

PHASE DIAGRAM OF THE SYSTEM $(\text{NH}_4)_2\text{SO}_4\text{-Cs}_2\text{SO}_4\text{-H}_2\text{O}$ AT 0°C J. BALEJ^a and V. G. SHEVCHUK^b^a *Institute of Inorganic Chemistry,
Czechoslovak Academy of Sciences, 160 00 Prague 6 and*^b *Institute of Engineering, Poltava, USSR*

Received September 2nd, 1974

A continuous series of solid solutions is produced at 0°C , whose solubility curve as well as distribution curve of ammonium ion between both phases have a course analogous to that found for temperatures of 25°C and 100°C . In order to achieve a steady composition of saturated liquid solutions, stirring of the solution with excess of a solid phase for 50 h is sufficient, whereas composition of the coexisting solid phase depends on time of stirring and on the direction of bringing the system to the equilibrium state. Different composition of coexisting solid solutions, established under different conditions is explained by slowness of the exchange processes in the solid phase at a low temperature. The course of the solubility curve at all the temperatures measured hitherto, allowed to express it by empiric equations valid for the whole temperature region of 0°C to 100°C .

In the previous paper¹ on the phase diagram of the system $(\text{NH}_4)_2\text{SO}_4\text{-Cs}_2\text{SO}_4\text{-H}_2\text{O}$ at 100°C , doubts were expressed about the reliability of data published for this system at 0°C according to Ushakov². The reason for it was both an extraordinary great dispersion of experimental data concerning the composition of saturated solutions, and a quite differing course of the distribution curve of the ammonium ion between the liquid and solid phases at this temperature, as compared with the course of the curve at 25°C and 100°C . While a nearly consistent course of this curve at 25°C and 100°C (refs.^{1,3,4}) puts this system according to the Roozeboom classification⁵ to the second group of systems with solid solutions, the distribution curve exhibits according to paper² at 0°C within the whole concentration range only a very small deviation from ideal behaviour with opposite distribution of experimental points around the diagonal than at 25°C and 100°C . We considered therefore useful to measure again solubility data of this system at 0°C .

EXPERIMENTAL

Reagents. The reagents were of A.R. grade purity (Lachema). Ammonium sulphate was recrystallized before use, cesium sulphate was used without any further purification. Both products were finally crystalline.

Working procedure. The saturated solutions were prepared by stirring a liquid solution with excess of the solid phase for a minimum period of 50 hours in glass vessels immersed into the stirred water-ice mixture. The systems examined were maintained at the temperature of 0°C

either within the whole period of mixing, or the temperature of equilibration was temporarily increased within 20 to 25°C, and afterwards again decreased down to 0°C, and at that temperature the system was again stirred for a minimum period of 50 hours before taking-off the samples. Total composition of the system was in minority of cases adjusted by direct mixing of a weighed amount of the two dry pure salts with appropriate amount of distilled water (procedure *A*). In most cases further amount of pure cesium sulphate (procedure *B*) or ammonium sulphate (procedure *C*) was added to the remainder of the system from the previous measurement so that it was possible in this way to approach the equilibrium composition of the system considered either from the side of cesium or ammonium sulphates. The data concerning the temperature conditions applied as well as direction of approaching the equilibrium state are given in Table I. Individual measured samples are ordered in the Table in such a way that the sample with a higher ordinal number in procedures *B* and *C* was prepared from the remainder of the sample with the preceding ordinal number and appropriate pure solid salt (No 2—6, 19 and 20); for samples denoted by a number and letter, series denoted by the same letter belong to one another (for instance, sample 8a was prepared from the remainder of sample 7a and admixture of pure ammonium sulphate, and analogously sample 10b from sample 9b *etc.*).

Analytical. The samples of coexisting liquid and solid phases were taken off analogously as in paper¹ (the "wet residue" method). Individual components in both phases were analyzed in the same way, *i.e.* the ammonium ion content titrimetrically according to Hanuš⁶, content of the total salt amount by evaporating all the water, and from the dry residue content of cesium sulphate was calculated after the portion belonging to ammonium sulphate having been subtracted.

RESULTS AND DISCUSSION

Composition of the saturated solutions of various contents of individual components, composition of "wet residues" coexisting with them, as well as composition of dry solid phases, which corresponds to the saturated solutions, are summarized in Table I, where experimental conditions of individual measurements during establishing the stationary state are likewise given. Solubility of ammonium sulphate itself at 0°C was taken from tables⁷, solubility of cesium sulphate at this temperature was calculated by means of the correlation equation derived¹ on the basis of tabular data⁸. The phase diagram of the system studied, constructed with use of the given data, is graphically presented in Fig. 1, in which also data according to Ushakov² are simultaneously given.

It follows from the results measured that course of the solubility curve is even at 0°C analogous to that at higher temperatures of 25°C [ref.^{3,4}] and 100°C [ref.¹], *i.e.* it shows two practically linear branches, if concentrations in weight % are expressed, with a relatively narrow transition region. This allows correlation of the solubility data by simple empiric equations. In the region having molar ratio of ammonium sulphate in the solid solution $x_{\text{NH}_4(\text{s})} > 0.5$ it is possible to express dependence of the content of this component (y , weight%) in the saturated solution upon the cesium sulphate content in the liquid solution (z , weight%) by relationship

$$y = 41.35 - 0.5111z, \quad (1)$$

TABLE I
Composition of Saturated Aqueous Solutions and Coexisting Solid Phases in the System $(\text{NH}_4)_2\text{SO}_4\text{-Cs}_2\text{SO}_4\text{-H}_2\text{O}$ at 0°C

No	Saturated aqueous solution			Wet residue			Dry solid phase			Conditions of equilibration
	$(\text{NH}_4)_2\text{SO}_4$ weight %	Cs_2SO_4 weight %	$x_{\text{NH}_4(\text{a})}$	$(\text{NH}_4)_2\text{SO}_4$ weight %	Cs_2SO_4 weight %	$(\text{NH}_4)_2\text{SO}_4$ weight %	Cs_2SO_4 weight %	$x_{\text{NH}_4(\text{s})}$		
1	41.38	0.00	1.000	—	—	100.00	0.00	1.000	50 h ^c (0°); A	
2	38.45	4.48	0.9592	—	—	—	—	—	50 h (0°); B	
3	37.14	7.55	0.9309	64.10	10.43	87.00	13.00	0.9483	65 h (0°); B	
4	35.37	11.90	0.8906	61.39	17.56	78.9	21.1	0.911	75 h (0°); B	
5	32.29	18.76	0.8250	51.24	21.74	74.9	25.1	0.888	100 h (0°); B	
6	32.74	19.83	0.8189	46.85	17.53	89.0	11.0	0.957	70 h (0°); A	
7a	3.21	59.59	0.1286	1.08	87.01	0.0	100.0	0.000	70 h (0°); A	
7b	4.65	58.37	0.1791	1.58	84.56	0.0	100.0	0.000	50 h (0°); C	
8a	6.02	56.37	0.2264	1.86	87.03	0.0	100.0	0.000	50 h (0°); C	
8b	9.30	5.381	0.3216	2.90	86.07	0.0	100.0	0.000	50 h (0°); C	
9a	14.07	49.08	0.4398	5.45	80.93	0.6	99.4	0.0163	50 h (0°); C	
9b	15.15	48.19	0.4628	8.78	76.44	4.2	95.8	0.1072	50 h (0°); C	
10a	18.26	44.82	0.5273	26.74	43.73	60.5	39.5	0.8075	50 h (0°); C	
10b	20.25	41.24	0.5735	35.81	39.06	64.8	35.2	0.8345	50 h (0°); C	

11a	21.03	39.83	0.5912	32.39	37.80	68.3	31.7	0.8551	75 h (0°); C
12a	22.28	37.08	0.6220	43.67	27.49	96.0	4.0	0.9850	75 h (0°); C
12a	25.75	30.70	0.6964	—	—	—	—	—	60 h (0°); C
12b	28.34	25.50	0.7527	58.45	15.39	98.0	2.0	0.9926	60 h (0°); C
13a	30.98	21.24	0.8002	56.88	13.54	99.3	0.7	0.9974	16 d ^d (22°) + 50 h (0°); C
13b	35.97	10.66	0.9026	63.83	6.84	97.9	2.1	0.9922	16 d (22°) + 50 g (0°); C
14a	33.68	15.63	0.8551	61.47	12.54	91.1	8.9	0.9656	100 h (0°); C
14b	36.18	10.83	0.9015	66.01	9.89	90.9	9.1	0.9647	100 h (0°); C
15	8.14	54.35	0.2909	5.16	77.53	2.5	97.5	0.0656	100 h (0°); A
16	7.71	55.92	0.2741	4.69	77.49	2.0	98.0	0.0529	150 h (0°); A
17	6.87	56.02	0.2514	4.55	85.86	3.7	96.3	0.0952	250 h (0°) + 9 d (22°) M + 50 h (0°); A
18	39.61	2.92	0.9738	66.25	1.5	100.0	0.0	1.000	100 h (0°); A
19	40.02	2.26	0.9798	66.0	1.41	99.8	0.2	0.9993	150 h (0°); A
20	37.63	7.06	0.9359	63.50	6.04	96.25	3.75	0.9860	250 h (0°) + 9 d (22°) + + 50 h (0°); C
21	0.00	62.45	0.000	—	—	0.00	100.00	0.000	

h = hours, d = days.

which is valid at the given temperature within $z \leq 45$ weight% of Cs_2SO_4 . For the second branch with excess of cesium sulphate in the solid phase, it is possible to express dependence of the content of this component upon the content of ammonium sulphate in the saturated solution by relation

$$z = 62.45 - 0.939y \quad (2)$$

valid for $y \leq 15.0$ weight% of $(\text{NH}_4)_2\text{SO}_4$. If we compare values of coefficients in the corresponding solubility branches at all measured temperatures of this system¹ between one another, we can find that these coefficients are linear functions of temperature in both linear sections of the solubility curves. Accordingly, the course of linear sections of the solubility curves of this system at arbitrary temperature within 0° to 100°C can be expressed by common equation

$$y = y^0 - 0.5111(1 + 7.01 \cdot 10^{-4}t) \cdot z, \quad (3)$$

and by

$$z = z^0 - 0.939(1 - 5.4 \cdot 10^{-4}t) \cdot y, \quad (4)$$

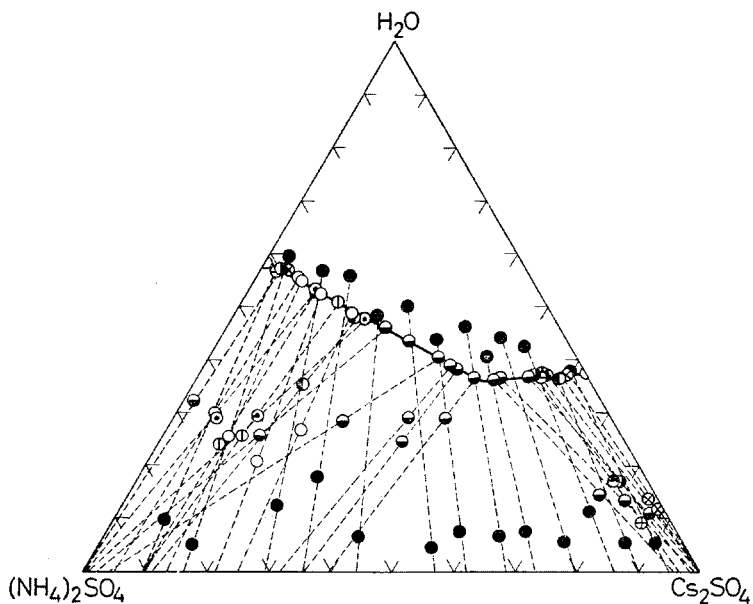


FIG. 1

Phase Diagram of the System $(\text{NH}_4)_2\text{SO}_4\text{-Cs}_2\text{SO}_4\text{-H}_2\text{O}$ at 0°C

Conditions of equilibration: \odot 50–70 h (0°) A; \bullet 100 h (0°) A; \ominus 150 g (0°) A; \oplus 250 h (0°) + 9 d (22°) + 50 h (0°) A; \circ 50–75 h (0°) B; \bullet 100 h (0°) B; \circ 60–75 h (0°) C; \oplus 100 h (0°) C; \ominus 250 g (0°) + 9 d (22°) + 50 h (0°) C; \oplus 16 d (22°) + 50 h (0°) C; \bullet Ushakov². Full line denotes course of solubility according to equations (1) and (2).

where y^0 and z^0 are solubilities of pure ammonium and cesium sulphates, respectively, at $t^\circ\text{C}$. By comparing with the composition of saturated solutions according to paper², it is evident that the previous data² are for the most part considerably far from the real state of saturation.

Whereas it is possible to conclude on the basis of the achieved data that compositions of the saturated solutions of the system in question are at 0°C unambiguously defined by the given results, it is not possible to say the same about the composition of coexisting solid phases. The results give evidence of the fact that even at this temperature a continuous series of solid solutions is produced, but from the course of tie lines connecting composition of saturated aqueous solutions and composition of taken-off samples of coexisting "wet residues", it is evident that composition of that "wet residue" and hence of the dry solid phase, achieved by extrapolation, considerably depends on reaction conditions under which the system of the total composition approached its equilibrium state. On the basis of the data achieved it is not possible to determine, whether the equilibrium state within the whole volume of the solid phase was in some cases attained.

From factors affecting composition of coexisting solid phases, determined analytically, time of stirring the solution with excess of the solid phase (see measurements 7a–8b and 15–17), temperature conditions during the equilibration (measurements 16 and 17), and direction of the change of the total composition of the system (see measurements 3–6 and 12a–13b) are applied. The intensity of stirring which may influence the results as well, was not examined.

Total recrystallization of starting solid phases of different composition is a condition of attaining the equilibrium composition in the whole mass of the coexisting solid phase in the formation of solid solutions. The process quoted, which consists of a series of transport and exchange processes in the solid phase, is very slow, parti-

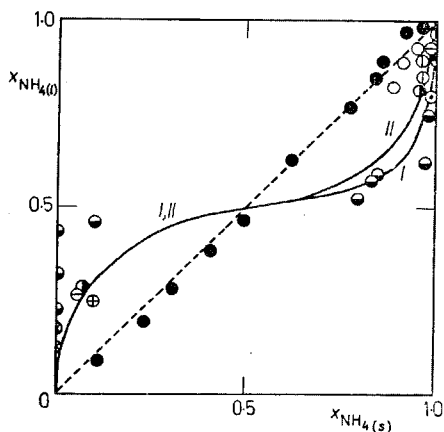


FIG. 2

Distribution Curve of Ammonium Ion between Liquid and Solid Solutions in the System $(\text{NH}_4)_2\text{SO}_4\text{-Cs}_2\text{SO}_4\text{-H}_2\text{O}$

Signification of Symbols is for 0°C the same as in Fig. 1. Full line denotes the course at 25° (I) and 100°C (II).

cularly at low temperatures. The equilibrium composition of a solid solution is therefore produced predominantly in the surface layer of the solid phase and its inside may be according to reaction conditions more or less far from the equilibrium composition. For that reason, composition of the solid phase samples taken off does not often as a whole correspond to the equilibrium composition, from which it can deviate to a different extent. The observed intersection of conodes is obviously due to a different choice of initial experimental conditions or to a different direction of bringing the system to its equilibrium state. The greatest differences in the composition of coexisting solid phases, which manifest themselves by a distinct intersection of conodes from appropriate regions of saturated aqueous solutions, were found for cases, when new composition of the system was adjusted by addition of either pure solid cesium sulphate or ammonium sulphate to the remainder of the system after a previous measurement. If solid cesium sulphate (process *B*) was added to the remainder of the preceding system, a higher relative content of this component in the solid solution than in the opposite case was established (procedure *C*). This means that no complete recrystallization of the solid phase, which inside contained the original starting solid component, occurred in the period of establishing the equilibrium state. In spite of this, composition of the aqueous solution corresponded to the equilibrium state of saturation, for it was present in a quasiequilibrium with the solid phase composition in the crystal surface, this fact being obviously sufficient for achieving fairly reliable data on the composition of saturated aqueous solutions.

The explanation given is obviously of more general validity and accounts for similar findings on the difference of composition of coexisting solid phases during formation of solid solutions, made by various authors, even when compositions of saturated liquid solutions are consistent between one another, and correspond to the state of saturation. Here, a question remains, whether real attaining of the equilibrium state in the composition of a coexisting solid solution within their whole volume is possible in an experimentally acceptable time, particularly at low temperatures. Another technique of the measurements than the commonly used stirring under excess of the solid phase might be needed.

The obtained results on the composition of coexisting solid solutions in the given system at 0°C cannot be on the basis of the given findings regarded as equilibrium ones. Nevertheless, it follows from them that even at this temperature shape of the distribution curve of the ammonium ion between liquid and solid solutions (Fig. 2) corresponds to that established at the temperatures of 25°C and 100°C and comes near to it more closely, the longer was the time of establishing the equilibrium state. The real equilibrium shape of the distribution curve of the ammonium ion most probably seems to be even at 0°C identical with the previously found course¹ for 25°C and 100°C. At the same time, this character of the distribution curve, which corresponds to systems belonging to the second group according to the Roozeboom

classification⁵, remained unchanged also for all estimated compositions of co-existing solid phases, whose conodes have a differing course. This is the reason for regarding as incorrect the data in paper², relating to the composition of co-existing solid phases of this system at 0°C, according to which the distribution curve of the ammonium ion has only negligible deviations from ideal behaviour within the whole concentration range. Our results show, even with respect to the given reservations, that a distinct point of inflexion appears on the distribution curve, which corresponds to a congruent dissolution of the solid solution of both components having molar fraction $x_{\text{NH}_4(s)} = 0.5$.

REFERENCES

1. Balej J., Shevchuk V. G.: This Journal 39, 3423 (1974).
2. Ushakov J. V.: Zh. Neorg. Khim. 18, 173 (1973).
3. Calvo C., Simons E. L.: J. Amer. Chem. Soc. 74, 1202 (1952).
4. Shevchuk V. G.: Zh. Neorg. Khim. 13, 1162 (1968).
5. Roozeboom H. W. B.: Z. Phys. Chem. (Leipzig) 8, 504 (1891).
6. Čůta F.: *Analytická chemie odměrná*, p. 295. Published by nakladatelství ČSAV, Prague 1956.
7. Seidell A.: *Solubilities of Inorganic and Metal Organic Compounds*, 3rd Ed., p. 1122. D. Van Nostrand, New York 1940.
8. *Spravochnik po Rastvorimosti Solevykh Sistem*, Vol. 3, p. 2167. Goskhimizdat, Moscow 1961.

Translated by J. Hejduk.