[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, RUTGERS UNIVERSITY]

The Ternary Aqueous Systems of Ammonium Sulfate with Cesium, Potassium and Rubidium Sulfates[1]

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The ternary systems $(NH_4)_2SO_4$-Cs_2SO_4-H_2O and $(NH_4)_2SO_4$-K_2SO_4-H_2O have been studied at 25°, the system $(NH_4)_2SO_4$-Rb_2SO_4-H_2O at 35°. All three show continuous solid solution. The first belongs to Roozeboom Type II, with a congruent crystallization point at 0.49 mole fraction $(NH_4)_2SO_4$; the latter two belong to Roozeboom Type I. The nature of the distribution of the components between liquid and solid phases indicates that of the systems studied, the one involving K_2SO_4 displays the largest deviation from ideal behavior, while the one involving Rb_2SO_4 displays the smallest deviation.

An examination of the lattice constants, unit cell volumes, and ionic radii available in the literature indicates that of the three possible binary solid solutions involving ammonium sulfate with the isomorphous, orthorhombic cesium, potassium and rubidium sulfates, the one with the latter should be the most nearly ideal. To gain some information concerning the nature of these solid solutions a study has been made of the distribution of their components in solubility equilibrium between an aqueous solution and the solid phase. The ternary system ammonium sulfate–potassium sulfate–water has already been investigated at 25° by Weston,[3] but from the experimental technique used it is doubtful that the data represent equilibrium conditions. Several points in this system have also been determined by Hill and Loucks[4] and by Fock,[5] and these fall close to the distribution curve shown in Fig. 1.

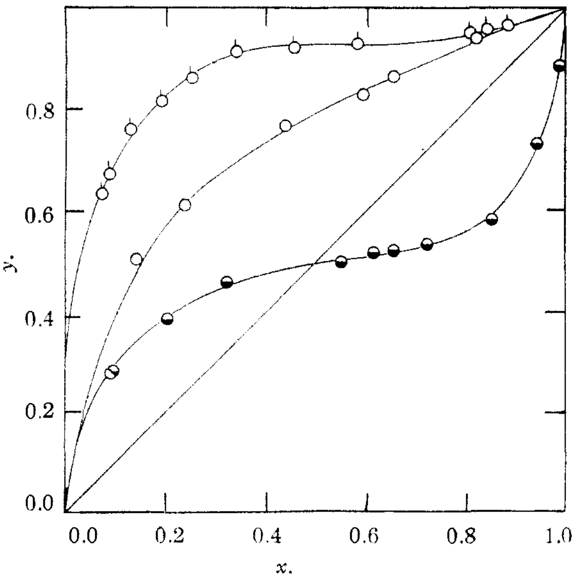

Fig. 1.—Distribution of $(NH_4)_2SO_4$ between liquid and solid solutions in the following systems: ⊖-⊖, $(NH_4)_2SO_4$-Cs_2SO_4-H_2O at 25°; ϕ-ϕ, $(NH_4)_2SO_4$-K_2SO_4-H_2O at 25°; O-O, $(NH_4)_2SO_4$-Rb_2SO_4-H_2O at 35°.

Materials.—C.p. grade ammonium and potassium sulfates were used without recrystallization. Cesium and rubidium sulfates were prepared as described previously.[6] All salts, after drying at 200° (the ammonium sulfate at 110°), were stored in glass-stoppered weighing bottles in a calcium chloride desiccator.

Solubility Determinations.—Complexes of known composition were made up by weight in 8-inch rubber stoppered ignition tubes which were agitated in a constant temperature bath maintained at 25.00 ± 0.05° (34.95 ± 0.05° for the rubidium system). The solid phase compositions were determined by algebraic extrapolation[7] of the tie-lines connecting the saturated aqueous solutions with either the original known complexes or with wet residue samples. The constancy of successive analyses indicated that two weeks of agitation were sufficient for equilibration. As a further check on the attainment of equilibrium, the method of duplicate complexes[8] was used in two cases.

In seeking an analytical technique it was desirable to find one that would not introduce contaminants which would complicate the subsequent recovery of the rubidium and cesium sulfates. To a weighed 1–2-ml. sample of the saturated solution in a crucible was added sufficient ethanol (3–8 ml.) to precipitate most of the dissolved salts. (Without the ethanol, alkali sulfate was lost mechanically during the subsequent ammonium sulfate volatilization through decrepitation of the large mixed crystals formed slowly during the evaporation of the aqueous solution.) The water content was determined by the loss in weight after overnight heating at 65°, followed by slow (3–4 days) drying at 110°. No ammonium sulfate was lost by this gentle treatment. The ammonium sulfate content was determined by the loss in weight after five hours in a muffle furnace during which time the temperature was gradually raised to 900–950°. Porcelain crucibles were used in the potassium system and platinum crucibles in the other two. A test of this method on known mixtures of ammonium sulfate with cesium and potassium sulfates showed an average error of less than 1 part per thousand.

Results.—The solubility data are shown in Table I. All three systems display continuous solid solution and, as shown in Fig. 1, in which the mole fraction of ammonium sulfate in the dissolved salts (y) is plotted against its mole fraction in the solid solution (x), the rubidium and potassium systems belong to Roozeboom Type I while the cesium system belongs to Type II.[9] On a triangular representation of the potassium sulfate system Weston's solubility data[3] lie on the same curve as those in Table I, but his tie-lines cross those obtained in this study. In view of the criteria used in this investigation, it is felt that the data herein presented represent the true equilibrium conditions for this system.

The distribution in the ammonium sulfate–rubidium sulfate system can be represented by the equation

$$\log y/(1 - y) = 0.61 + 0.80 \log x/(1 - x) \quad (1)$$

over the range of x values from 0.15 to 0.85, and for

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[3] A. Weston, *J. Chem. Soc.*, **121**, 1223 (1922).

[4] A. E. Hill and C. M. Loucks, THIS JOURNAL, **59**, 2094 (1937).

[5] Fock, *Z. Krist.*, **28**, 337 (1897).

[6] W. C. von Dohlen and E. L. Simons, THIS JOURNAL, **73**, 461 (1951).

[7] A. E. Hill and J. E. Ricci, *ibid.*, **53**, 4306 (1931).

[8] A. E. Hill and N. Kaplan, *ibid.*, **60**, 550 (1938).

[9] B. Roozeboom, *Z. physik. Chem.*, **8**, 521 (1891).

the ammonium sulfate–cesium sulfate system a similar equation, with an intercept of −0.03 and a slope of 0.22, is applicable over the range of x values from 0.25 to 0.85. Equation (1) is of the form proposed by Hill, Durham and Ricci[10]

$$\log R_I = \log K + m \log R_S \qquad (2)$$

in which R_I and R_S represent the mole ratios of the more soluble to the less soluble salt in the liquid and solid phases, respectively. K represents the square root of the ratio of the activity product constants of the two salts (for uni-divalent salts in which the univalent ions are the exchangeable ones), and m is a constant whose deviation from unity represents the deviation of the system from ideal behavior.

TABLE I

SYSTEMS $(NH_4)_2SO_4$–H_2O- AND Cs_2SO_4, K_2SO_4 OR Rb_2SO_4 AT 25° OR 35°

Liquid solution Wt. % $(NH_4)_2SO_4$	Liquid solution Wt. % Cs_2SO_4	Density	C, original complex R, wet residue Wt. % $(NH_4)_2SO_4$	C, original complex R, wet residue Wt. % Cs_2SO_4	Solid solution Wt. % $(NH_4)_2SO_4$
(1) Cs_2SO_4 at 25°					
43.41		1.226			100.0
40.08	6.49	1.281	C 45.09	6.02	99.0
36.22	13.70	1.355	R 93.28	4.17	96.2
31.69	22.03	1.443	C 35.67	21.07	92.7
28.01	29.20		R 54.55	22.37	85.6
23.61	37.31	1.620	R 76.74	23.26	76.7
21.32	41.75	1.688	C 25.03	41.03[a]	67.4
21.36	41.74	1.688	C 25.01	41.06[b]	66.7
18.71	46.01	1.727	R 40.12	50.20	48.3
18.25	47.01	1.773	R 40.44	59.46	40.5
18.13	47.08		C 21.05	49.51	37.1
17.24	48.10	1.790	C 19.16	51.18	30.8
15.38	50.30	1.808	C 15.12	56.74	14.5
12.16	53.44	1.853	C 11.69	58.12	8.4
8.16	57.23	1.909	C 7.61	62.07	3.7
	64.54	2.005			0.0
(2) K_2SO_4 at 25°					
	K_2SO_4			K_2SO_4	
43.41					100.0
40.62	2.06		C 45.26	3.25	85.6
39.88	2.47		R 49.44	6.38	80.8
39.28	2.82		C 42.60	4.65	76.6
36.92	3.83		C 38.22	8.01	51.0
35.81	4.14		C 35.98	5.99[a]	40.9
35.86	4.15		C 35.97	5.99[c]	39.3
35.67	4.26		R 36.36	13.92	39.2
32.25	5.09		C 31.89	11.10	28.3
28.25	6.02		C 27.55	12.48	20.3
23.42	7.15		C 22.75	13.49	15.5
19.37	8.04		C 18.64	14.56	10.2
13.99	9.03		C 13.47	15.14	6.8
12.22	9.35		C 11.74	15.67	5.8
	10.79				0.0
(3) Rb_2SO_4 at 35°					
	Rb_2SO_4			Rb_2SO_4	
44.33					100.0
38.21	4.81		C 41.05	7.10	69.8
31.85	9.98		C 33.45	13.97	48.3
29.26	12.16		C 30.34	16.00	42.0
25.51	15.35		R 27.21	72.01	27.1
17.23	22.25		C 17.03	25.34	13.1
13.05	25.71		R 8.00	87.69	7.6
5.99	31.37		C 5.94	34.80	5.0
	36.27				0.0

[a] $(NH_4)_2SO_4$ initial solid phase. [b] Cs_2SO_4 initial solid phase. [c] K_2SO_4 initial solid phase.

On the basis of the above m values, the ammonium sulfate–rubidium sulfate system is more nearly ideal in its behavior than the ammonium sulfate–cesium sulfate system, and both systems display negative deviations from ideality. In the absence of any data on the activity coefficients of ammonium and cesium sulfates in their saturated aqueous solutions it is not possible to compare the intercepts observed for the systems involving these salts with the actual log K values. The deviation from ideality of the ammonium sulfate–potassium sulfate system is so great (as indicated by the distorted form of its distribution plot in Fig. 1) that its distribution can be represented by an equation of the form of equation (1) only over a limited range of x values (0.50 to 0.90).

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[10] A. E. Hill, G. S. Durham and J. E. Ricci, THIS JOURNAL, **62**, 2723 (1940).