354. *The System Manganese Sulphate–Thorium Sulphate–Water at* 30°. *A New Type of Double Salt.*

By Robert M. Caven.

It was shown by the author and Mitchell (J., 1925, **127**, 527, 2549) that $MnSO_4$, but not $CuSO_4$ or $NiSO_4$, forms a double salt with $Al_2(SO_4)_3$ at 30° : and it appeared from the form of the graph that the limits within which the manganese double salt is formed are narrow, and that this salt is not much less soluble in the solution from which it separates than are its constituent single salts.

It appeared interesting, therefore, to discover whether double sulphates are formed by combination of bivalent and quadrivalent sulphates; and a start was made with $MnSO_4$ and $Th(SO_4)_2$. Moreover, $Th(NO_3)_4$ is known to form double salts with the nitrates of Mg, Zn, Co, Ni, and Mn, of the type $M^{++}Th(NO_3)_6,8H_2O$ (Meyer and Jacoby, *Z. anorg. Chem.*, 1901, **27**, 359).

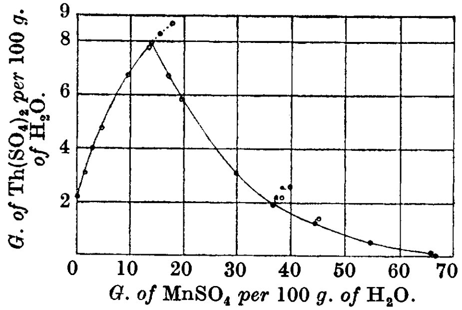
EXPERIMENTAL.

The materials employed were A.R. $MnSO_4,5H_2O$ and $Th(SO_4)_2,8H_2O$, the purity of which was proved by analysis. For the analysis of solutions containing these, alternative methods were available. The Mn might be estimated by the bismuthate method, and the Th calc. after estimation of total SO_4. This method was used in the earlier work, but was found unsuitable when the proportion of Th was small. All the recorded results were obtained by precipitating Th as iodate in presence of HNO_3, converting this into $Th(OH)_4$

by NH_3 aq., and weighing it as ThO_2, a double pptn. being employed, unless the hydroxide was white, to ensure freedom from Mn.

The complete pptn. of SO_4 from $Th(SO_4)_2$ in acid solution is well known to present difficulty owing to the existence of thorisulphate ions. Therefore, NH_3 aq. was always added in excess before $BaCl_2$, and the liquid heated with HCl aq. after pptn. until the $BaSO_4$ appeared white. Even in that case it was found necessary to allow the liquid to stand over-night for pptn. to be complete. The explanation of this appears to be that the $Th(OH)_4$ pptd. by NH_3 aq. contains a little sulphate, which, on acidification, forms thorisulphate ions from which SO_4 is only slowly pptd. by $BaCl_2$. This supposition is borne out by the fact that the direct pptn. of $Th(OH)_4$ from aq. solution of the pure sulphate by NH_3 gives a high value for Th; *e.g.*, Th found by direct ammonia pptn. = 41·33, 41·39, and 41·40%, whilst Th found by pptn. as iodate subsequently decomp. by NH_3 = 40·82% [Calc. for $Th(SO_4)_2,8H_2O$: Th, 40·86%]. SO_4 estimated in same sample = 33·81% ≡ 40·87% Th.

System $MnSO_4$–$Th(SO_4)_2$–H_2O *at* 30°.



The results obtained, showing the effect of increasing amounts of $MnSO_4$ on the solubility of $Th(SO_4)_2$, were plotted on the same scale as that employed by Barre (*Compt. rend.*, 1910, **150**, 1599) for the NH_4–Th double sulphates at 16° (cf. Mellor, "Comprehensive Treatise, etc.," Vol. VII, p. 245); and it soon appeared that an increase of solubility of $Th(SO_4)_2$ was produced by $MnSO_4$ similar to that caused by $(NH_4)_2SO_4$. Double salt, however, did not immediately separate when a sufficiency of $MnSO_4$ to produce it was present; instead, a metastable state resulted, with $Th(SO_4)_2$ remaining alone as solid phase. The formation of double salt in presence of $Th(SO_4)_2$ has not been observed.

The double salt first appeared in the following way. As much $Th(SO_4)_2$, $8H_2O$ as possible was dissolved in a nearly satd. solution of $MnSO_4$ at an elevated temp.; the solution was then filtered hot and stirred in the thermostat at 30°. A fine cryst. powder gradually separated, which was subsequently shown to be the double salt. A characteristic, however, of this double salt formation is its slowness, except with high concns. of $MnSO_4$. Indeed, several hrs. may elapse before there is visible sign of crystn., and about 14 days may be necessary for a state of equil. to be reached. This is illustrated by the points α and β on the figure. The point α represents the state of a solution from which double salt has been separating for 7 days, and the point β the same solution 3 days later, when a condition of equil. is being approached, but is not yet reached.

The slow rate at which equil. was reached gave rise to experimental difficulty. In former recorded expts. by the author and his co-workers, it was found sufficient to stir the solutions in loosely covered bottles in the thermostat, because separation of crystals occurred more rapidly than evaporation at 30°; but in this case it became evident that evaporation must be prevented.

Indeed, in one expt. the solution became dry before equil. was reached. Consequently, the following mechanism, designed by Prof. Thomas Gray and executed by Mr. Alex. Hossack, was constructed. A hollow, rectangular brass frame of square cross-section was made to carry three wide-mouthed stoppered bottles of 400-c.c. capacity, which were screwed into position after their stoppers had been made water-tight with paraffin wax. The frame was caused to rotate horizontally in a carrier fixed to the bottom of the thermostat, by means of a pair of toothed wheels and a vertical spindle set revolving by an electric motor. Thus, the bottles were plunged lengthwise continuously through the water in the thermostat at a speed sufficient to mix their contents and stir the water but not to agitate its surface. The thermostat was heated and controlled electrically (Cranston, J., 1930, 1458) at 30° ± 0·1°.

By this means solutions could be agitated for an unlimited time, and portions withdrawn successively for analysis. These portions were first transferred to a stoppered test-tube which was immersed in the thermostat water up to its rim until suspended matter had settled, and the supernatant liquid was then decanted into a weighing bottle or quickly filtered, with suction, if necessary.

When the lowest point on the double-salt curve had been fixed, successive higher points were obtained by the addition of small quantities of H_2O, which could be continued as long as any double salt remained undissolved. These points were obtained more easily than the first because equil. is reached more quickly by solution than by crystn. The triple point, at which the solution was in equil. with double salt and $Th(SO_4)_2$, was reached by adding $Th(SO_4)_2$ and a calc. quantity of H_2O to the mixture after the highest point on the double-salt curve had been obtained. Microscopic examination showed the solid phase to be a mixture.

The System $MnSO_4$–$Th(SO_4)_2$–H_2O *at* 30°.

$Th(SO_4)_2$.	$MnSO_4$.	Solid phase.
2·14	—	A
3·03	1·41	
3·94	2·93	
4·69	4·54	
6·64	9·33	
7·75	13·54	
*8·23	15·49	
*8·66	17·68	
7·91	13·79	A, B
6·65	16·94	B
5·82	19·86	
3·11	29·75	
α2·58	39·82	
β2·17	38·47	
1·87	36·78	
1·20	44·62	
1·38	45·27	
0·50	54·59	
0·135	65·67	B, C
—	66·41	C

* Metastable.

A = $Th(SO_4)_2,8H_2O$; B = $MnSO_4,Th(SO_4)_2,7H_2O$; C = $MnSO_4,5H_2O$.

The Double Salt $MnSO_4,Th(SO_4)_2,7H_2O$.—For analysis and study of properties, a quantity of *double salt* prep. as above was filtered off with suction, washed twice with cold H_2O, and dried in air on a porous plate for 2 days. It was a pure white powder consisting of microscopic prisms. By gentle ignition, it lost all its H_2O without other change, for when anhyd. it dissolved completely in H_2O. After being heated to dull redness, it appeared pale pink when cold, but this change involved no loss of SO_3 since the product was still sol. in H_2O [Found: $MnSO_4$, 21·74; $Th(SO_4)_2$, 59·98, 60·08, mean 60·03; H_2O, 18·00; SO_4, 41·05; $MnSO_4 : Th(SO_4)_2 : H_2O$ = 1·000 : 0·983 : 7·012.

$MnSO_4,Th(SO_4)_2,7H_2O$ requires $MnSO_4$, 21·53; $Th(SO_4)_2$, 60·49; H_2O, 17·97; SO_4, 41·08%].

It is seen from the figure that the range of double-salt formation is large, the limits being $MnSO_4 : Th(SO_4)_2 = 5 : 1$ and 1360 : 1.

Thus the double salt cannot be crystallised from an equimol. solution of its component salts, nor recrystallised from water; its aq. solution yielded a mixture when evaporated at room temp.

Since the purity of the double salt is proved by the analytical figures for H_2O and SO_4, it appears that the $Th(SO_4)_2$ is about 0·8% low, and the $MnSO_4$, which depends upon it, correspondingly high. This is probably due to the slight solubility of the $Th(IO_3)_4$ in the liquid from which it is pptd.

Summary.

The double salt $MnSO_4,Th(SO_4)_2,7H_2O$ crystallises from aqueous solution at 30° in microscopic prisms. The limits of its formation are $MnSO_4 : Th(SO_4)_2 = 5 : 1$ and 1360 : 1. Consequently the salt cannot be recrystallised from water.

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