CCCXXXII.—*Equilibrium in the Systems* $ZnSO_4$–Na_2SO_4–H_2O *at* $0°$ *and* $25°$; $MnSO_4$–Na_2SO_4–H_2O *at* $0°$, $25°$, *and* $35°$; *and* $CoSO_4$–K_2SO_4–H_2O *at* $25°$.

By ROBERT MARTIN CAVEN and WILLIAM JOHNSTON.

KOPPEL and GUMPERZ (*Z. physikal. Chem.*, 1905, **52**, 409) have investigated the double salts formed by sodium sulphate with a series of the sulphates of the bivalent metals. These double sulphates are formed, not at $0°$, but at higher temperatures. However, while Koppel and Gumperz were mainly interested in the double salts formed, the present authors are more concerned with the type of isotherms given by the various systems. Thus, whilst Koppel (*Z. physikal. Chem.*, 1903, **42**, 1) showed that the double salt $CuSO_4$,Na_2SO_4,$2H_2O$ does not crystallise below $16·7°$ from a solution of its component salts, the authors (J., 1927, 2358) investigated the isotherms of the system $CuSO_4$–Na_2SO_4–H_2O at $0°$, $25°$, and $37·5°$.

Koppel and Gumperz (*loc. cit.*) have shown that the double salt $ZnSO_4$,Na_2SO_4,$4H_2O$ is formed from a solution of its component salts only above $8·7°$. They did not, however, examine the system completely at any given temperature, so it was decided to investigate the isotherms at $0°$ and $25°$.

Geiger (Thesis, Berlin, 1904) alleged that the double salt of manganese sulphate and sodium sulphate existed in two hydrated forms : $MnSO_4$,Na_2SO_4,$4H_2O$ and $MnSO_4$,Na_2SO_4,$2H_2O$. According to Marignac (*Ann. Min.*, 1856, **9**, 22), the dihydrate of manganese sodium sulphate crystallises from a solution not below $36·5°$, and a tetrahydrate by free evaporation at the ordinary temperature ; these results were accepted by Koppel (*loc. cit.*).

Schreinemakers and Provije (*Proc. K. Akad. Wetensch. Amsterdam*, 1913, **15**, 326) investigated the system $MnSO_4$–Na_2SO_4–H_2O at $35°$, and noted the formation of two double salts ($9MnSO_4$,$10Na_2SO_4$ and $MnSO_4$,$3Na_2SO_4$) according to the composition of the mother-liquor. It was therefore decided to investigate this system at this temperature as well as at $0°$ and $25°$.

The system $CoSO_4$–K_2SO_4–H_2O has been investigated at $25°$ in order to compare it with the systems $NiSO_4$–K_2SO_4–H_2O (Caven and Johnston, J., 1926, 2628) and $CuSO_4$–K_2SO_4–H_2O (Caven and Mitchell, J., 1924, **125**, 1428) at the same temperature.

EXPERIMENTAL.

The System $ZnSO_4$–Na_2SO_4–H_2O *at* $0°$ *and* $25°$.—For the investigation at $0°$, saturated solutions of the two salts were made at

atmospheric temperature, and various proportions of these solutions were placed successively in a flask fitted with a stirrer and kept immersed in ice and water; the mixtures were stirred for 3 days before portions of the solutions were separated and analysed. For the system at $25°$, saturated solutions of the two salts were made at $40°$, and solutions as above placed in a flask immersed in a thermostat at $25° \pm 0·01°$. Zinc was determined by means of standard potassium

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System $ZnSO_4$–Na_2SO_4–H_2O at $0°$ and $25°$.
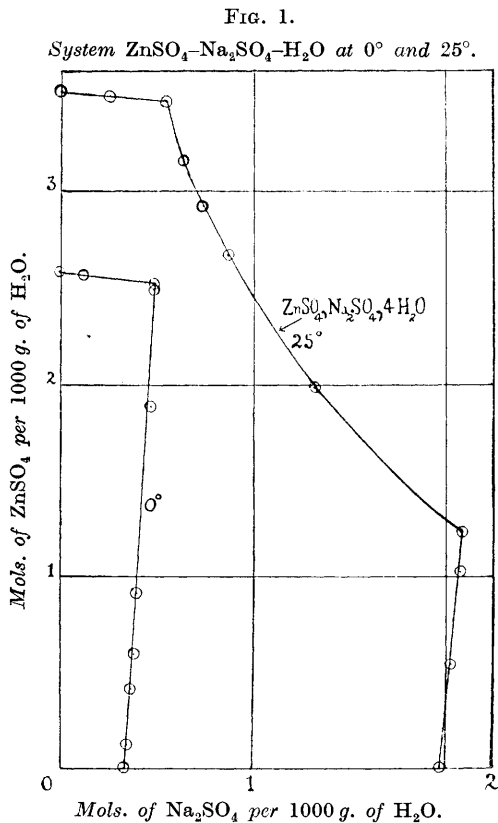
ferrocyanide solution, and sodium sulphate was calculated after determination of total sulphate.

The results are expressed as mols. per 1000 g. of water, and are shown by means of rectangular co-ordinates (Fig. 1).

The System $MnSO_4$–Na_2SO_4–H_2O *at* $0°$, $25°$, *and* $35°$.—For this system at $0°$, saturated solutions of the two salts were made at room temperature, and the same procedure as above was carried out. A slightly different procedure was necessary at $25°$. The solubility

TABLE I.

The System $ZnSO_4$–Na_2SO_4–H_2O at 0° and 25°.

(Z = Zinc sulphate; N = Sodium sulphate; D = Double salt.)

Temperature 0°.			Temperature 25°.		
Mols. of $ZnSO_4$ per 1000 g. of H_2O.	Mols. of Na_2SO_4 per 1000 g. of H_2O.	Solid phase.	Mols. of $ZnSO_4$ per 1000 g. of H_2O.	Mols. of Na_2SO_4 per 1000 g. of H_2O.	Solid phase.
—	0·331	N.	—	1·972	N.
0·128	0·347	N.	0·543	2·023	N.
0·414	0·366	N.	1·073	2·084	N.
0·600	0·381	N.	1·226	2·087	N. & D.
0·914	0·388	N.	1·987	1·322	D.
1·886	0·463	N.	2·669	0·871	D.
2·494	0·485	N.	2·922	0·745	D.
2·521	0·492	N. & Z.	3·157	0·641	D.
2·568	0·122	Z.	3·463	0·551	D. & Z.
2·589	—	Z.	3·504	0·255	Z.
			3·518	—	Z.

of manganese sulphate decreases above 27°, and there was therefore no advantage in preparing solutions above this temperature. Consequently, solutions of sodium sulphate saturated at 40° and of manganese sulphate saturated at 25° were used. To ensure the presence of a solid phase on the manganese sulphate portion of the isotherm, solid tetrahydrated manganese sulphate (the hydrate stable at 25°) was added to different mixtures of the above solutions. These mixtures were placed in a flask as above, immersed in a thermostat at 25 ± 0·01°, and stirred for 4 days, after which it was found that equilibrium had been reached. At the sodium sulphate end of the isotherm, different proportions of the above solutions were taken, and the mixtures stirred for 3 days. Both solid and liquid phases were analysed. For the experiment at 35°, various proportions of solutions of the two salts saturated at 40° were used, whilst to ensure the presence of the appropriate solid phase, anhydrous sodium sulphate was added at the sodium end of the isotherm and monohydrated manganese sulphate at the manganese end. These mixtures were stirred for 4 days. Both solid and liquid phases were analysed, manganese being estimated volumetrically by the Volhard method, and sodium sulphate calculated after determination of total sulphate.

The results are expressed as mols. per 1000 g. of water (Fig. 2). The results at 25° and 35° are also expressed as g. per 100 g. of solution, and plotted on the triangular diagram in order to show the composition of the double salt (Figs. 3 and 4).

The double salt obtained by us at 25° from an equimolecular solution of its constituent salts was washed with water at the same

temperature, air-dried, and analysed (Found: $MnSO_4$, 45·77; Na_2SO_4, 43·15; H_2O, 11·08. Calc. for $MnSO_4,Na_2SO_4,2H_2O$: $MnSO_4$, 45·88; Na_2SO_4, 43·18; H_2O, 10·94%).

FIG. 2.

System $MnSO_4$–Na_2SO_4–H_2O at 0°, 25°, and 35°.

Mols. of Na_2SO_4 per 1000 g. of H_2O.
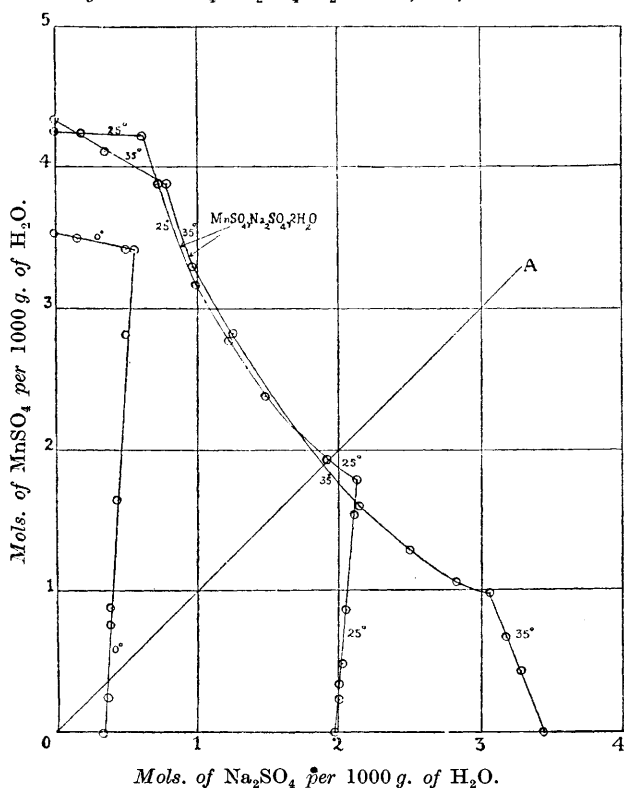
TABLE II.

The System $MnSO_4$–Na_2SO_4–H_2O at 0°.

(M = Manganese sulphate; N = Sodium sulphate.)

Mols. of MnSO₄ per 1000 g. of H₂O.	Mols. of Na₂SO₄ per 1000 g. of H₂O.	Solid phase.	Mols. of MnSO₄ per 1000 g. of H₂O.	Mols. of Na₂SO₄ per 1000 g. of H₂O.	Solid phase.
—	0·331	N.	2·818	0·520	N.
0·254	0·369	N.	3·413	0·566	N. & M.
0·773	0·389	N.	3·424	0·509	M.
0·897	0·383	N.	3·499	0·158	M.
1·650	0·445	N.	3·533	—	M.

FIG. 3.
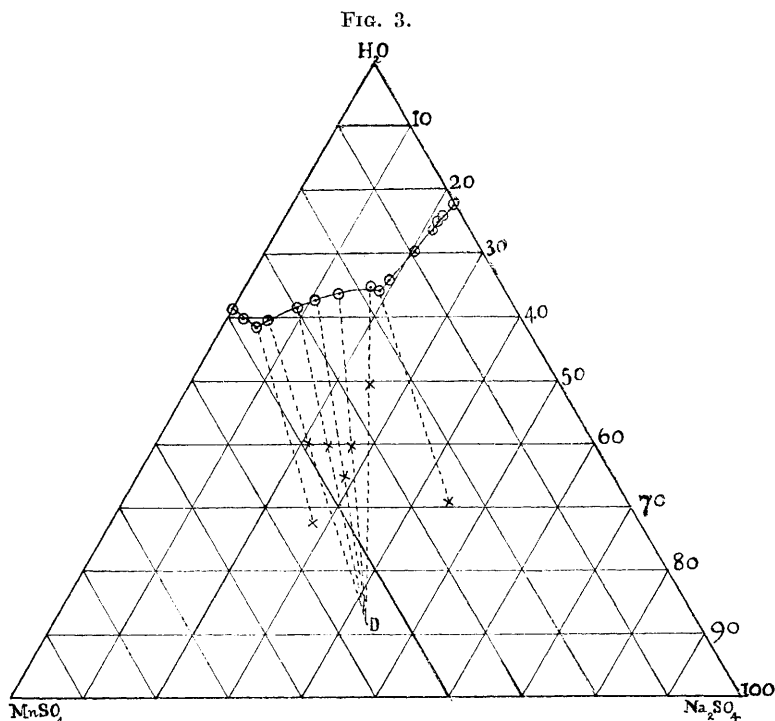
Equilibrium diagram for the system $MnSO_4$–Na_2SO_4–H_2O *at* 25°.
   The composition of the double salt is shown by the co-ordinates of the point D, *at which broken lines drawn through the moist residues intersect, to be* $MnSO_4,Na_2SO_4,2H_2O$.

TABLE III.

The System $MnSO_4$–Na_2SO_4–H_2O at 25° and 35°.

(M = Manganese sulphate ; N = Sodium sulphate ; D = Double salt.)

Temperature 25°.			Temperature 35°.		
Mols. of $MnSO_4$ per 1000 g. of H_2O.	Mols. of Na_2SO_4 per 1000 g. of H_2O.	Solid phase.	Mols. of $MnSO_4$ per 1000 g. of H_2O.	Mols. of Na_2SO_4 per 1000 g. of H_2O.	Solid phase.
—	1·972	N.	—	3·440	N.
0·246	2·004	N.	0·431	3·288	N.
0·349	2·003	N.	0·674	3·175	N.
0·491	2·029	N.	0·980	3·063	N. & D.
0·861	2·054	N.	1·055	2·830	D.
1·536	2·108	N.	1·287	2·504	D.
1·786	2·132	N. & D.	1·602	2·144	D.
1·928	1·917	D.	2·821	1·256	D.
2·381	1·494	D.	3·299	0·978	D.
2·767	1·232	D.	3·875	0·790	D. & M.
3·169	1·001	D.	4·109	0·359	M.
3·889	0·742	D.	4·334	—	M.
4·220	0·618	D. & M.			
4·248	0·195	M.			
4·252	—	M.			

FIG. 4.

Equilibrium diagram for the system MnSO$_4$–Na$_2$SO$_4$–H$_2$O at 35°.

The composition of the double salt is shown by the co-ordinates of the point D, at which broken lines drawn through the moist residues intersect, to be MnSO$_4$,Na$_2$SO$_4$,2H$_2$O.

TABLE IV.

The System MnSO$_4$–Na$_2$SO$_4$–H$_2$O at 25°.

(D.S. = MnSO$_4$,Na$_2$SO$_4$,2H$_2$O.)

Solutions.			Moist solids.			
MnSO$_4$.	Na$_2$SO$_4$.	H$_2$O.	MnSO$_4$.	Na$_2$SO$_4$.	H$_2$O.	Solid phase.
—	21·89	78·11	—	—	—	
2·81	21·54	75·65	—	—	—	
3·94	21·28	74·78	—	—	—	
5·44	21·16	73·40	—	—	—	Na$_2$SO$_4$,10H$_2$O.
9·14	20·53	70·33	—	—	—	
15·15	19·55	65·30	—	—	—	
17·15	19·26	63·59	24·50	44·95	30·55	Na$_2$SO$_4$,10H$_2$O & D.S.
18·62	17·42	63·96	26·26	24·64	49·10	
22·88	13·51	63·61	33·24	26·87	39·89	
26·23	11·00	62·77	37·26	28·81	33·93	D.S.
29·52	8·78	61·70	36·58	23·97	39·45	
34·69	6·23	59·08	39·20	20·94	39·86	
36·94	5·09	57·97	45·01	28·10	26·89	D.S. & MnSO$_4$,4H$_2$O.
38·43	1·66	59·91	—	—	—	MnSO$_4$,4H$_2$O.
39·10	—	60·90	—	—	—	

TABLE V.

The System $MnSO_4$–Na_2SO_4–H_2O at 35°.

(D.S. = $MnSO_4,Na_2SO_4,2H_2O$.)

Solutions.			Moist solids.			
$MnSO_4$.	Na_2SO_4.	H_2O.	$MnSO_4$.	Na_2SO_4.	H_2O.	Solid phase.
—	32·83	67·17	—	—	—	Na_2SO_4.
4·25	30·49	65·26	3·26	47·92	48·82	
6·55	29·05	64·40	5·45	40·51	54·04	
9·35	27·49	63·16	8·41	38·47	53·12	Na_2SO_4 & D.S.
10·21	25·75	64·04	20·43	31·06	48·51	
12·54	22·96	64·50	15·62	24·90	59·48	
15·64	19·70	64·66	23·09	25·78	51·13	D.S.
26·56	11·12	62·32	28·87	15·31	55·82	
30·43	8·49	61·08	32·65	13·93	53·42	
34·46	6·62	58·92	45·73	6·65	47·62	D.S. & $MnSO_4,H_2O$.
37·12	3·05	59·83	39·60	3·01	57·39	$MnSO_4,H_2O$.
39·56	—	60·44	—	—	—	

The System $CoSO_4$–K_2SO_4–H_2O *at* 25°.—For this system at 25°, saturated solutions of the two salts were made at 40°, and various proportions placed in a flask fitted with a stirrer, and immersed in a thermostat at 25° $\pm$ 0·01°. The mixtures were stirred for 3 days, and liquid phases only analysed. Cobalt was estimated by precipitation as ammonium phosphate, and ignition to pyrophosphate. Potassium sulphate was calculated after determination of total sulphate.

The results are expressed as mols. per 1000 g. of water (Fig. 5).

TABLE VI.

The System $CoSO_4$–K_2SO_4–H_2O at 25°.

(C = Cobalt sulphate; K = Potassium sulphate; D = Double salt.)

Mols. of $CoSO_4$ per 1000 g. of H_2O.	Mols. of K_2SO_4 per 1000 g. of H_2O.	Solid phase.	Mols. of $CoSO_4$ per 1000 g. of H_2O.	Mols. of K_2SO_4 per 1000 g. of H_2O.	Solid phase.
—	0·680	K.	1·372	0·321	D.
0·150	0·737	K.	2·205	0·240	D.
0·239	0·780	K. & D.	2·557	0·212	D. & C.
0·458	0·531	D.	2·536	0·190	C.
0·950	0·388	D.	2·433	—	C.
1·095	0·361	D.			

Conclusions.

The Zinc–Sodium System (Fig. 1).—1. No double salt is formed at 0°. This is in agreement with the work of Koppel and Gumperz. The isotherm simply shows the influence of each salt on the solubility of the other.

2. The double salt $ZnSO_4,Na_2SO_4,4H_2O$ is formed over a considerable range at 25°.

3. At both 0° and 25°, the solubility of sodium sulphate is increased by addition of zinc sulphate.

4. At both 0° and 25°, the solubility of zinc sulphate is decreased by addition of sodium sulphate. This is in contrast to the system $CuSO_4$–Na_2SO_4–H_2O (Caven and Johnston, *loc. cit.*) where both at 0° and 25° the solubility of copper sulphate is increased by addition of sodium sulphate.

The Manganese–Sodium System (Fig. 2).—1. No double salt is formed at 0°.

2. The double salt $MnSO_4,Na_2SO_4,2H_2O$ (Fig. 3) is the stable salt at 25°, and is formed over a considerable range.

3. $MnSO_4,Na_2SO_4,2H_2O$ (Fig. 4) is also formed at 35° over a wider range. No evidence was found of the formation of the double salts $MnSO_4,3Na_2SO_4$ and $9MnSO_4,10Na_2SO_4$ (Schreinemakers and Provije, *loc. cit.*), or of $MnSO_4,Na_2SO_4,4H_2O$.

4. A study of the isotherms at 25° and 35° (Fig. 2) shows the interesting fact that the double-salt portion of the 25°-isotherm is nearly coincident along all its length with the double-salt portion of the 35°-isotherm. This indicates that the solubilities of the double salt at these two temperatures are almost identical. A closer inspection of the place where the equimolecular line 0A (Fig. 2) cuts the isotherms shows that the solubility of the double salt $MnSO_4,Na_2SO_4,2H_2O$ is slightly less at 35° than at 25°.

5. At all three temperatures the solubility of manganese sulphate is decreased by addition of sodium sulphate. This fact is of much greater interest on more particular examination, for the solid phases are different at the different temperatures. The decrease is least at 25° where the solid phase is $MnSO_4,4H_2O$, and is greatest, being much accentuated, at 35° where the solid phase is $MnSO_4,H_2O$. An intermediate decrease is shown at 0°, where the solid phase is $MnSO_4,7H_2O$. Thus these isotherms show the effect of addition of sodium sulphate on the solubilities of the hepta-, tetra-, and mono-hydrated forms of manganese sulphate.

6. The solubility of $MnSO_4,H_2O$ at 35° is slightly greater than that of $MnSO_4,4H_2O$ at 25°.

FIG. 5.
System Co(Cu,Ni)SO₄–K₂SO₄–H₂O *at* 25°.
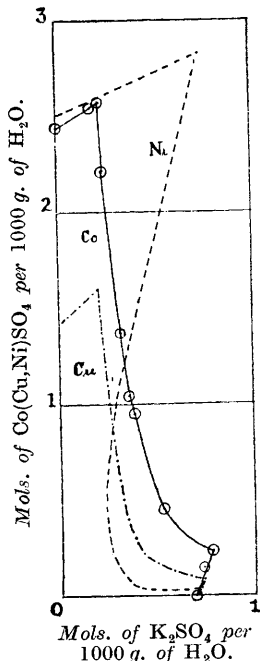
7. At $0°$ and $25°$ the solubility of sodium sulphate is increased by addition of manganese sulphate. At $35°$ it is much decreased by increasing quantities of manganese sulphate. Here again there is a change of solid phase from the decahydrated to the anhydrous state.

The Cobalt–Potassium System (Fig. 5).—1. The double salt $CoSO_4,K_2SO_4,6H_2O$ is formed over a wide range at $25°$.

2. The solubility of each single salt is increased by addition of the other.

3. The isotherm is of the general type obtainable for double salts of the form $M^{II}SO_4,M^I_2SO_4,6H_2O$. It closely resembles the isotherm for the system $CuSO_4–K_2SO_4–H_2O$ at $25°$ (Caven and Mitchell, *loc. cit.*), but differs considerably from the corresponding isotherm for the system $NiSO_4–K_2SO_4–H_2O$ (Caven and Johnston, J., 1926, 2628), which deviates appreciably from the typical isotherm (see Fig. 5).