444. *The System* $MnSO_4$–H_2SO_4–H_2O.

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The system $MnSO_4$–H_2SO_4–H_2O has been investigated at 0°, 20°, 25°, 45°, 65°, and 95·7°, and the following succession of solid phases observed : $MnSO_4,5H_2O$, $MnSO_4,H_2O$, $MnSO_4,H_2SO_4,H_2O$, $MnSO_4,H_2SO_4$, and $MnSO_4,3H_2SO_4$. The pentahydrate does not exist in contact with saturated solutions above 24·5°, and the lower formation temperature of $MnSO_4,H_4SO_4$ is very close to 65°. The microscopical appearance of solid phases together with details of solubility measurements and analytical procedures are given. Conditions under which transitions between hydrates and/or acid sulphates occur in condensed sulphate systems have been examined, and lead to an empirical method for distinguishing between normal and acid sulphates whether hydrated or not.

SOLID–LIQUID phase equilibria in condensed metal sulphate–sulphuric acid–water systems may show one or both of two general features : (*a*) progressive dehydration of normal sulphate hydrates as the temperature is raised and/or the acid concentration increased, and (*b*) formation of acid sulphates. Polythermal equilibrium data provide comparisons of hydrate–lower hydrate, hydrate–acid sulphate and acid sulphate–higher acid sulphate transitions and, while reliable results for (*a*) are numerous, examples of (*b*) either alone or in conjunction with (*a*) have received much less attention. Manganese sulphate is one such case, only one isotherm at 12·6° having been reported (Montemartini and Losana, *Ind. chim., Roma*, 1928, **4**, 107). The following succession of solid phases with increasing acid concentration is claimed : $MnSO_4,5H_2O$, $MnSO_4,4H_2O$, $MnSO_4,H_2O$, $MnSO_4$, $MnSO_4,H_2SO_4,H_2O$, $MnSO_4,H_2SO_4$, $MnSO_4,3H_2SO_4$. Data for this system over the range 0—95·7° are now presented, and the above three types of transition compared for this and other systems for which sufficient reliable data are available.

EXPERIMENTAL

"AnalaR" materials were used throughout, the manganese sulphate being in the form of the metastable tetrahydrate (B.D.H.). Mixtures of the desired composition were prepared from previously analysed materials by weighing in small tubes or flasks. These were closed with rubber stoppers carrying glass stirrers and 6″ stirrer glands lubricated with stiff grease. Thus absorption of atmospheric moisture by the solutions during stirring to equilibrium was negligible. The time to reach equilibrium varied from a few hours at 95·7° to a fortnight at low temperatures and high acid concentrations. Owing to comparatively small changes in solubility with temperature and the absence of marked supersaturation, it was not possible to bring the initial tetrahydrate solid phase completely into solution before transference to the thermostat bath, but fortunately inter-solid phase transitions were moderately rapid and progress towards equilibrium could be readily observed by microscopical examination. The establishment of equilibrium was judged both microscopically and by agreement between solubility results for duplicate experiments. Electrically heated water-thermostats controlled within ±0·02° by electronic relays (Taylor, *J.*, 1951, 232) were used at 20°, 25°, 45°, and 65°, gas heating at 95·7° ± 0·2°, and a well-lagged bath of melting ice at 0°. A layer of liquid paraffin minimised evaporation at the higher temperatures. Samples of saturated solutions were withdrawn for analysis by means of a pre-heated micro-filter stick of No. 3 porosity and a pipette of suitable volume; the samples were weighed in a closed vessel and diluted to a standard volume with distilled water. When a sample of the moist solid phase was required, as much as possible of the remaining liquid was removed with water-pump suction *via* the filter stick without removal of the solubility vessel from the thermostat. Since all the solid phases were well crystallised and settled rapidly, this sampling procedure could be carried out so quickly that absorption of moisture by the deliquescent phases was negligible except at very high acid concentrations at 95·7°. Even then absorption was very slight.

Although none of the crystals except $MnSO_4,5H_2O$ and $MnSO_4,H_2O$ could be isolated in the dry state for refractive index measurements, the appearance and optical properties of all of them when viewed, in contact with mother-liquor, with a polarising microscope were sufficiently characteristic to allow of their certain identification. These observations always agreed with tie-line information, and thus analyses of moist solid phases could frequently be dispensed with. Indeed, isothermal invariant points could be recognised with complete certainty microscopically, but not so from tie-lines unless the two solid phases were present in roughly equal amounts.

Analytical Procedure.—The samples were analysed for manganese and free sulphuric acid, water being determined by difference. For manganese, the bismuthate procedure (Vogel, "Quantitative Inorganic Analysis," Longmans, Green & Co., 1948, p. 358) was shown to be accurate over the range of manganese concentrations and of $MnSO_4 : H_2SO_4$ ratios encountered in this work if 15 minutes were allowed for the oxidation at room temperature. Typical results with standard potassium permanganate solution reduced with sulphur dioxide as a known source of manganese are shown in Table 1. For sulphuric acid, titration with standard sodium carbonate solution and a bromocresol-green–methyl-red mixed indicator proved highly accurate provided carbon dioxide was removed by boiling just before the true end-point. Since the latter is delayed when carbonate is run into an acid solution, a preliminary titration was necessary. The indicator contained 0·09 g. of bromocresol-green and 0·06 g. of methyl-red in 100 ml. of 80% alcohol, and changed from bluish-pink through grey to green with increasing pH. The very sharp grey-to-green change was always taken as the end-point. Results for known H_2SO_4–$MnSO_4$ mixtures are given in Table 1.

TABLE 1.

Taken : MnSO$_4$, mg.	Taken : Wt.-ratio H_2SO_4 : $MnSO_4$	Found : MnSO$_4$, mg.
6·04	1000	5·93
30·2	100	30·08
75·5	0	75·53
151·0	0	151·4

Taken : 0·5N-H_2SO_4, ml.	Taken : Wt.-ratio $MnSO_4$: H_2SO_4	Found : 0·5N-Na_2CO_3, ml.
25·0	0·0	25·00
25·0	0·048	24·99
25·0	0·96	24·99
25·0	4·8	25·01
25·0	9·6	25·00
25·0	14·4	25·00

RESULTS.

Microscopical Appearance of Solid Phases.—$MnSO_4,5H_2O$ is pink, triclinic, with the same habit as that of perfectly formed $CuSO_4,5H_2O$ crystals (cf. Hammel, *Ann. Chim.*, 1939, **11**, 247). $MnSO_4,H_2O$ forms minute birefringent bipyramids or four-sided prisms which in bulk appear almost white. $MnSO_4,H_2SO_4,H_2O$ forms 1—2-mm., pink, six-sided plates whose opposite edges and side faces are parallel, none of the side faces being perpendicular to the plane of the hexagon. Extinction is symmetrical and multiple twinning frequent. The acute bisectrix is

TABLE 2. *The System* $MnSO_4$–H_2SO_4–H_2O.

Solution $MnSO_4$, %	Solution H_2SO_4, %	Moist solid phase $MnSO_4$, %	Moist solid phase H_2SO_4, %	Extra-polated tie-lines, $MnSO_4$, %	Solid phase
At 0°.					
13·10	27·90	—	—	—	A + B
At 20°.					
30·61	8·98	—	—	—	A + B
0·47	69·64	—	—	—	B + C
0·37	89·09	—	—	—	C + D
At 24·5°.					
* 39·3	0·0	—	—	—	A + B
At 25°.					
38·81	0·23	—	—	—	B
25·08	12·98	70·0	3·92	89·45	B
7·07	34·34	63·95	10·43	88·71	B
2·71	43·26	—	—	—	B
0·58	56·18	57·93	19·52	88·49	B
0·39	62·39	—	—	—	B
0·41	66·90	57·62	23·55	88·7	B
0·53	70·09	53·32	36·06	83·2	B + C
0·53	70·00	53·26	32·54	99·1	B + C
0·42	70·90	48·21	41·50	74·9	C
0·28	72·89	39·1	47·50	77·87	C
0·19	84·90	39·04	51·57	99·1	C
0·33	88·20	36·94	54·50	96·2	C
0·42	89·30	31·41	64·20	54·5	C + D
0·34	89·54	23·93	72·80	35·2	D
0·20	90·90	27·00	71·00	34·78	D
0·09	92·08	23·73	73·60	35·95	D
0·02	96·29	26·24	72·91	34·10	D
At 45°.					
38·49	0·0	—	—	—	B
18·40	19·54	—	—	—	B
2·63	44·75	—	—	—	B
5·22	62·20	—	—	—	B
0·81	70·30	—	—	—	B + C
0·25	77·70	—	—	—	C
0·27	83·80	—	—	—	C
0·74	90·02	—	—	—	C + D
0·75	90·05	—	—	—	C + D
0·41	91·59	—	—	—	D
0·08	96·92	—	—	—	D
At 65°.					
35·88	0·0	—	—	—	B
16·78	20·40	—	—	—	B
2·87	45·93	—	—	—	B
0·89	61·73	—	—	—	B
1·26	70·70	—	—	—	B + C
0·54	76·10	—	—	—	C
0·44	83·41	—	—	—	C
0·94	89·20	38·65	53·44	95·07	C
1·35	90·70	—	—	—	C + E
1·31	90·80	43·91	54·34	56·07	E
1·30	90·91	—	—	—	E + D
1·04	91·68	24·93	72·90	35·07	D
0·72	92·79	—	—	—	D
At 95·7°.					
25·87	0·0	—	—	—	B
2·06	69·41	59·39	24·06	89·79	B
2·48	71·20	—	—	—	B + C
2·11	72·28	40·20	47·26	76·75	C
1·70	88·40	37·25	54·60	94·68	C
1·89	88·50	45·19	51·70	65·92	C + E
1·79	89·15	45·20	52·27	62·07	E
1·61	90·58	—	—	—	E
1·52	91·41	—	—	—	E
1·43	92·40	42·44	55·30	66·17	E
1·38	93·0	—	—	—	E
1·35	93·63	44·70	53·59	67·10	E
1·34	94·49	44·16	54·21	71·61	E
1·39	95·87	47·18	51·80	74·36	E

* Krepelka and Rejha, *Coll. Czech. Chem. Comm.*, 1933, **5**, 67.

Solid phases : A = $MnSO_4,5H_2O$
B = $MnSO_4,H_2O$
C = $MnSO_4,H_2SO_4,H_2O$
D = $MnSO_4,3H_2SO_4$
E = $MnSO_4,H_2SO_4$

almost perpendicular to the plate, the optic axial angle is small, and the optical sign negative. $MnSO_4,H_2SO_4$ occurs as very small pink birefringent parallelepipeds or short six-sided prisms with several end faces. $MnSO_4,3H_2SO_4$ forms highly birefringent four-sided prisms which are biaxial negative, with the slow ray across the prism. Extinction is not symmetrical.

Phase Equilibria.—Table 2 contains all the solubility and tie-line measurements, the column headed " Extrapolated tie-lines, $MnSO_4$, % " giving the points where the mathematically extrapolated tie-lines cut either the $MnSO_4$–H_2O or the $MnSO_4$–H_2SO_4 side of the equilateral triangle as the case may be. These points have direct significance regarding the composition of solid

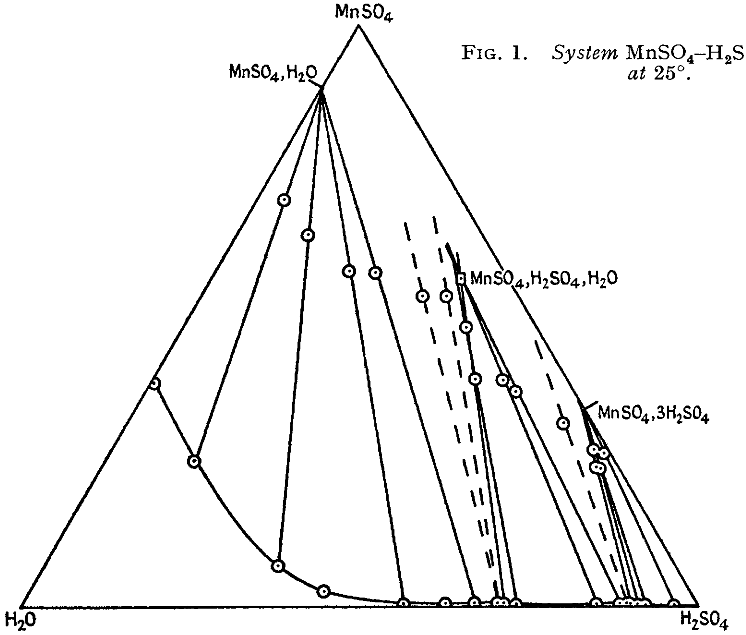

FIG. 1. *System* $MnSO_4$–H_2SO_4–H_2O *at* 25°.

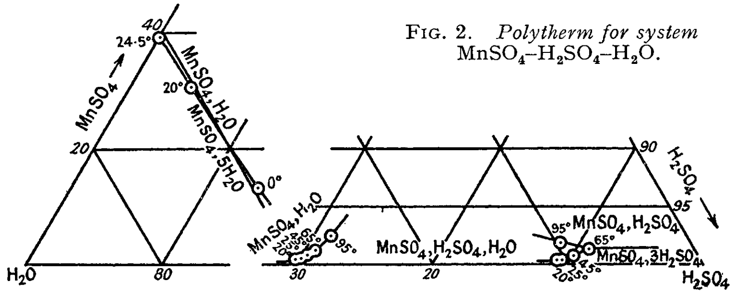

FIG. 2. *Polytherm for system* $MnSO_4$–H_2SO_4–H_2O.

phases B, D, and E (theor.: 89·3, 33·9, and 60·6% of $MnSO_4$ respectively), but not for the ternary compound C whose composition must be judged from the appropriate tie-line convergence point inside the triangle. Compositions are by weight. Typical tie-line convergence is shown on the 25° isotherm in Fig. 1, and the polytherm projection diagram in Fig. 2. The $MnSO_4,H_2SO_4$–$MnSO_4,3H_2SO_4$ isothermal invariant point at 95·7° is unknown, but the corresponding univariant line on the polytherm must run from the lower formation point of $MnSO_4,H_2SO_4$ passing very near to the last point on the 95·7° isotherm. This is the direction given in Fig. 2.

DISCUSSION

In view of (1) the presence of not more than 30% of liquid phase in samples of moist solid phases, (2) the reliability of the analytical procedures, and (3) the use of mathematical extrapolation to eliminate drawing errors, the position of the tie-lines is considered accurate in all cases except at very high acid concentrations at 95·7°. The composition of the solid phases B, C, and D as deduced from tie-line convergence is, therefore, quite unambiguous, but this is not so for the solid E. Composition $MnSO_4,H_2SO_4$ for E is, however, preferred on several grounds. The relevant tie-lines should converge for this composition at the point $MnSO_4$ 60·6% on the $MnSO_4$–H_2SO_4 side of the triangle, and the most reliable line, *i.e.*, that which makes the largest angle with this side, does in fact run to the point 62·07% (see Table 2), while the tie-line from the neighbouring invariant solution runs to the point 65·92%. The latter implies that the solid E must contain less than 65·92% $MnSO_4$ and could not, therefore, be $MnSO_4$ or $2MnSO_4,H_2SO_4$. That four of the tie-lines in question do actually run to points with higher $MnSO_4$ contents is believed due to the fact that they run almost parallel to the $MnSO_4$–H_2SO_4 side of the triangle, and in consequence errors as small as 0·2% in the water content of the moist solid phase points would have a major effect on the gradient of the corresponding tie-lines. The observed displacement of the latter from convergence at $MnSO_4$ 60·6% is consistent with the absorption of about 10 mg. of water by the moist solid phases during sampling and this is considered not improbable. It is unlikely that the displacement is due to the presence in addition to E of a second solid phase, *viz.*, $MnSO_4$ or $2MnSO_4,H_2SO_4$, because (1) the solid phase was microscopically homogeneous, (2) experiment showed that the anhydrous sulphate, prepared by heating the pentahydrate *in vacuo* at 200° (controlled by analysis), is rapidly converted into E when heated with 98·6% H_4SO_2 at temperatures between 95° and the boiling point, and (3) true equilibrium was undoubtedly established and there could, therefore, be no question of E's slowly changing into another phase. Furthermore, the composition $2MnSO_4,H_2SO_4$ for E would require the moist solid phases to contain about 40% of mother-liquor, but, in view of the well-crystallised nature of E and the method of sampling, the figure 25% as required by $MnSO_4,H_2SO_4$ is considered much more probable. Little significance can be attached to the 65° tie-line for E, which runs to $MnSO_4$ 56%, owing to the extremely small range of stability of E at this temperature. The solid phase in this instance may have contained a small amount of phase D which would account for the low $MnSO_4$ content.

There is no evidence for the occurrence as stable solid phases of the tetrahydrate or anhydrous normal sulphates as reported by Montemartini and Losana (*loc. cit.*) at 12·6°. As mentioned above, $MnSO_4,H_2SO_4$ is still present as stable solid phase in 98% acid even at the boiling point, and it seems unlikely, therefore, that the anhydrous normal sulphate ever appears in the ternary system at atmospheric pressure. These authors also claim the existence of $MnSO_4,H_2SO_4$ at 12·6°, but from Table 2 it is clear that the lower formation temperature of this phase is only very slightly less than 65°. The present solubility results differ considerably from those of the authors mentioned. All the moist acid sulphate phases dissolved in water with evolution of heat greatly in excess of that due to adhering mother-liquor alone, thus suggesting the presence of covalent H_2SO_4 molecules (or $H_3O^+HSO_4^-$ in the case of $MnSO_4,H_2SO_4,H_2O$) as structural units in the lattices.

It will be seen from Fig. 2 that the water content of all points on the univariant line where $MnSO_4,5H_2O$ and $MnSO_4,H_2O$ co-exist in contact with saturated solutions increases with rise in temperature. This behaviour is common to all inter-hydrate transitions in systems showing the feature (*a*) mentioned above for which reliable data are available (a total of 18 examples) and may therefore be considered characteristic of this type of transition. An alternative statement of this water requirement is that, on traversal of the hydrate saturation surfaces at constant water content in the direction of rising temperatures, the path must pass from a higher to a lower hydrate surface and never the reverse. It is noteworthy that the transition $MnSO_4,H_2SO_4,H_2O \rightleftharpoons MnSO_4,H_2SO_4$ involving acid sulphates also conforms to the water condition, as does a similar example in the ferric sulphate system.

Analogously, for this and other systems showing feature (*b*), paths over the acid sulphate saturation surfaces at constant sulphuric acid content in the direction of rising temperature always pass from a higher to a lower acid sulphate surface. This corresponds to a rise in the free acid content of all points on the univariant lines with rise in temperature. Thirteen examples have been found altogether. The transitions $MnSO_4,H_2O \rightleftharpoons MnSO_4,H_2SO_4,H_2O$

and $MnSO_4,H_2SO_4,H_2O \rightleftharpoons MnSO_4,3H_2SO_4$, and a similar example from the ferric sulphate system, also conform to the acid sulphate case.

It appears therefore that the direction of the appropriate univariant lines could be used to characterise the three types of transition, and thus to distinguish between normal and acid sulphates, whether hydrated or not, in cases where tie-line convergence is ambiguous. Corresponding transitions in systems of the type M_2O–P_2O_5–H_2O, though only a few examples are available, appear to conform to the same criteria as apply in sulphate systems. In MCl–HCl–H_2O systems only a minority of hydrate transitions conform.

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