

# A STUDY OF THE SYSTEMS $\text{CuSO}_4\text{-NiSO}_4\text{-H}_2\text{O}$ AND $\text{CuSO}_4\text{-CoSO}_4\text{-H}_2\text{O}$ .

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Received April 12, 1938.

PRASAD AND TENDULKAR<sup>1</sup> have shown that the nickel-copper matte obtained by roasting the nickel ore contains most of the nickelous oxide in the passive state. Consequently when the matte is treated with dilute sulphuric acid nearly the whole of copper oxide and very little of nickel oxide go into solution. These authors have also suggested that the small amount of nickel in solution may be due to (i) the presence of small quantities of nickelic oxide in the matte and (ii) the action between nickel oxide and aqueous solution of copper sulphate. However, another factor which may influence the relative amounts of copper and nickel salts in the leached solution is the mutual effect of the solubilities of nickel and copper sulphates.

A search of literature revealed that although the system alkali sulphate—nickel sulphate—water has been studied in great detail practically no data is available on the study of the system  $\text{CuSO}_4\text{-NiSO}_4\text{-H}_2\text{O}$ . Mitscherlich<sup>2</sup> found that monoclinic or triclinic crystals separate out of a solution containing both the salts depending upon their relative proportions. Fock<sup>3</sup> gave more details about the conditions under which the two types of crystals are obtained and confirmed the observations of Mitscherlich. Double sulphates having the formula  $\text{CuSO}_4 \cdot 2\text{NiSO}_4 \cdot x\text{H}_2\text{O}$  have been obtained from mixed solutions of the component salts by Etard,<sup>4</sup> Dufet,<sup>5</sup> Boisbaudran<sup>6</sup> and Hauer.<sup>7</sup>

In order to investigate the effect of adding increasing quantities of copper sulphate on the solubility of nickel sulphate, the system nickel sulphate,

<sup>1</sup> *J.C.S.*, 1931, 1407.

<sup>2</sup> *Pogg. Ann.*, 1827, **11**, 326 ; 1828, **12**, 146.

<sup>3</sup> *Zeit. Kryst.*, 1897, **28**, 385.

<sup>4</sup> *Compt. Rend.*, 1878, **87**, 602.

<sup>5</sup> *Ibid.*, 1878, **86**, 880.

<sup>6</sup> *Ann. Chim. Phys.*, 1869, **18**(4), 288.

<sup>7</sup> *Pogg. Ann.*, 1865, **125**, 638.

copper sulphate and water, was studied at 40°. A study of the system, cobalt sulphate, copper sulphate and water, was a natural sequel and it was also investigated in the same manner and at the same temperature as the above-mentioned system. This system has been investigated by Crockford and Brawley<sup>8</sup> at 0° and 25°. They found that at both these temperatures the solids consist of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  and a series of solid solutions in which the copper salt is partially replaced by  $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ .

#### *Experimental.*

It was ascertained that 40 g. of nickel sulphate, 35 g. of cobalt sulphate and 20 g. of copper sulphate are more than sufficient to form saturated solutions in 25 c.c. of water. These chemicals were Kahlbaum's extra pure substances and were used after testing their purity. The different mixtures were kept in well-stoppered glass bottles and shaken in a water thermostat at 40° for more than 90 hours. The metal rack holding the bottles was rotated by means of an electric motor. After shaking the mixture for the above length of time it was assumed that equilibrium was reached. The liquid was separated from the solid phase and it was analysed.

The amounts of copper, nickel and cobalt were estimated by the electro-deposition method using a rotating platinum gauze cathode and a platinum gauze anode. From the weights of the metals deposited the corresponding amounts of the sulphates were calculated. The results obtained for the systems  $\text{CuSO}_4\text{—NiSO}_4\text{—H}_2\text{O}$  and  $\text{CuSO}_4\text{—CoSO}_4\text{—H}_2\text{O}$  are given in Tables I and II and are represented by means of triangular diagrams given in Figs. 1 and 2.

It will be seen from Table I that when the concentration of copper sulphate increases from 0.00 g. to 8.47 g. (Nos. 1 to 4) the solubility of nickel sulphate decreases from 32.33 g. to 26.10 g. per 100 g. of the solution. Similarly when the concentration of nickel sulphate increases from 0.00 g. to 21.52 (Nos. 9 to 19) the solubility of copper sulphate decreases from 23.00 g. to 11.73 g. per 100 g. of the solution. Nos. 5 to 8 show that the composition of the solution is nearly constant.

Applying the phase rule,  $F = C - P + 2$ , to the present system it will be seen that there are three components, copper sulphate, nickel sulphate and water and the phases are vapour, solution and either one or two solid hydrates. The system will be bivariant in the first case and univariant in the second; in the latter case the composition of the solution will remain practically constant at constant temperature. The data on the

<sup>8</sup> *J. Phys. Chem.*, 1932, 36, 1534.

TABLE I.

$\text{CuSO}_4 - \text{NiSO}_4 - \text{H}_2\text{O}$  at  $40^\circ$ .

No.	Liquid				Solid		Solid Phase
	% $\text{NiSO}_4$	% $\text{CuSO}_4$	% $\text{H}_2\text{O}$	% $\text{NiSO}_4$	% $\text{CuSO}_4$	% $\text{H}_2\text{O}$	
1	32.33	..	67.67	55.24	..	44.76	$\text{NiSO}_4, 7 \text{H}_2\text{O}$
2	30.92	2.21	66.87	55.24	..	44.76	„
3	27.41	6.56	66.03	55.24	..	44.76	„
4	26.10	8.47	65.43	55.24	..	44.76	„
5	25.28	9.68	65.04	45.32	11.36	43.32	$\text{NiSO}_4, 7 \text{H}_2\text{O}$ and solid solution
6	25.30	9.70	65.00	39.25	18.40	42.35	„
7	25.10	9.87	65.03	35.22	23.09	41.69	„
8	25.20	9.90	64.90	31.25	27.69	41.06	„
9	21.52	11.73	66.75	..	63.94	36.06	$\text{CuSO}_4, 5 \text{H}_2\text{O}$
10	19.86	12.59	67.55	..	63.94	36.06	„
11	18.18	13.80	68.02	..	63.94	36.06	„
12	16.85	14.56	68.59	..	63.94	36.06	„
13	14.74	15.65	69.61	..	63.94	36.06	„
14	12.71	16.63	70.66	..	63.94	36.06	„
15	10.37	17.80	71.83	..	63.94	36.06	„
16	8.57	19.01	72.42	..	63.94	36.06	„
17	5.42	20.00	74.58	..	63.94	36.06	„
18	2.70	21.19	76.11	0.22	63.69	36.09	„
19	..	23.00	77.00	..	63.94	36.06	„

TABLE II.

*System CuSO<sub>4</sub> - CoSO<sub>4</sub> - H<sub>2</sub>O at 40°.*

No.	Liquid				Solid		Solid Phase
	% CoSO <sub>4</sub>	% CuSO <sub>4</sub>	% H <sub>2</sub> O	% CoSO <sub>4</sub>	% CuSO <sub>4</sub>	% H <sub>2</sub> O	
1	31.90	..	68.10	55.16	..	44.84	CoSO <sub>4</sub> , 7 H <sub>2</sub> O
2	30.14	2.00	67.86	52.23	3.39	44.38	„
3	27.99	3.65	68.36	49.04	7.10	43.86	Solid solution
4	25.00	7.30	67.70	47.57	8.79	43.64	„
5	23.39	9.06	67.55	46.96	9.51	43.53	„
6	22.04	10.50	67.46	45.40	11.31	43.29	„
7	21.44	11.38	67.18	42.53	14.64	42.83	„
8	19.63	12.50	67.87	37.56	20.40	42.04	Solid solution & CuSO <sub>4</sub> , 5 H <sub>2</sub> O
9	19.34	12.64	68.02	27.72	31.81	40.47	„
10	19.76	12.46	67.76	0.00	63.94	36.06	CuSO <sub>4</sub> , 5 H <sub>2</sub> O
11	18.18	13.24	68.58	1.22	62.53	36.24	„
12	16.75	14.45	68.80	0.00	63.94	36.06	„
13	15.20	15.29	69.51	0.00	63.94	36.06	„
14	11.51	17.01	71.48	0.44	63.43	36.13	„
15	9.79	17.96	72.25	0.00	63.94	36.06	„
16	4.88	20.12	75.00	2.26	61.32	36.42	„
17	2.55	21.33	76.11	1.19	62.56	36.25	„
18	..	22.92	77.08	..	63.94	36.06	„

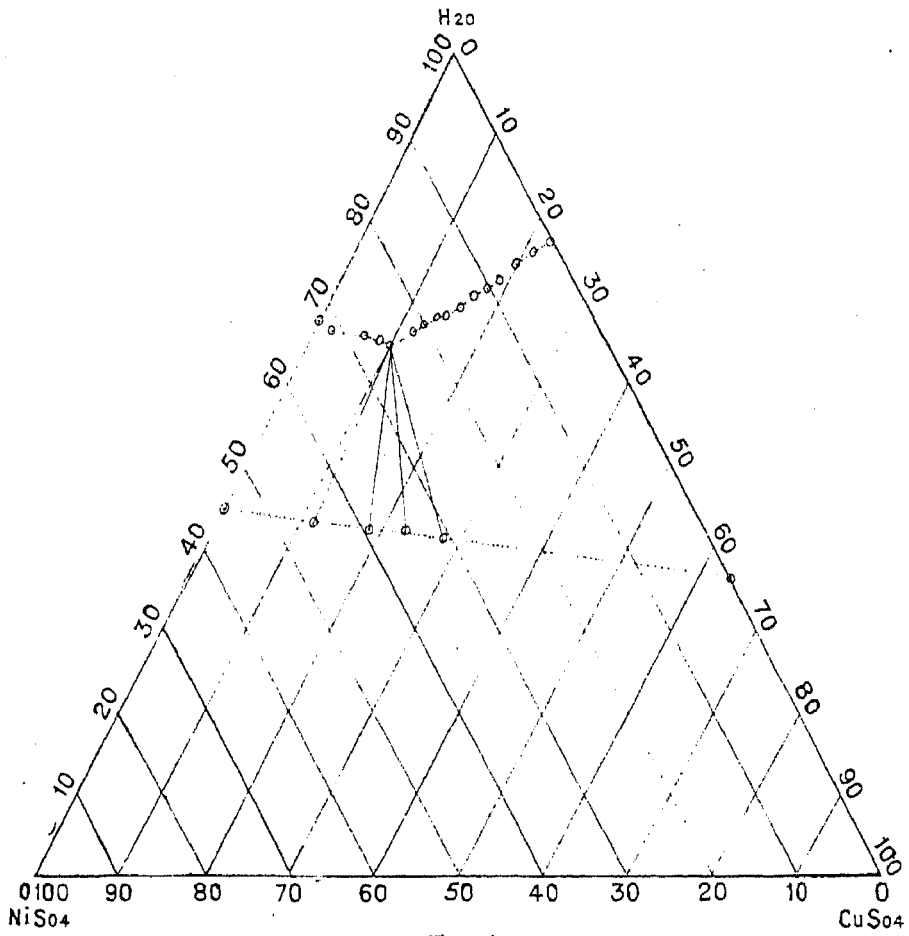


FIG. 1.

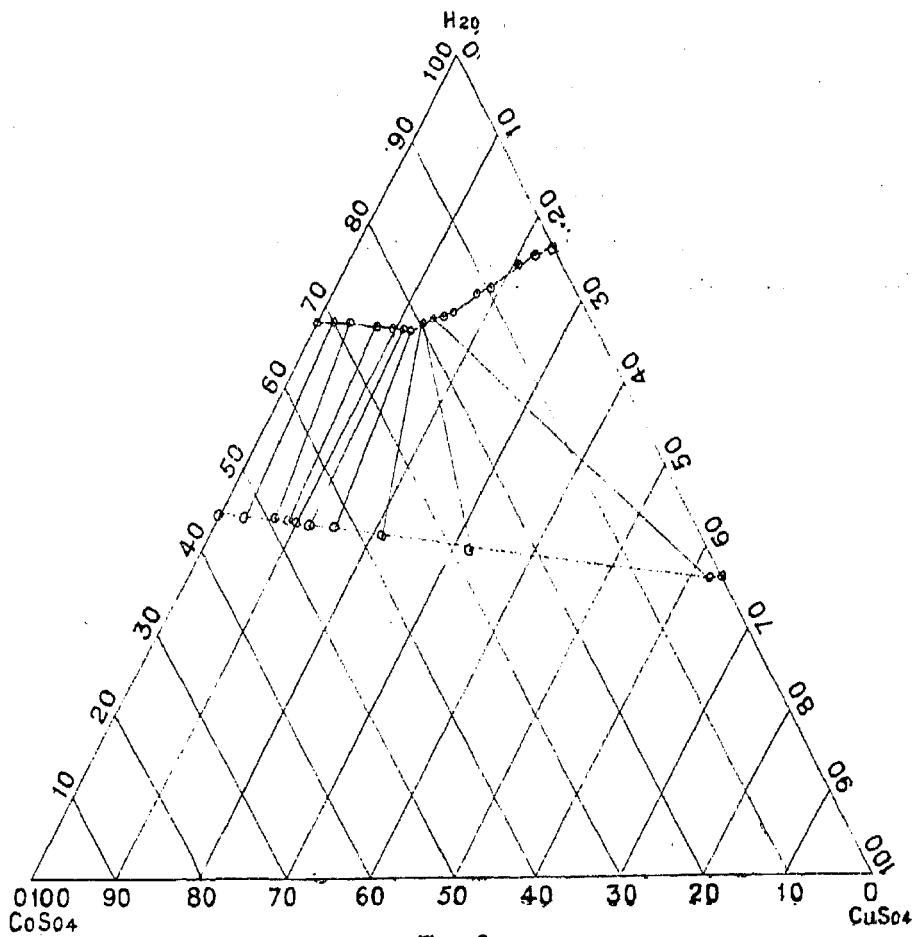


FIG. 2.

composition of the solid is in accordance with the above-mentioned conclusions. The residue in Nos. 1 to 4 consists of only  $\text{NiSO}_4, 7\text{H}_2\text{O}$  and in Nos. 9 to 19 of only  $\text{CuSO}_4, 5\text{H}_2\text{O}$ ; Nos. 5 to 8 contain the two solid hydrates in varying proportions.

Table II shows that the solubility of cobalt sulphate falls from 31.90 g. to 21.44 g. (Nos. 1 to 7) per 100 g. of solution when the concentration of copper sulphate increases from 0.00 g. to 11.38 g. Similarly when the concentration of cobalt sulphate is increased from 0.00 g. to 18.18 g. the solubility of copper sulphate decreases from 22.92 g. to 13.24 g. (Nos. 11 to 18) per 100 g. of the solution. Nos. 8 and 9 show nearly a constant composition.

The composition of the residues in Nos. 1 and 2 and those in Nos. 10 to 18 shows that they consist of only  $\text{CoSO}_4, 7\text{H}_2\text{O}$  and  $\text{CuSO}_4, 5\text{H}_2\text{O}$ , respectively, and that the system is bivariant. Solids in Nos. 8 and 9 contain both copper and cobalt sulphates and the system is univariant. This is supported by the constancy of the composition of the solutions. The solids in Nos. 3 to 7 also contain both copper and cobalt sulphates but the composition of the solution varies in the different mixtures. This leads to the conclusion that the solid phases in these cases are solid solutions and the system is bivariant. The existence of solid solutions in this system has also been found by Crockford and Brawley who studied it at low temperatures. This data also shows that if the solid consists of two phases—one being the hydrated salt and the other solid solution—the composition of the liquid is constant.

Figs. 1 and 2 show that the curves consist of two branches. This shows that there are no possibilities of the formation of double salts of copper sulphate and nickel sulphate and those of copper sulphate and cobalt sulphate under these conditions.