

CCCXLV.—*Equilibrium in the Systems Nickel Sulphate–Potassium Sulphate–Water, Zinc Sulphate–Potassium Sulphate–Water, and Manganese Sulphate+Potassium Sulphate–Water at 25°.*

By ROBERT MARTIN CAVEN and WILLIAM JOHNSTON.

THE experiments here described are a continuation of the work of Caven and Mitchell (J., 1924, 125, 1428) to determine the limits of existence of double salts of the type $M^uSO_4.M^vSO_4.6H_2O$ in equilibrium with solutions containing their component salts, and to obtain evidence of the existence of the double salts in these solutions.

Lipscomb and Hulett (*J. Physical Chem.*, 1916, 20, 75) have examined the system $ZnSO_4-K_2SO_4-H_2O$ at 25°, and obtained results which differ from ours in showing potassium sulphate to cause a decrease in the solubility of zinc sulphate.

It has already been shown (*loc. cit.*) that the double salts $CuSO_4.M^vSO_4.6H_2O$ ($M^v = K$ or NH_4) are stable over wide ranges of temperature and relative concentrations of the component salts. Moreover, the continuous increase in solubility of each of the three simple salts caused by the addition of the second component up to the triple point, at which the double salt separates, was believed to indicate the presence of a considerable amount of the double salt, or its ions, in solution.

EXPERIMENTAL.

The Systems $NiSO_4-K_2SO_4-H_2O$ and $ZnSO_4-K_2SO_4-H_2O$ at 25°.

For the nickel system, solutions of the two salts were made at 40°, and various proportions of the two solutions placed successively in a flask, fitted with a stirrer, and kept in a thermostat at $25^\circ \pm 0.1^\circ$. The mixtures were stirred for 3 days, and then portions of the solutions and solid phases were separated and analysed.

The nickel was determined volumetrically by adding an excess of potassium cyanide and titrating back with standard nickel sulphate solution in presence of ammonia, diphenylglyoxime being used as indicator (Kelly and Conant, *Ind. Eng. Chem.*, 1916, 8, 804). The potassium was calculated after determination of the total sulphate.

The procedure for the zinc system was the same as for the nickel system. The zinc was estimated volumetrically by the potassium ferrocyanide method, and the total sulphate determined.

The quantities in the tables are expressed as g. per 100 g. of solution (for the solutions) or of moist solid (for the "rests").

TABLE I.

The System NiSO₄-K₂SO₄-H₂O at 25°.

Solutions.			Rests.			Solid phase.
K ₂ SO ₄ .	NiSO ₄ .	H ₂ O.	K ₂ SO ₄ .	NiSO ₄ .	H ₂ O.	
10.59	Nil.	89.41	—	—	—	K ₂ SO ₄ .
11.16	0.33	88.51	39.63	14.59	45.78	
4.93	1.35	93.72	25.00	20.75	54.25	Double salt.
4.15	3.90	91.95	24.35	21.85	53.80	
4.11	10.15	85.74	25.75	25.50	48.75	
4.75	15.66	79.59	32.50	31.32	36.18	
5.62	19.33	75.05	31.61	31.58	36.81	
6.82	23.09	70.09	32.22	32.76	35.02	
8.26	27.90	63.84	11.20	42.60	46.20	
6.30	27.92	65.78	1.45	48.75	49.80	Double salt and NiSO ₄ ·7H ₂ O.
3.82	27.87	68.31	0.55	50.32	49.13	
Nil.	27.94	72.06	—	—	—	NiSO ₄ ·7H ₂ O.

TABLE II.

The System ZnSO₄-K₂SO₄-H₂O at 25°.

Solutions.			Rests.			Solid phase.
K ₂ SO ₄ .	ZnSO ₄ .	H ₂ O.	K ₂ SO ₄ .	ZnSO ₄ .	H ₂ O.	
10.59	Nil.	89.41	—	—	—	K ₂ SO ₄ .
10.71	1.11	88.18	80.08	0.25	19.67	
10.94	1.91	87.15	43.35	26.00	30.65	
6.52	4.73	88.75	32.09	29.37	38.54	Double salt.
5.99	5.40	88.61	31.04	28.69	40.27	
3.19	25.11	71.70	27.01	32.51	40.48	
2.27	33.08	64.65	26.08	35.21	38.71	
1.95	35.58	62.47	22.75	36.00	41.25	
1.82	36.00	62.18	25.51	36.23	38.26	
1.85	36.39	61.78	11.58	50.33	38.09	
1.44	36.42	62.14	0.58	48.95	50.47	Double salt and ZnSO ₄ ·7H ₂ O.
Nil.	36.61	63.39	—	—	—	

The System MnSO₄-K₂SO₄-H₂O at 25°.

As the system MnSO₄-H₂O shows a transition point at 27°, where after the solubility decreases, there was no advantage in preparing solutions of manganese sulphate above this temperature. Saturated solutions of the two salts were therefore made at room temperature and mixed in various proportions; the mixtures were then evaporated isothermally at 25° by a filtered current of air. When sufficient solid phases had separated, the solutions were transferred to the reaction-vessel and stirred for 3 days.

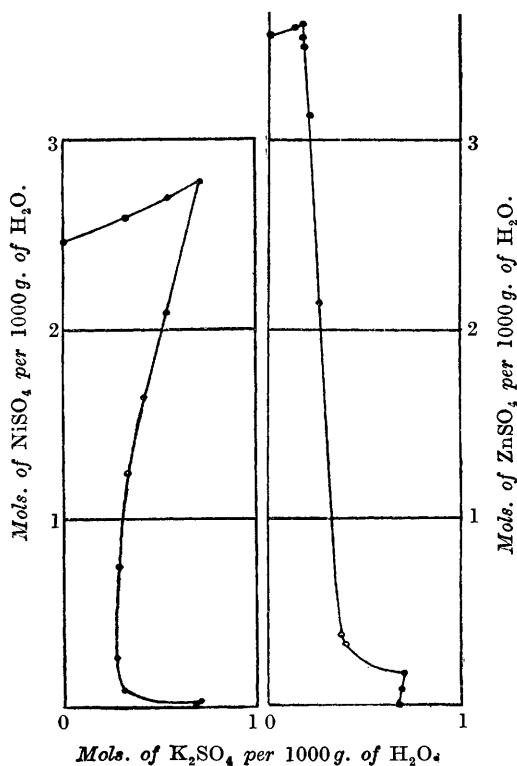
The manganese was estimated volumetrically with permanganate by the Volhard method, the total sulphate determined, and the potassium sulphate calculated.

TABLE III.

Solutions.			Rests.			Solid phase.
K ₂ SO ₄ .	MnSO ₄ .	H ₂ O.	K ₂ SO ₄ .	MnSO ₄ .	H ₂ O.	
10.59	Nil.	89.41	—	—	—	K ₂ SO ₄ .
11.27	6.30	82.43	74.62	1.78	23.40	
12.04	15.22	72.74	77.46	3.66	18.98	
12.31	16.58	71.11	53.33	20.71	25.96	K ₂ SO ₄ and double salt.
10.06	19.27	70.67	30.91	30.83	38.26	
5.27	30.47	64.26	29.02	35.01	35.97	Double salt.
4.30	35.58	60.12	31.42	37.23	31.35	
4.20	37.28	58.52	28.42	37.75	33.83	
4.15	37.92	57.93	11.88	47.42	40.70	
3.03	38.21	58.76	1.25	56.66	42.09	Double salt and MnSO ₄ ·4H ₂ O.
2.46	38.42	59.12	0.83	58.42	41.75	
1.87	38.54	59.59	0.66	57.35	42.99	MnSO ₄ ·4H ₂ O.
0.43	39.03	60.55	0.17	60.01	39.82	
Nil.	39.10	60.90	—	—	—	

FIG. 1.

FIG. 2.

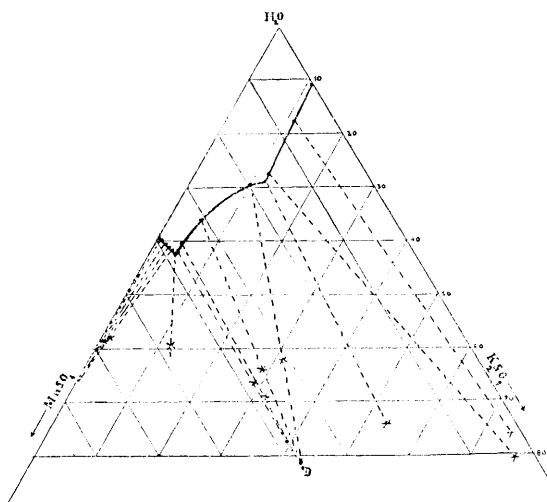


Conclusions.

1. Increase in solubility of potassium sulphate is observed when increasing quantities of nickel, zinc, or manganese sulphate are present, until the triple point is reached; and, reciprocally, increase in solubility of each of these three bivalent sulphates appears with increasing quantities of potassium sulphate up to the triple point in each case, although this increase is small with manganese sulphate.

These facts are shown for the nickel and zinc systems in Figs. 1 and 2, respectively, for which quantities are calculated, not as in

FIG. 3.



Equilibrium Diagram K_2SO_4 - $MnSO_4$ - H_2O at 25° .

The composition of the double salt is shown, by the co-ordinates of the point D at which broken lines drawn through "rests" intersect, to be $MnSO_4, K_2SO_4, 4H_2O$.

the tables, where the percentage compositions of the solutions are shown with varying amounts of water, but as mols. of each salt per 1000 g. of water.

The manganese system is represented by a triangular diagram (Fig. 3), in order to show how the composition of the double salt is arrived at; but on this diagram, which corresponds with the figures in the table, the small increase in solubility of manganese sulphate does not appear.

2. The range of existence of each double salt at 25° is as follows:

Nickel potassium sulphate, from 0.031 to 3.8 mols. of $NiSO_4$ to 1 mol. of K_2SO_4 .

Zinc potassium sulphate, from 0.19 to 21.3 mols. of ZnSO_4 to 1 mol. of K_2SO_4 .

Manganese potassium sulphate, from 1.5 to 10.4 mols. of MnSO_4 to 1 mol. of K_2SO_4 .

3. The relations between these concentrations in the case of the nickel double salt lead to a curious result which is seen when the figures are plotted on a rectangular diagram. Thus the double salt may be in equilibrium with the same concentration of potassium sulphate but with widely different concentrations of nickel sulphate; and the curve changes its direction so that its upper part is vertically above some of the lower part.

4. The shorter range in the case of the manganese double salt results chiefly from the large quantity of manganese sulphate which must be present before double salt formation can begin. This salt, however, cannot properly be compared with the others, because it has the composition $\text{MnSO}_4 \cdot \text{K}_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$, as indicated by Fig. 3. This result accords with the conclusions of Tutton (*J.*, 1893, **63**, 342; 1896, **69**, 344).

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ROYAL TECHNICAL COLLEGE,
GLASGOW.

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