62.46	2.09	53.50
16	17.00	62.90	2.33	59.65
17	17.14	63.51	1.89	68.32
18	17.27	63.87	2.09	81.65
19	17.30	64.13	2.03	88.91
20	17.32	64.29	1.44	91.75
21	17.33	64.45	1.87	92.86
22	17.31	65.15	1.94	94.14
23	18.57	69.94	1.92	94.99
24	18.82	72.49	2.05	96.39
25	20.81	80.49	1.97	98.13
26	22.54	86.85	2.16	98.84
27	25.04	100.00	2.01	100.00

The equilibrium relation is graphically represented in Fig. 2 by using the data in Table IV.

As may be seen, the solubility curve in Fig. 2 is quite similar to that in Fig. 1. In the upper part of the figure, at the point B on the curve AB, the solid solution becomes saturated with ammonium chromate, and it corresponds to 61.66 molal percentage of ammonium chromate in the liquid solution and 16.75 in the solid solution.

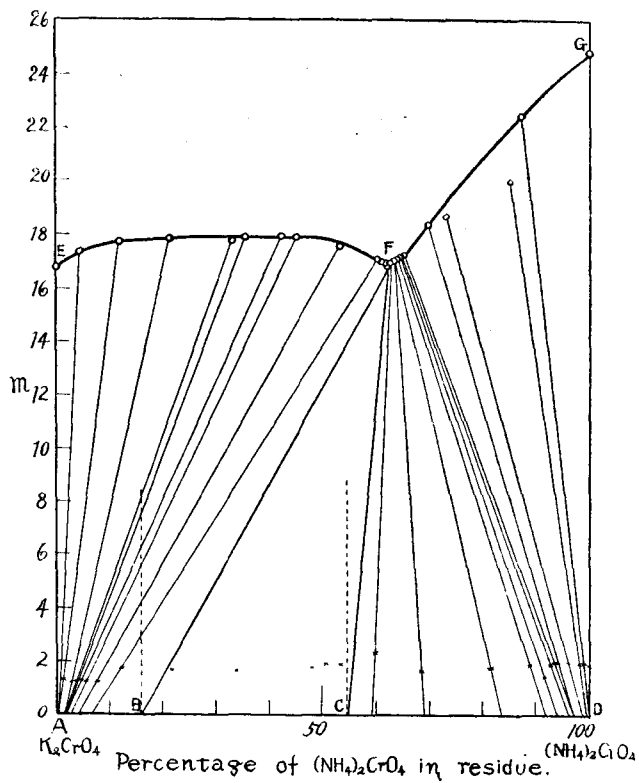
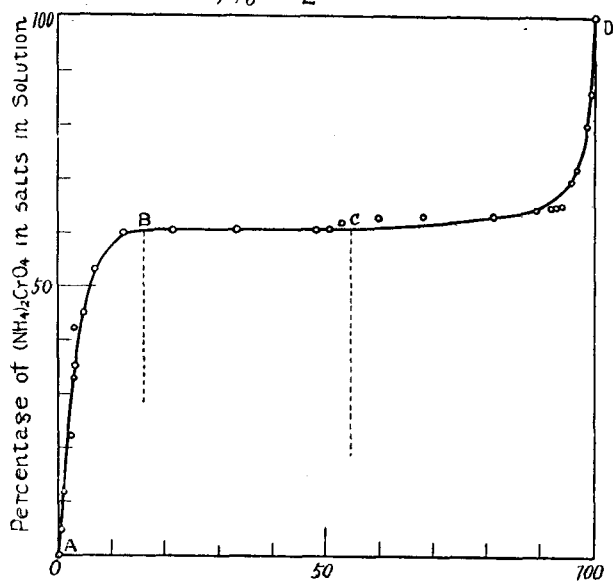
The composition of the residue which corresponds to the point C is estimated to be 55.50 in molal percentage of ammonium chromate. Thus in this system, at 25° C., no solid solution of ammonium chromate and potassium chromate, which contains the former in molal percentages between 16.75 and 55.50, exists.

The curve, CD, refers to the second series of the solid solutions.

In the lower part of the figure, the curve, EF, represents the compositions of liquid solutions which are in equilibrium with the first series of solid solutions denoted by the points on the horizontal line AB. The compositions of these solutions change gradually from  $[(\text{NH}_4)_2\text{K}_2\text{CrO}_4]$ .



Fig 2



16.62 H<sub>2</sub>O to  $[(\text{NH}_4)_2\text{K}_2\text{CrO}_4] \cdot 16.82 \text{ H}_2\text{O}$ .

The curve, FG, represents the compositions of liquid solutions which are in equilibrium with the second series of solid solutions denoted by the points on the line CD, and the compositions of these liquid solutions change gradually from  $[(\text{NH}_4)_2\text{K}_2\text{CrO}_4] \cdot 16.82\text{H}_2\text{O}$  to  $[(\text{NH}_4)_2\text{K}_2\text{CrO}_4] \cdot 25.04\text{H}_2\text{O}$ .

#### SUMMARY.

1. The equilibrium in the following systems have been studied at 25° C.:

(1)  $(\text{NH}_4)_2\text{CrO}_4$ ,  $(\text{NH}_4)_2\text{SO}_4$  and  $\text{H}_2\text{O}$  ;

(2)  $(\text{NH}_4)_2\text{CrO}_4$ ,  $\text{K}_2\text{CrO}_4$  and  $\text{H}_2\text{O}$ .

2. In each system, two series of solid solutions are formed with a gap. The gaps are respectively :

(1) 2.90–21.50 in molal percentage of ammonium chromate.

(2) 16.75–55.50 in molal percentage of ammonium chromate.

3. In the liquid solutions in equilibrium with the two kinds of solid solutions, the amount of ammonium chromate in molal percentage of the total salts are respectively :

(1) 8.56,

(2) 61.66.

4. In each case, the solubility curve consists of two branches, and the mols of water to one mol of solid solution vary as follows :

	Ammonium chromate side.	The other side.
(1)	9.71–25.11	9.56–9.71
(2)	16.82–25.04	16.62–16.82.

The writer wishes to express his gratitude to Prof. Osaka for all his advice.