CCCXVII.—*Equilibrium in the Systems* $MnSO_4$–K_2SO_4–H_2O *and* $MnSO_4$–$(NH_4)_2SO_4$–H_2O *at* 0°; *also in the System* $CuSO_4$–Na_2SO_4–H_2O *at* 0°, 25°, *and* 37·5°.

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THE authors have previously shown (J., 1926, 2628), from an investigation of the system $MnSO_4$–K_2SO_4–H_2O at 25°, that at this temperature the double salt is tetrahydrated ($MnSO_4,K_2SO_4,4H_2O$). Since manganese sulphate itself crystallises with $4H_2O$ at 25°, and with $7H_2O$ at 0°, it was decided to investigate the hydration of its potassium double salt at 0°, in the expectation that it might then be hexahydrated, and thus conform to the general type: $M''SO_4,M'_2SO_4,6H_2O$. Moreover, since manganese ammonium sulphate conforms to this general type, even at 25°, it was decided also to investigate the system $MnSO_4$–$(NH_4)_2SO_4$–H_2O at 0°, and thus to compare the kinds of isotherm obtained in the two cases. Further, this system was investigated at 25° by Schreinemakers (*Chem. Weekblad*, 1909, **6**, 131), and in the present paper his results are compared with those obtained by the authors (*loc. cit.*) for the system $MnSO_4$–K_2SO_4–H_2O at the same temperature.

Also, in order to study the influence of the water of crystallisation of the double salt on the type of isotherm obtained, it was decided to investigate the system $CuSO_4$–Na_2SO_4–H_2O at various temperatures, the double salt in this case always crystallising with $2H_2O$. This system has already been studied by several workers. Diacon (*Jahresber.*, 1866, 61) investigated it at 0°, and his results show that the double salt $CuSO_4,Na_2SO_4,2H_2O$ does not exist at this temperature in contact with solutions of its component salts. Nevertheless, the continuous increase in solubility of each of the two single salts caused by addition of the other salt up to the triple point indicates the presence of a considerable amount of the double salt or its ions in solution. Koppel (*Z. physikal. Chem.*, 1903, **42**, 1) showed that below 16·7° the double salt does not crystallise from a solution of its component salts; and from his results he drew a series of isotherms, showing an increased range of double salt formation above this temperature, which do not seem to be justified. Moreover, these hypothetical isotherms indicate that, from 0° to about 30°, whilst the solubility of sodium sulphate is increased by the addition of copper sulphate, that of copper sulphate is decreased by the addition of sodium sulphate. This conclusion contradicts Diacon's results at 0°. Massink investigated the same system at 20° (*Z. physikal. Chem.*, 1916, **92**, 351),* and showed a short range of double salt formation, with continuous increase of solubility of each of the single salts on addition of the other, up to the corresponding triple point. He gave, however, only one point within the double-salt range.

In view, therefore, of the conflicting and inadequate results of previous workers, the authors felt justified in investigating this system at 0° and 25°; and, since sodium sulphate is decahydrated below 33° and anhydrous above that temperature, they also decided to investigate the system above 33° (at 37·5°), to discover what

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* According to an abstract of this paper (*Chem. Weekblad*, 1917, **14**, 756), Massink also investigated the system at 35°. Reference to the original paper shows that 35° is mentioned, but that the results supposed to be obtained at that temperature are missing.

influence the change in hydration of sodium sulphate had upon the isotherm.

EXPERIMENTAL.

The Systems $MnSO_4$–K_2SO_4–H_2O *and* $MnSO_4$–$(NH_4)_2SO_4$–H_2O *at* 0°.

For the manganese–potassium system, 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 a mixture of ice and water. The mixtures were stirred for 3 days before portions of the solutions were separated and analysed. The manganese was estimated volumetrically by the Volhard method, the total sulphate determined, and the potassium sulphate calculated. The same procedure was carried out with the manganese–ammonium system, except that, as the solid phases are known, they were not analysed. The ammonia and total sulphate were determined.

In Table I, the results for the manganese–potassium system at 0° are expressed as g. per 100 g. of solution or of moist solid, and the triangular diagram is used to determine the composition of the double salt (Fig. 1). In Table II, the same results, and those for the manganese–ammonium system at 0°, are expressed as mols. per 1000 g. of water; and these results are then compared graphically by means of rectangular co-ordinates with those previously obtained by Schreinemakers and the authors at 25° (Figs. 2 and 3).

The System $CuSO_4$–Na_2SO_4–H_2O *at* 0°, 25°, *and* 37·5°.

For this system at 0°, the procedure was as above, although only the liquid phases were analysed. Copper was estimated iodometrically, and total sulphate determined. For the systems at 25° and 37·5°, solutions of the two salts were made at temperatures about 15° above those required, and various proportions of the two solutions were placed in a flask, fitted with a stirrer, and kept in a thermostat at 25° ± 0·1° or 37·5° ± 0·1°. The solutions were stirred for 3 days before portions were separated and analysed. The results are expressed in Table III, and in Fig. 4 by means of rectangular co-ordinates, those of Diacon and Massink being also included in the same figure.

Conclusions.

Manganese Double Sulphates.—The following points arise :

1. Manganese potassium sulphate crystallises at 0°, as well as at 25°, with $4H_2O$.

2. Its isotherm at 0° resembles the corresponding isotherm at 25°. except that it shows a more rapid increase in solubility of

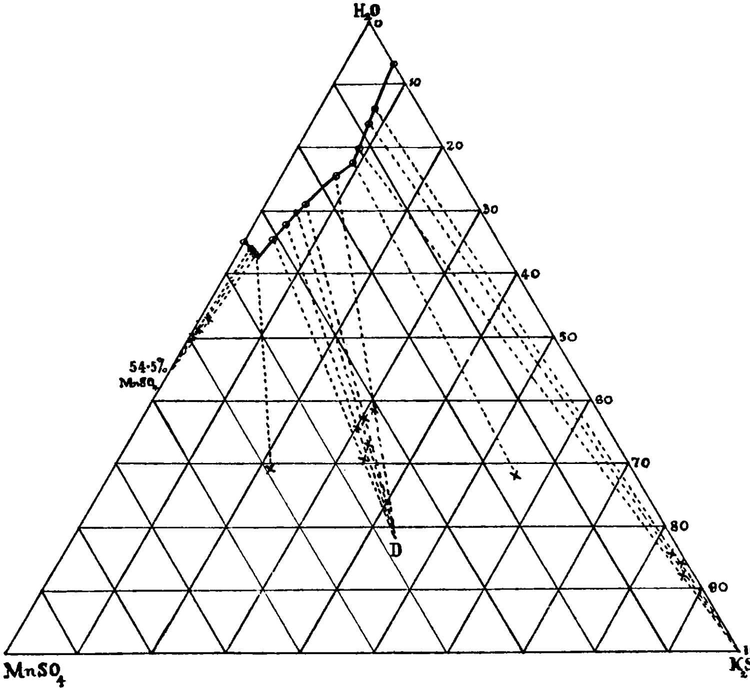
TABLE I.

The System $MnSO_4$–K_2SO_4–H_2O *at* 0°.

D.S. = Double salt.

Solutions.			Moist solids.			
K_2SO_4.	$MnSO_4$.	H_2O.	K_2SO_4.	$MnSO_4$.	H_2O.	Solid phase.
—	34·78	65·22	—	—	—	$MnSO_4,7H_2O$.
1·68	34·49	63·83	0·42	49·31	50·27	
1·85	34·53	63·62	0·70	48·00	51·30	
2·81	34·38	62·81	1·24	45·85	52·91	
3·35	34·30	62·35	21·52	49·49	28·99	$MnSO_4,7H_2O$ and D.S.
4·00	30·28	65·72	33·46	36·00	30·54	D.S.=$MnSO_4,K_2SO_4,4H_2O$.
4·48	27·62	67·90	30·31	34·46	35·23	
5·00	25·50	69·50	32·84	34·50	32·66	
5·54	23·64	70·82	30·46	32·98	36·56	
7·69	17·39	74·92	30·82	30·60	38·58	
8·88	13·68	77·44	55·60	16·90	27·50	D.S. and K_2SO_4.
8·48	11·80	79·72	86·00	1·82	12·18	K_2SO_4.
7·97	8·21	83·82	82·81	1·52	15·67	
7·75	6·21	86·04	84·55	1·11	14·34	
6·82	—	93·18	—	—	—	

FIG. 1.



Equilibrium diagram $MnSO_4$–K_2SO_4–H_2O *at* 0°.

The composition of the double salt is shown by the co-ordinates of the point D, *at which broken lines drawn through the " rests " intersect, to be* $MnSO_4,K_2SO_4,4H_2O$. *Broken lines drawn through rests for the single salts intersect at points showing* $MnSO_4,7H_2O$ (% $MnSO_4$ = 54·5) *and* K_2SO_4 (100%).

TABLE II.

The Systems $MnSO_4$–K_2SO_4–H_2O *and* $MnSO_4$–$(NH_4)_2SO_4$–H_2O *at* 0°.

(M = Manganese sulphate; K = Potassium sulphate; A = Ammonium sulphate; D = Double salt.)

Mols. of K_2SO_4 per 1000 g. of H_2O.	Mols. of $MnSO_4$ per 1000 g. of H_2O.	Solid phase.	Mols. of $(NH_4)_2SO_4$ per 1000 g. of H_2O.	Mols. of $MnSO_4$ per 1000 g. of H_2O.	Solid phase.
—	3·533	M	—	3·533	M
0·151	3·580	M	0·168	3·623	M
0·167	3·594	M	0·251	3·665	M and D
0·257	3·624	M	0·260	3·565	D
0·308	3·642	M and D	0·261	3·525	D
0·349	3·051	D	0·531	1·868	D
0·379	2·698	D	1·069	0·769	D
0·413	2·430	D	1·315	0·531	D
0·447	2·211	D	1·864	0·377	D
0·589	1·537	D	3·551	0·167	D
0·659	1·169	D and K	3·993	0·138	D
0·611	0·978	K	5·135	0·075	D
0·546	0·649	K	5·229	0·081	D and A
0·517	0·478	K	5·254	0·017	A
0·420	—	K	5·327	—	A

FIG. 2.

A.

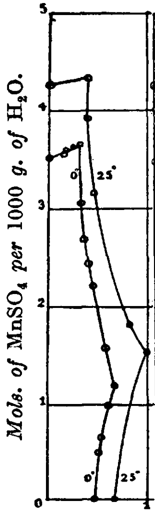
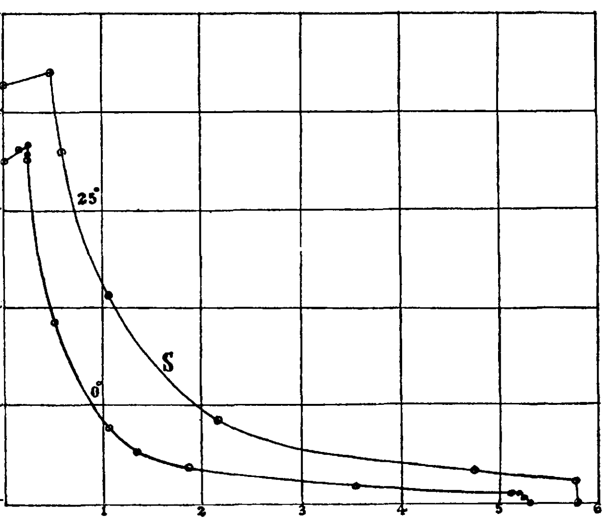


FIG. 3.

System $MnSO_4$–$(NH_4)_2SO_4$–H_2O *at* 0° *and* 25°.



B.

Mols. of $(NH_4)_2SO_4$ *per* 1000 *g. of* H_2O.

S = *Curve drawn from results of Schreinemakers at* 25°.

Double salt is $MnSO_4,(NH_4)_2SO_4,6H_2O$ *at both temperatures.*

A. *System* $MnSO_4$–K_2SO_4–H_2O *at* 0° *and* 25°.

B. *Mols. of* K_2SO_4 *per* 1000 *g. of* H_2O.

Double salt is $MnSO_4,K_2SO_4,4H_2O$ *at both temperatures.*

TABLE III.

The System $CuSO_4$–Na_2SO_4–H_2O *at* 0°, 25°, *and* 37·5°.

(D.S. = Double salt.)

Temperature : 0°.

Mols. per 1000 g. of H_2O.		
$CuSO_4$.	Na_2SO_4.	Solid phase.
—	0·387	$Na_2SO_4,10H_2O$.
0·213	0·415	
0·415	0·450	
0·590	0·468	
1·047	0·526	$Na_2SO_4,10H_2O$ + $CuSO_4,5H_2O$.
0·998	0·306	$CuSO_4,5H_2O$.
0·970	0·175	
0·929	—	

Temperature : 25°.

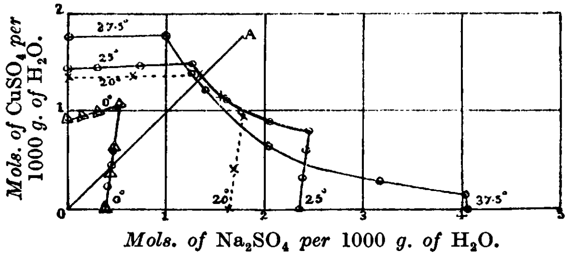
Mols. per 1000 g. of H_2O.		
$CuSO_4$.	Na_2SO_4.	Solid phase.
—	2·353	$Na_2SO_4,10H_2O$.
0·256	2·394	
0·593	2·432	
0·781	2·461	$Na_2SO_4,10H_2O$ + D.S.
0·847	2·057	D.S. = $CuSO_4,Na_2SO_4,2H_2O$.
0·979	1·717	
1·068	1·603	
1·457	1·323	$CuSO_4,5H_2O$.
1·449	0·765	
1·433	0·325	
1·428	—	

Temperature : 37·5°.

Mols. of $CuSO_4$ per 1000 g. of H_2O.	Mols. of Na_2SO_4 per 1000 g. of H_2O.	Solid phase.
—	4·066	Na_2SO_4.
0·162	4·046	Na_2SO_4 + D.S.
0·280	3·183	D.S. = $CuSO_4,Na_2SO_4,2H_2O$.
0·678	2·049	
0·821	1·800	
1·209	1·406	
1·402	1·242	
1·770	1·007	D.S. + $CuSO_4,5H_2O$.
1·754	—	$CuSO_4,5H_2O$.

FIG. 4.

System $CuSO_4$–Na_2SO_4–H_2O.



Diacon's results at 0° *are indicated thus* △.
Massink's ,, ,, 25° ,, ,, ,, ×, *and the isotherm by a broken line.*
OA *A line of equimolecular proportions to show solubility of double salt.*

manganese sulphate with addition of potassium sulphate up to the triple point. Some difference would be expected, since at 0° the solid phase is $MnSO_4,7H_2O$, whereas at 25° it is $MnSO_4,4H_2O$.

3. The 0°-isotherm of the potassium system differs greatly from that of the ammonium system, the range of double salt formation

in the case of the latter being much the greater. This is traceable to two factors : (*a*) the much greater solubility of ammonium sulphate, (*b*) the fact that the ammonium double salt crystallises with $6H_2O$, whereas the potassium double salt crystallises with $4H_2O$.

4. The 0°-isotherm of the ammonium system resembles the 25°-isotherm, as shown by Schreinemakers's results. Two points, however, should be noted : (*a*) The increase in solubility of manganese sulphate caused by ammonium sulphate at 25° is accentuated at 0° (compare the potassium system at 0° and 25°); (*b*) the decrease in solubility of ammonium sulphate caused by manganese sulphate at 25° is accentuated at 0°.

5. The isotherms for manganese ammonium sulphate, but not for the corresponding potassium salt, closely resemble those for the analogous copper salt (Caven and Mitchell, J., 1924, **125**, 1428).

Copper Sodium Sulphate.—A study of the results for the $CuSO_4$–Na_2SO_4–H_2O system shows a number of interesting points (see Fig. 4) :

1. Diacon's results at 0° have been confirmed : there is no formation of double salt, but an increase in solubility of each single salt is caused by the presence of the other.

2. At 25°, the range of double salt formation is fairly wide. The addition of each component increases the solubility of the other up to the corresponding triple point where the double salt begins to crystallise. In the case of copper sulphate, this increase is slight but definite, in agreement with Massink's results, but in contradiction to those of Koppel.

3. At 37·5°, the range of double salt formation is greatly increased. It is to be noted, however, that although copper sulphate still shows a slight increase of solubility in presence of sodium sulphate, sodium sulphate now shows a decrease of solubility in presence of copper sulphate. A change in the form of the isotherm here is to be expected owing to the change of hydration of solid sodium sulphate.

4. The increase in range of double salt formation with rise of temperature is connected with some remarkable relationships seen when the isotherms of different temperatures are compared. Thus, although the solubilities of the single salts at 20° are less than at 25°, the double salt curve at 20°, according to Massink, appears to coincide through part of its course with the corresponding curve of the authors at 25°; and the double salt curve at 37·5°, according to the authors' results, actually falls within the corresponding curve at 25°, and even recedes from it at the sodium sulphate end because of the shortness of the solubility curve of sodium sulphate which has become anhydrous. It is evident, moreover, that the extent of the

double salt curve at 37·5° is connected with the greatly increased solubility of sodium sulphate at that temperature.

5. Thus it is concluded from the authors' results at 25° and 37·5° that the solubility of the double salt decreases with rise of temperature; and it may be supposed that the solubility at 20° is actually slightly greater than that at 25°, although Massink's result compared with the authors' does not show this.

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