

On the Equilibrium in the System of Copper Sulphate, Ammonium Sulphate, Potassium Sulphate, and Water at 25.0°C.

By

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On the equilibrium in a quaternary system consisting of water and three salts with a common ion, we find not a few laborious works in the literature, most of which are due to J. H. van't Hoff, F. A. H. Schreinemakers, and their co-workers.¹ In certain cases, only the component salts appeared as the residue, while in others some double salts existed also. In the literature, however, there has been reported, so far as the author knows, no case in which a solid solution existed as a residue.

It is well known that, in the systems, $(\text{NH}_4)_2\text{SO}_4-\text{CuSO}_4-\text{H}_2\text{O}$ and $\text{K}_2\text{SO}_4-\text{CuSO}_4-\text{H}_2\text{O}$, the double salts, $(\text{NH}_4)_2\text{SO}_4.\text{CuSO}_4.6\text{H}_2\text{O}$ and $\text{K}_2\text{SO}_4.\text{CuSO}_4.6\text{H}_2\text{O}$, can respectively exist.² Ammonium sulphate and potassium sulphate are completely isomorphous and form solid solutions in all possible proportions, and so are also these double salts. According to A. Fock³ these two series of solid solutions, single and double salts, give continuous solubility curves of the same type.

¹ van't Hoff, *Z. anorg. Chem.*, **47**, 251-253 (1905); Schreinemakers, *Z. phys. Chem.*, **66**, 687 (1909); *ibid.*, **65**, 586 (1909); *ibid.*, **71**, 109 (1919).

² Schreinemakers and de Baat, *Proc. K. Akad. Wetensch Amsterdam*, **17**, 533 (1914); J. E. Trevor, *Z. phys. Chem.*, **7**, 469 (1891); Meerburg, *J. Chem. Soc., A.*, **II**, 380 (1911); Fräulein W. C. de Baat, *Z. phys. Chem.*, **66**, 693 (1909).

³ A. Fock, *Z. phys. Chem.*, **12**, 661 (1893); *ibid.*, **24**, 536, R. (1897); *J. Chem. Soc., A.*, **II**, 480 (1897); Seidell, *Solubilities of Inorganic and Organic Substances*, 261, 271.

From these facts we can expect the interesting role which those two series of solid solutions would play in the equilibrium of the system of copper, ammonium, and potassium sulphates and water. Thus, the author took up the study of that system from the standpoint of the phase rule.

Purification of the Materials.

The sulphates of copper, ammonium, and potassium were recrystallised thrice from somewhat acidic, ammoniacal, and neutral solutions respectively of commercial pure salts, washed well with water, and dried. These salts thus prepared were sufficiently pure for the present work.

Methods of Analysis.

The compositions of solutions and residues were determined in the following ways: The total sulphate radical was determined as barium sulphate, of which the precipitation was effected by the cautious addition of the barium chloride or by the rapid method according as the solution was rich in copper or not.

Copper was estimated by the iodometry, using 1/10- and 1/30-normal thiosulphate solutions, which were standardised against iodine purified in the following way: Pure iodine was precipitated from a potassium iodide solution by addition of water, then distilled from water suspension and finally dried in a desiccator containing conc. sulphuric acid.

Ammonia was distilled by the addition of caustic soda into a known volume of normal sulphuric acid, which was then titrated with 2/10-normal carbonate-free caustic soda solution by using methyl orange as indicator.

All the analytical operations were carried out under as much the same conditions as possible throughout the experiment. Potassium and water were estimated by difference.

Methods of Experiments.

In such a quaternary system as that under consideration, when two solid phases exist, the system becomes bivariant and in a given temperature it has only one degree of freedom. At 25° we may

have the following two different cases of this kind of equilibrium, in which the solid phases are respectively :

- (A) $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, $\text{CuSO}_4 \cdot (y(\text{NH}_4)_2(1-y)\text{K}_2)\text{SO}_4 \cdot 6\text{H}_2\text{O}$;
(B) $\text{CuSO}_4 \cdot (y(\text{NH}_4)_2(1-y)\text{K}_2)\text{SO}_4 \cdot 6\text{H}_2\text{O}$, $(x(\text{NH}_4)_2(1-x)\text{K}_2)\text{SO}_4$.

For convenience, we designate the solid solutions of the double salts by S_1 and those of the single sulphates by S_2 .

The experimental method adopted for case A was as follows:—

In an Erlenmeyer flask of a capacity of about 59 c.c., certain amounts of the potassium and ammonium salts were completely dissolved in water at 60° , and then an excess of finely powdered copper sulphate was added. The flask was made to rotate in a thermostat at 25.0° for at least three days ; usually the equilibrium was attained after two days' rotation. Then the flask was left at a stillstand in the same thermostat for a while until the solid phases had settled, when the solution was taken out by a pipette through a cotton filter and divided into six weighing tubes. The residue was separated from the solution and the adhering mother liquor was removed by pressing and rubbing it between folded filter paper as rapidly as possible ; then it was dissolved in water to a definite volume.

In this case the residue consisted always of two species of crystals differing in colour and size. The copper sulphate appeared as large deep blue triclinic crystals, the habitus was somewhat columnar, often attaining a size of about 7 mm. It was mechanically separated and on analysis proved to be the pure hydrate, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$. On the other hand, the solid solution consisted of very fine, light blue crystals, which appeared as rhombus forms under the microscope ; after removing the copper sulphate crystals they were found to be represented by the formula assigned to the solid solution S_1 . The composition of the solid solution varied continuously with that of the liquid phase.

The experiment for the case B was carried out in a quite different way. In the previous case A, the procedure was very simple, as, though there appeared two solid phases, one of them was only a single salt of a definite composition. Now, in the case B the matter is far more complicated, because the co-existence of two kinds of solid solutions is expected. The preliminary examinations were undertaken as follows:— A comparatively small quantity of copper sulphate, and ammonium and potassium sulphates in different proportions were mixed with water in an Erlenmeyer flask, and the mixture

was made to attain equilibrium at 25.0° as in the other case. The composition of the solutions varied continuously whenever in the residue the copper radical, in the molecular relation, was less than half the total sulphate radical, and there was no indication of the existence of more than two solid phases. In a case when the residue contained the copper radical in a quantity the exact moiety of the total sulphates, the water of crystallization almost satisfied the requirement for the solid solution, S_1 . Moreover, when the residue contained a very small quantity of copper, the co-existence of the solid solution, S_2 , could be directly confirmed. Both of these solid solutions were very fine crystals discriminated from each other by their rhombus and orthogonal shapes under the microscope, but to the naked eyes the mixture appeared homogeneous.

For the determination of the compositions of these residues, the mutual separation of them for analysis would have given the most accurate and simplest method, but the simple mechanical separation was impossible. The utilization of the difference of a physical property, i.e. the specific gravities of the substances, suggested itself, but preliminary experiments proved the futility of it.

Now as the direct separation of the mixed residue ended in failure, some other method had to be sought. If we get a residue which contains a large quantity of one of the solid solutions and a very small part of the other, we can determine at least approximately the composition of the former, but this is a tedious and speculative method. If we have two kinds of residues which correspond to the one and same solution and yet contain the two solid solutions in different proportions, we can determine the compositions of the two phases at the same time, as we now obtain two equations for two unknown quantities. This method is more interesting and practicable than the above method, and was adopted in the second experiment. This method is based on the following consideration.

The residue (1) consists of a large part of the solid solution S_2 of the single salts and a small part of the other solid solution S_1 . The residue (2), on the contrary, contains a relatively very large quantity of the latter. Let the molecular ratio of copper, ammonium, and potassium sulphates in the residue (1) be $a : b : c$, and that in (2) $a' : b' : c'$, then we have the following relations.

In the residue (1) containing 1 mole of copper sulphate, we have

- (b/a) = moles of total ammonium sulphate,
 $(b/a - y)$ = moles of ammonium sulphate contained in the solid solution S_2 ,
 $(b/a + c/a)$ = moles of total ammonium and potassium sulphates,
 $(b/a + c/a - 1)$ = moles of ammonium and potassium sulphates forming the solid solution S_2 ,
 $(b/a + c/a - 1)x$ = moles of ammonium sulphate in the solid solution S_2 ,

therefore,

$$(b/a + c/a - 1)x = (b/a - y).$$

Similarly for the residue (2), we have

$$(b'/a' + c'/a' - 1)x = (b'/a' - y).$$

From these two equations, we have

$$\begin{aligned}
 x &= (ba' - b'a) / ((b+c)a' - (b'+c')a) \\
 y &= ((c-a)b' - (c' - a')b) / ((b+c)a' - (b'+c')a).
 \end{aligned}$$

In order to diminish errors in the calculation, the residues must have in their compositions as large a difference as possible. For this purpose the experiment was carried out in the following way:— The quantities of the sulphates and water were taken in such proportions that the residue (2) was deposited when they attained the equilibrium state. They were put in a special tube of H-form of about 100 c.c. capacity, and were made to form a solution at 60°, then the tube was set in rotation in the thermostat at 25.0° for about 24 hours. Now, nearly all the residue was collected in one limb of the tube and the solution was divided almost equally between both limbs. By means of a curved glass rod a piece of cleaned cotton cloth of about 5 cm. square was put into the lateral part of the tube in such a manner that it made complete contact with the glass wall. To the limb, where only a small portion of the residue was present, a finely powdered mixture of ammonium and potassium salts, which was roughly calculated to make the residue (1), was added. The H-tube was warmed to dissolve the salts as much as possible, then cooled by shaking it in cold water to have the deposition of the solid solutions,

during these operations care being taken that the contents of the two limbs should not be mixed up. Finally the tube was made to rotate in the thermostat round an axis parallel to the lateral part of the tube. In this way the equilibrium in each of the two parts and also between them was effected without much mixing of residues with each other. At first, however, failures occurred very often, as when a large cloth was inserted, the equilibrium between the two parts was reached very slowly, while if a smaller one was used, the residue in the two parts became mixed up. But by introducing a modifications in the shape of the H-tube, namely by somewhat tapering the lateral tube toward the places where it opens into the side tubes, the difficulty was removed. After three weeks' revolution the solutions and the residues in both limbs were taken out and subjected to analysis. This method gave a satisfactory result as expected from the preliminary experiments, but the error was naturally much higher than in the former case A.

Results.

The results obtained in the experiments for the simple case A are given in the following tables.

TABLE I.

Composition of solution saturated with copper sulphate and solid solution S_1 in gram percentages.

No.	CuSO_4	$(\text{NH}_4)_2\text{SO}_4$	K_2SO_4	H_2O
1	19.32	...	2.82	77.86
2	19.36	0.83	2.58	77.23
3	19.37	1.11	2.66	76.86
4	19.45	1.66	2.12	76.77
5	19.36	2.01	2.11	76.52
6	19.32	2.64	1.92	76.12
7	19.51	2.82	1.69	75.98
8	19.38	3.34	1.44	75.84
9	19.46	3.81	1.04	75.69
10	19.50	4.17	0.85	75.48
11	19.50	4.64	0.63	75.23
12	19.46	4.83	0.48	75.23
13	19.47	5.33	...	75.20

The following table was deduced from these data.

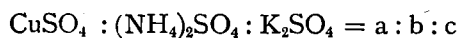
TABLE 2.

In this table the composition of solution is represented by the formula $100\text{mH}_2\text{O}\cdot\text{XCuSO}_4\cdot\text{Y}(\text{NH}_4)_2\text{SO}_4\cdot(100-\text{X}-\text{Y})\text{K}_2\text{SO}_4$.

No.	X.	Y.	(100-X-Y).	m.
1	88.22	...	11.78	31.49
2	85.23	4.41	10.36	30.11
3	83.68	5.82	10.50	29.40
4	83.14	8.56	8.30	29.07
5	81.66	10.22	8.12	28.58
6	79.62	13.15	7.23	27.78
7	79.75	13.93	6.32	27.49
8	87.38	16.30	5.32	27.17
9	77.76	18.41	3.83	26.79
10	77.02	19.89	3.09	26.40
11	75.95	21.81	2.24	25.95
12	75.63	22.68	1.69	25.89
13	75.14	24.86	...	25.70

TABLE 3.

Molecular ratios of sulphates in the residue.



No.	a	b	c
1
2	41.37	3.17	25.98
3	45.91	3.67	21.04
4	43.21	7.12	20.86
5	43.67	7.10	14.57
6	38.13	16.38	21.16
7	46.93	12.03	12.61
8	39.87	21.00	15.03
9	42.63	21.97	9.48
10	42.09	26.13	7.68
11	42.43	27.76	4.27
12	41.46	31.96	3.71
13

TABLE 4.

Molar fraction of ammonium sulphate in total alkali sulphates.

No.	In aqueous solution.	In solid solution.
I
2	29.80	10.88
3	35.56	14.86
4	50.79	25.47
5	55.62	32.74
6	64.51	43.62
7	68.74	48.83
8	75.36	58.29
9	82.85	69.86
10	86.56	77.29
11	90.63	86.68
12	93.05	89.60
13	100.00	100.00

The results for the case B are in the following.

TABLE 5.

Composition of solution saturated with two solid solutions, namely S_1 and S_2 , in gram percentages.

No.	$CuSO_4$	$(NH_4)_2SO_4$	K_2SO_4	H_2O
1	1.30	...	11.14	87.56
2	1.35	1.71	11.07	85.87
3	1.35	2.23	10.92	85.50
4	1.36	4.17	10.54	83.93
5	1.34	6.59	10.07	82.00
6	1.35	7.97	10.28	80.40
7	1.27	10.47	9.45	78.81
8	1.20	12.83	8.96	77.01
9	1.08	17.88	8.16	72.88
10	0.92	20.77	7.60	70.71
11	0.89	22.35	7.20	69.56
12	0.82	25.49	6.20	67.49
13	0.64	28.62	5.13	65.61

14	0.55	33.44	4.02	61.99
15	0.43	37.18	3.58	58.81
16	0.40	40.16	2.06	57.38
17	0.37	43.10	...	56.53

TABLE 6.

In this table the composition of solution is represented by the formula $100\text{mH}_2\text{O} \cdot \text{XCuSO}_4 \cdot \text{Y}(\text{NH}_4)_2\text{SO}_4 \cdot (100 - \text{X} - \text{Y})\text{K}_2\text{SO}_4$.

No.	X.	Y.	(100 - X - Y).	m.
1	11.27	...	88.73	67.41
2	9.93	15.26	74.81	56.10
3	9.59	19.19	17.22	53.90
4	8.46	31.35	60.19	46.28
5	7.28	43.01	49.76	39.22
6	6.61	47.19	46.20	34.92
7	5.60	56.02	38.38	30.91
8	4.80	62.23	32.97	27.37
9	3.59	71.66	24.75	21.40
10	2.80	76.10	21.10	19.00
11	2.58	78.27	19.15	17.86
12	2.20	82.56	15.24	16.04
13	1.61	86.62	11.77	14.56
14	1.24	90.53	8.23	12.30
15	0.88	92.39	6.73	10.71
16	0.79	95.48	3.73	10.00
17	0.70	99.30	...	9.55

TABLE 7.

Molecular ratios of sulphates in the residues.

No.	a	:	b	:	c	:	a'	:	b'	:	c'
1
2	0.28		0.54		89.98		17.44		1.21		63.54
3	0.41		0.36		90.73		19.49		1.53		69.98
4	0.21		0.62		90.54		21.68		2.32		56.41
5	5.33		1.80		82.06		14.88		2.90		66.27
6	4.83		2.79		81.22		16.02		4.15		63.34
7	6.30		4.72		79.01		21.57		8.26		52.52

8	2.98	10.92	77.78	25.65	11.10	42.30
9	2.95	10.06	74.55	30.05	16.54	32.59
10	5.34	18.32	70.55	23.37	20.42	40.93
11	7.62	21.46	64.72	33.56	21.92	23.72
12	6.43	25.84	61.45	35.24	24.39	18.66
13	2.83	31.12	64.07	32.34	36.40	22.42
14	6.84	40.93	49.70	36.53	30.83	12.20
15	3.72	66.83	37.40	37.64	36.24	7.35
16	3.26	83.81	22.63	37.58	36.29	5.29
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TABLE 8.

Molar fraction of ammonium sulphate in total alkali sulphates.

No.	In aqueous solution	In single solid solution S_2	In double solid solution S_1^1
1
2	16.93	0.58	5.34
3	21.23	0.37	7.03
4	34.27	0.66	9.55
5	46.34	1.29	14.76
6	50.54	2.42	18.14
7	59.34	3.50	32.03
8	65.39	11.69	30.63
9	74.32	16.84	44.33
10	78.29	18.24	57.71
11	80.35	21.74	57.48
12	84.43	26.93	63.24
13	88.02	31.70	65.49
14	91.64	42.59	76.91
15	93.22	63.30	86.33
16	96.25	78.45	88.28
17	100.00	100.00	100.00

From the data in Tables 2 and 6, neglecting water, Fig. 1 was obtained, and from data in Tables 4 and 8, Fig. 2.

In Fig. 1, the angular points, A, B, and C, represent CuSO_4 , $(\text{NH}_4)_2\text{SO}_4$, and K_2SO_4 , respectively, and the straight lines, BC and HK, the single solid solutions S_2 and the double solid solutions S_1

respectively. The curves, DE and FG, represent the solutions saturated with $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and the double solid solutions and those saturated with the double and single solid solutions respectively. The relation between the compositions of the solutions and the residue is expressed by the tie lines connecting the corresponding points.

In Fig. 2, the horizontal and vertical sides represent the molar fraction of ammonium sulphate in the total alkali sulphates in the solid solutions and in the aqueous solutions respectively, and those three curves, representing the three cases respectively, show the relative distribution of the two alkali sulphates between solid and liquid solutions.

Summary.

The equilibrium in the system of copper, potassium, and ammonium sulphates and water at 25°C . has been studied and the relation between the composition of aqueous solutions and that of the solid solutions determined when the residue is a mixture of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and $\text{CuSO}_4 \cdot (\text{NH}_4, \text{K})_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ and also when it is a mixture of $(\text{NH}_4, \text{K})_2\text{SO}_4$ and $\text{CuSO}_4 \cdot (\text{NH}_4, \text{K})_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$.

In the latter case, where the single and double solid solutions are mixed in the residue, it was difficult to determine the compositions of those solid solutions separately. Thus a new experimental method was devised to remove that difficulty, and it proved to be satisfactory.

This work was suggested by Prof. Y. Osaka and carried out under his direction. The author wishes to take this opportunity to thank him for his helpful suggestions and kind instructions.

Fig. 1.

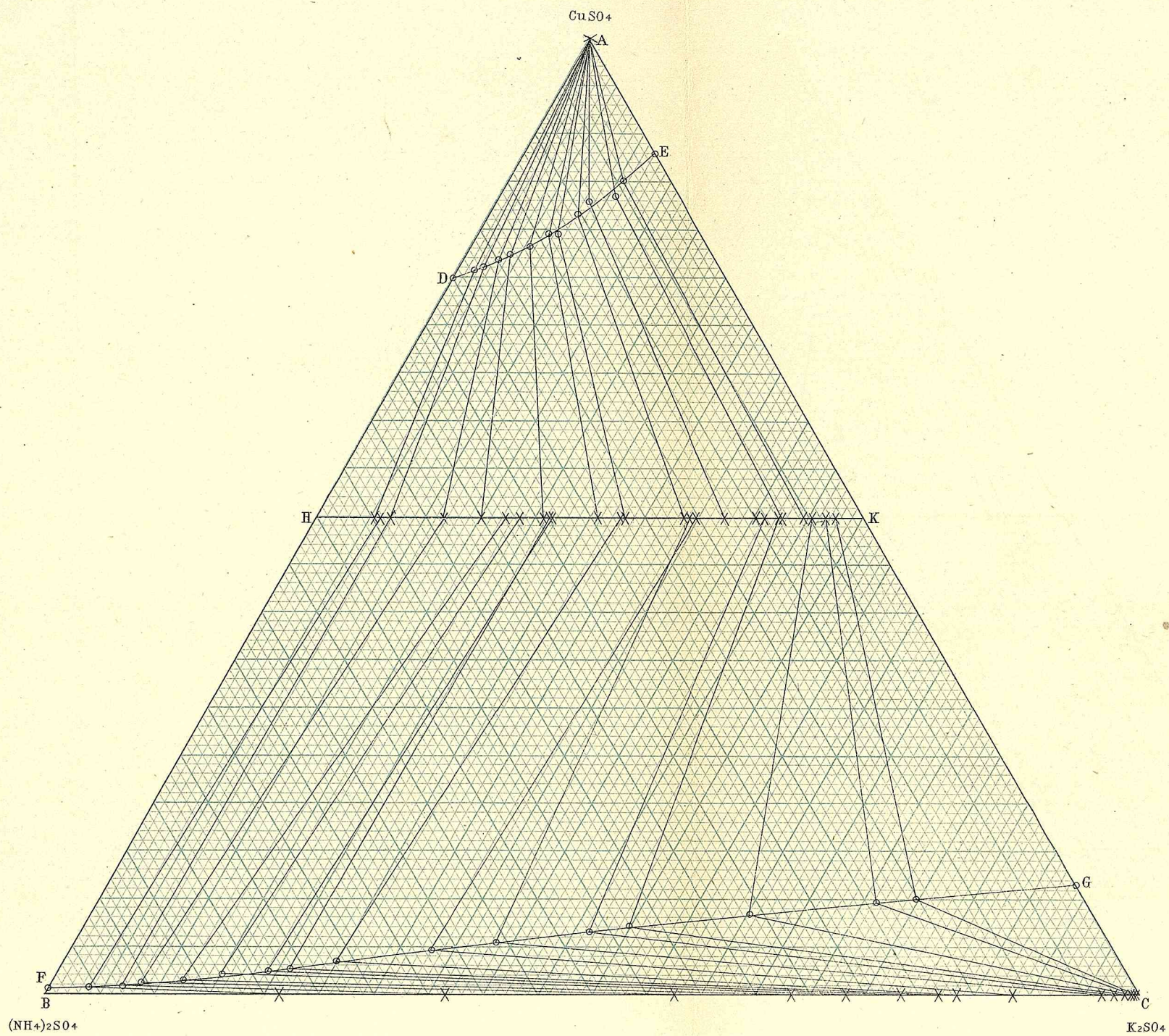


Fig. 2.
Molar fraction of ammonium sulphate in total alkali sulphate.

