A STUDY OF THE RECIPROCAL SALT PAIR: [K_2, $(NH_4)_2$] – [SO_4, CrO_4] AT 25°C.

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In a systematic study of a reciprocal salt pair, it is necessary to know the solubilities of the four single salts and the equilibria of the systems of two salts with a common ion and water, previous to the study of the equilibrium of the system in question. In the present case of $[K_2, (NH_4)_2]-[SO_4, CrO_4]$, the necessary data for those equilibria are found in literature.[1] As to the systems of two salts with a common ion, the following facts are to be remarked, all being observed at 25°. Potassium sulphate and potassium chromate, and ammonium sulphate and potassium sulphate form a complete series of solid solutions under the liquid solutions respectively, with no gap. Ammonium chromate and ammonium sulphate, and ammonium chromate and potassium chromate form each two series of solid solutions with a gap. The gaps are respectively 2.90 – 21.50 and 16.75 – 55.50 in molar percentage of ammonium chromate.

Materials. The four salts were "extra pure" preparations of E. Merck and have been tested for their purity according to Merck's "*Prüfung der chemischen Reagenzien auf Reinheit.*" Ordinary distilled water was used.

Methods of Analysis. The chromate was estimated by the ordinary method of iodometry. The ammonium was determined by distillation of the sample with caustic soda into a known volume of a standard sulphuric acid and titrating back the excess of the acid with a standard alkali solution, using methyl orange as indicator. The sulphate was determined as barium sulphate. The potassium and water were found by difference.

Experimental Procedure. The experiments were carried out in the following way. Into a solution in equilibrium with two kinds of solid solutions of two salts having a common ion, another salt was added in different proportions and in such an amount that, when the equilibrium was attained, two or three solid phases remained as residue. The mixture in an Erlenmeyer flask of a capacity of about 30 c.c. was made to rotate in a thermostat at 25.0° for at least two days. When the equilibrium was attained, the flask was allowed to stand still in the same thermostat until the suspended matter had settled. Then about 5 c.c. of the solution were taken out by a pipette through a cotton filter into a weighing bottle and subjected to analysis.

(1) Single salts: Landolt-Börnstein-Roth-Scheel, "Physikalische Tabellen"; Comey, "Dictionary of Chemical Solubilities of Inorganic Compounds"; Seidell, "Solubilities of Inorganic and Organic Compounds." As to the solubility of ammonium chromate at 25° it is 33.62 grams per 100 grams water, according to Araki (*Mem. Coll. Sci. Kyoto Imp. Univ.*, (A) 8, No. 3 (1925)), but the writer has found it to be 39.60.

The system of potassium sulphate, potassium chromate and water: Fock, Seidell's "Solubilities," 2d. ed. p. 559; M. Amadori, "Tables annuelles de constantes et données numériques" 3, 341.

The system of ammonium sulphate, potassium sulphate and water: Fock, Seidell's "Solubilities," 2d. ed. p. 556.

The systems of ammonium chromate, potassium chromate and water, and of ammonium chromate, ammonium sulphate and water: S. Araki, loc. cit.

The composition of the solution was represented by the formula:

$$100m\ H_2O\cdot x(NH_4)_2\cdot(100-x)K_2\cdot y(SO_4)\cdot(100-y)CrO_4$$

and it was graphically represented by using a square diagram after E. Janecke.[1]

When it was crystallographically confirmed by a Zeiss polarising microscope that there were two phases in the residue, they were separated from the solution by a centrifugal filter machine and then the two kinds of solid solutions mechanically separated from each other as completely as possible.

The two kinds of residues, each of which contained a little of the other and also some of the mother liquor, were analysed. As the pure residues are anhydrous, the amount of the mother liquor adhereing to them was easily calculated from the amount of water contained in the impure residues. The compositions of the anhydrous impure residues were represented by the formula:

$$x(NH_4)_2\cdot(100-x)K_2\cdot ySO_4\cdot(100-y)CrO_4$$

and plotted in the square diagram. Then the points representing the pure solid phases must lie on the extension of the line connecting the two points. Thus, to find the composition of each of the pure solid phases, the materials were mixed in such calculated proportions that when the equilibrium was reached, the liquid solution of the same composition as above was in equilibrium with only one solid phase having its position on the extension line. When such a mixture attained its equilibrium, the residue was microscopically examined and when the residue was found not to be homogeneous, the experiment was repeated with somewhat modified proportions of the materials. This process was repeated until only one solid phase was detected and then it was taken as one of the solid phases in equilibrium with the given liquid solution.

The results are given in the following table and graphically represented in Fig. 1.

No.	Liquid solution.			Solid solution.			
				A.		B.	
	m	x	y	x	y	x	y
1	9.71	100.00	91.44	100.00	97.10	100.00	78.50
2	10.64	91.51	79.37	73.75	92.29	98.28	11.88
3	12.46	88.12	69.32	42.14	88.89	96.72	11.37
4	14.85	77.30	41.15	24.15	84.93	92.86	9.39
5	14.85	66.05	21.29	21.07	77.32	89.86	7.17
6	15.01	59.51	14.19	17.57	71.66	69.42	6.40
7	15.08	52.04	9.79	37.56	41.41	60.20	9.38
8	15.71	42.61	7.59	37.41	14.61	48.16	7.83
9	15.24	45.17	3.63	—	—	49.76	3.30
10	16.82	61.66	0.00	16.76	0.00	55.50	0.00

(1) *Z. anorg. Chem.*, **51** (1906), 132.

The liquid solutions represented by the points on the curve CC′ have always two kinds of solid solutions as the residue which are represented by the points on the lines AA′ and BB′. The crosses on the diagram represent some mixtures of two solid phases and served to find the compositions of the single solid solutions, as above stated.

Fig. 2 represents a model of this system.

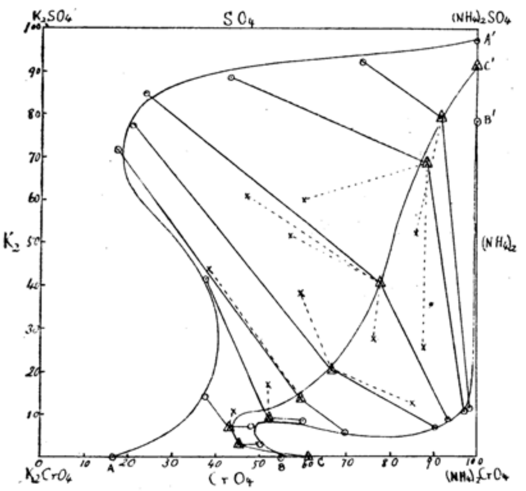

Fig. 1.

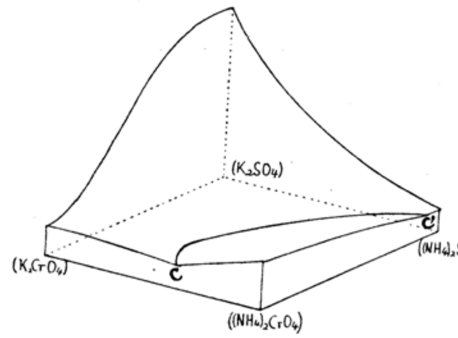

Fig. 2.

Summary.

The equilibrium of the reciprocal salt pair $[K_2, (NH_4)_2]-[SO_4, CrO_4]$ was studied at 25°.

There exist two complete series of solid solutions in equilibrium with liquid solutions.

The compositions of the solid solutions have been determined by a special method.

The equilibrium of the system has been graphically represented using Janecke's square diagram.

In conclusion the writer wishes to express his sincere thanks to Prof. Y. Osaka for his valuable suggestions and kind instructions.

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