221. *Equilibria in the Systems* $(NH_4)_2SO_4$–$NiSO_4$–H_2O, $(NH_4)_2SO_4$–$CoSO_4$–H_2O, $(NH_4)_2SO_4$–$ZnSO_4$–H_2O, Na_2SO_4–$NiSO_4$–H_2O, *and* Na_2SO_4–$CoSO_4$–H_2O, *at* 25°.

By Robert M. Caven and W. Kidston Gardner.

The isotherms of a number of systems of the type M'_2SO_4–$M''SO_4$–H_2O, where M′ is Na, K, or NH_4, and M″ is Mn, Ni, Co, Cu, or Zn, have been studied by one of the authors and his co-workers (J., 1924, **125**, 1428; 1926, 2628; 1927, 2358, 2902; 1928, 2506), and the five systems whose isotherms are described in the present paper complete the series. The polytherms of the systems $(NH_4)_2SO_4$–$NiSO_4$–H_2O and $(NH_4)_2SO_4$–$CoSO_4$–H_2O have been investigated by Benrath (*Z. anorg. Chem.*, 1928, **208**, 169).

It is well known that all double salts of ammonium sulphate with bivalent metallic sulphates, crystallising from water near room temperature, contain $6H_2O$, whilst those with sodium sulphate contain only 2 or $4H_2O$. In the present work it has been unnecessary to analyse the solid phases, qualitative examination of them being sufficient, since Koppel (*Z. physikal. Chem.*, 1905, **52**, 385) has shown that the double sulphates of sodium with nickel and cobalt crystallise with $4H_2O$.

Experimental.

The method adopted was the usual one of making saturated solutions of the two salts at 30°, and placing successively various proportions of the two solutions in a suitable bottle kept in a thermostat at 25°. The bottle was loosely covered, and fitted with a stirrer; and the mixture was stirred for three days, before a portion of the solution was withdrawn for analysis, stirring, withdrawal, and analysis being continued till constancy was obtained.

The following methods of analysis were adopted.

System $(NH_4)_2SO_4$–$NiSO_4$–H_2O. The nickel was estimated volumetrically by the cyanide method of Kelly and Conant (*Ind. Eng. Chem.*, 1916, **8**, 804). The ammonium was at first calculated after estimation of the total sulphate, but later it was found more convenient to estimate it directly by adding excess of sodium hydroxide to the solution and distilling the ammonia into an excess of standard hydrochloric acid.

System Na_2SO_4–$NiSO_4$–H_2O. The nickel was estimated by precipitation and weighing as nickel dimethylglyoxime, and the sodium was calculated after estimation of total sulphate.

The results for the system Na_2SO_4–$NiSO_4$–H_2O were obtained at 25·5°.

System $(NH_4)_2SO_4$–$NiSO_4$–H_2O *at* 25° (Fig. 1).

$(NH_4)_2SO_4$.	$NiSO_4$.	Solid phase.
—	2·490	$NiSO_4,7H_2O$
0·2020	2·498	
0·2727	2·505	$NiSO_4,7H_2O$ & D.S.
0·2839	2·337	D.S.
0·2296	0·2287	
0·4976	0·0534	
0·8136	0·0353	
1·375	0·0237	
2·104	0·0159	
2·471	0·0136	
3·241	0·0088	
3·808	0·0057	
5·813	—	$(NH_4)_2SO_4$

D.S. = Double salt : $(NH_4)_2SO_4,NiSO_4,6H_2O$.

System $(NH_4)_2SO_4$–$CoSO_4$–H_2O *at* 25° (Fig. 2).

$(NH_4)_2SO_4$.	$CoSO_4$.	Solid phase.
—	2·441	$CoSO_4,7H_2O$
0·2868	2·430	$CoSO_4,7H_2O$ & D.S.
0·3156	2·352	D.S.
0·3522	1·744	
0·3986	1·678	
0·4488	1·054	
0·4677	0·9419	
0·4644	0·9404	
0·4655	0·9069	
0·5989	0·5916	
1·375	0·1581	
2·534	0·0967	
3·061	0·0606	
4·689	0·0370	
5·826	—	$(NH_4)_2SO_4$

D.S. = Double salt : $(NH_4)_2SO_4,CoSO_4,6H_2O$.

System $(NH_4)_2SO_4$–$ZnSO_4$–H_2O *at* 25° (Fig. 3).

$(NH_4)_2SO_4$.	$ZnSO_4$.	Solid phase.
—	3·571	$ZnSO_4,7H_2O$
0·1313	3·560	$ZnSO_4,7H_2O$ & D.S.
0·1703	3·160	D.S.
0·2628	2·100	
0·3248	1·429	
0·4680	0·6220	
0·6054	0·3176	
0·8511	0·1708	
1·288	0·0930	
1·913	0·0795	
2·993	0·0291	
3·742	0·0183	
5·826	—	$(NH_4)_2SO_4$

D.S. = Double salt : $(NH_4)_2SO_4,ZnSO_4,6H_2O$.

System Na_2SO_4–$NiSO_4$–H_2O *at* 25·5° (Fig. 4).

Na_2SO_4.	$NiSO_4$.	Solid phase.
—	2·619	$NiSO_4,7H_2O$
0·5041	2·530	
0·7152	2·514	
0·7661	2·501	
0·8818	2·487	
1·144	2·449	
1·286	2·416	
1·391	2·395	
1·535	2·374	
1·636	2·353	$NiSO_4,7H_2O$ & D.S.
1·715	2·074	D.S.
1·933	1·872	
2·169	1·818	D.S. & $Na_2SO_4,10H_2O$
2·145	1·319	$Na_2SO_4,10H_2O$
2·144	1·153	
2·066	—	

D.S. = Double salt : $Na_2SO_4,NiSO_4,4H_2O$.

Fig. 1.

Fig. 3.

Fig. 2.

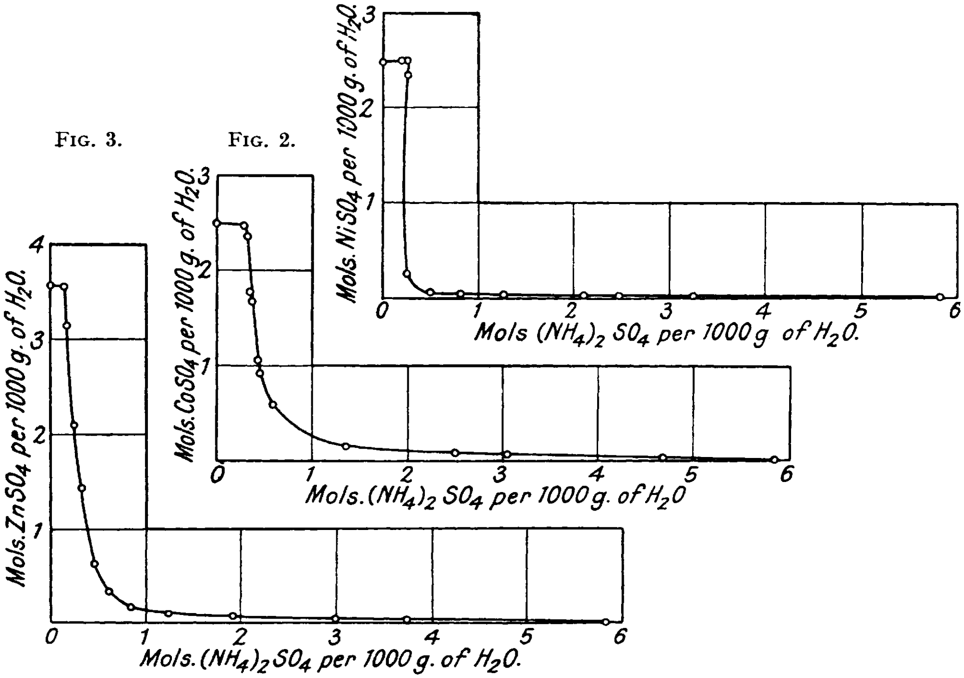


Fig. 1.—*System* $(NH_4)_2SO_4$–$NiSO_4$–H_2O *at* 25°. **Fig. 2.**—*System* $(NH_4)_2SO_4$–$CoSO_4$–H_2O *at* 25°. **Fig. 3.**—*System* $(NH_4)_2SO_4$–$ZnSO_4$–H_2O *at* 25°.

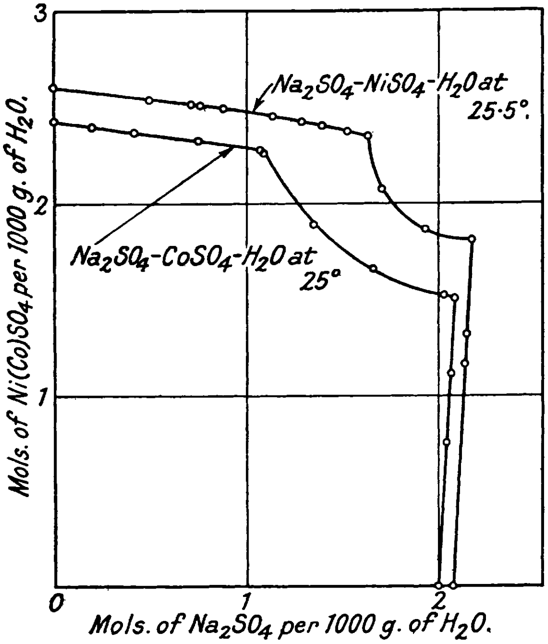
System $(NH_4)_2SO_4$–$CoSO_4$–H_2O. The ammonium was at first estimated by distillation, and the cobalt calculated after estimation of total sulphate. As the quantity of cobalt in the solution decreased, however, it was found better to estimate this directly by precipitating it as hydrated sesquioxide with bromine and caustic soda, and igniting and reducing the precipitate to metallic cobalt before weighing; the ammonium was then calculated after estimation of total sulphate.

System Na_2SO_4–$CoSO_4$–H_2O. The cobalt was estimated directly as in the above system, and the sodium calculated after estimation of total sulphate.

System $(NH_4)_2SO_4$–$ZnSO_4$–H_2O. The ammonium was at first estimated by distillation, and the zinc calculated after estimation of total sulphate. As the quantity of zinc in the solution decreased, this metal was estimated by precipitation and weighing as zinc ammonium phosphate, and the ammonium calculated after estimation of total sulphate.

FIG. 4.

System Na_2SO_4–$NiSO_4$–H_2O *at* 25·5°.
System Na_2SO_4–$CoSO_4$–H_2O *at* 25°.



System Na_2SO_4–$CoSO_4$–H_2O *at* 25° (Fig. 4).

Na_2SO_4.	$CoSO_4$.	Solid phase.
—	2·433	$CoSO_4,7H_2O$
0·1983	2·406	
0·4220	2·372	
0·7565	2·327	
1·075	2·275	$CoSO_4,7H_2O$ & D.S.
1·096	2·266	D.S.
1·356	1·891	
1·663	1·665	
2·035	1·517	
2·092	1·510	$Na_2SO_4,10H_2O$ & D.S.
2·069	1·119	$Na_2SO_4,10H_2O$.
2·044	0·7501	
1·988	—	

D.S.=Double salt: $Na_2SO_4,CoSO_4,4H_2O$.

The results obtained are given in the tables as mols. per 1000 g. of water, and are plotted with rectangular co-ordinates in Figs. 1, 2, 3, and 4.

CONCLUSIONS.

1. The isotherms obtained for the systems Na_2SO_4–$NiSO_4$–H_2O, Na_2SO_4–$CoSO_4$–H_2O are quite different from those of the sulphates of the same bivalent metals with ammonium sulphate. This is in accordance with the results recorded previously.

2. There is a marked similarity between the isotherms of the systems Na_2SO_4–$NiSO_4$–H_2O and Na_2SO_4–$CoSO_4$–H_2O (Fig. 4). In each case addition of sodium sulphate decreases the solubility of the bivalent sulphate, whilst addition of the bivalent sulphate increases the solubility of the sodium sulphate up to the triple point. The work of Caven and Johnston (J., 1928, 2506) on the systems Na_2SO_4–MSO_4–H_2O (M = Zn, Mn, or Cu) shows the same effects on the solubilities of the sulphates.

3. The isotherms of the systems $(NH_4)_2SO_4$–MSO_4–H_2O (M = Ni, Co, or Zn) (Figs. 1, 2, 3) are alike in that no increase of solubility of ammonium sulphate is observed on addition of bivalent sulphate. In fact, in each case the slightest addition of bivalent sulphate causes the double salt to separate as solid phase. From this it appears that none of the corre-

sponding double salts $(NH_4)_2SO_4,MSO_4,6H_2O$ is perceptibly soluble in a saturated solution of ammonium sulphate.

4. Addition of ammonium sulphate to nickel sulphate causes a slight increase in its solubility, whilst addition of ammonium sulphate to cobalt sulphate or to zinc sulphate causes a slight decrease in the solubility of these sulphates to the triple point.

After the triple point the decrease in the solubility of the double salt is very rapid as the proportion of ammonium sulphate increases up to about 1 mol. per litre in the case of the cobalt and zinc double salts, and 0·25 mol. per litre in the case of the nickel double salt.

5. The double salts of the type $(NH_4)_2SO_4,M''SO_4,6H_2O$ have a much greater range of formation than those of the type $Na_2SO_4,M''SO_4,4H_2O$.

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[*Received, May* 17*th*, 1933.]