

CCCXLIII.—*The Hydrates of Manganous Oxalate.*

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IN the course of experiments on the rates of change of metastable systems consisting of salt hydrates with their saturated solutions, determinations have been made of the solubility curves and densities of the two known hydrates of manganous oxalate. This salt forms a dihydrate, stable in contact with its saturated solution between 0° and 100°, and a trihydrate, unstable over this range.

Preparation of the Hydrates.—The dihydrate was prepared by two methods: (1) by the action of potassium permanganate on oxalic acid (Coltman, *Ind. Eng. Chem.*, 1924, **16**, 606); (2) by loss of water from the trihydrate. No difference was observed in the properties of the dihydrate prepared in these two ways. The trihydrate was obtained by mixing ice-cold dilute solutions of manganous sulphate and oxalic acid, the former being in excess; the mixture was kept at 0°, and under these conditions a crystalline product separated in 12 hours. This was filtered off and washed thoroughly with ice-cold water immediately before use.

Solubility Determinations.—The oxalate content of the saturated solution was determined by titration with potassium permanganate which had been standardised on potassium hydrogen oxalate, sodium oxalate, and the dihydrate, $\text{MnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$.

Saturation of the solution was effected by mechanical stirring in a flask immersed in a thermostat; samples were removed for analysis by filtration through an asbestos filter attached to the point of a pipette. No difficulty was experienced in the case of the dihydrate, as stirring could be continued until a constant value was obtained. In the case of the trihydrate there is an obvious difficulty in that decomposition is concurrent with the process of dissolution. The true saturation value can be obtained by working under conditions such that the rate of dissolution is much greater than that of recrystallisation of the solute as dihydrate. Now, direct experiment in a dilatometer showed that the rate of decomposition exhibits a pronounced induction period; *e.g.*, at 25° only 1% of the trihydrate decomposes in the first 5 hours, although after 50% of the trihydrate has changed into dihydrate, the rate of decomposition is 1% in 10 minutes. The corresponding figures at 36° are 1% in the first 11 minutes and 7.6% in 10 minutes. Accordingly, at the higher temperatures, an attempt was made to saturate the solution before the induction period was completed by making a thick suspension of the trihydrate crystals in water

and agitating this by a very rapidly rotating mechanical stirrer. During the induction period, the ratio of the surfaces of dihydrate to trihydrate crystals is very small, and therefore it was assumed that, so long as constant results could be obtained within the period of induction, these represent the true solubility. In this way values up to 30° were obtained.

Results.—The averages of the values found at each temperature are given in the table; in no case did the individual values differ by more than 1% among themselves. The solubilities (*s*) are expressed as g. of anhydrous manganous oxalate in 100 g. of saturated solution.

Dihydrate.				Trihydrate.			
<i>t.</i>	<i>s.</i>	<i>t.</i>	<i>s.</i>	<i>t.</i>	<i>s.</i>	<i>t.</i>	<i>s.</i>
0.0°	0.0198	25.0°	0.0308	0.0°	0.0326	20.1°	0.0582
6.3	0.0225	30.3	0.0335	6.3	0.0388	25.0	0.0669
12.8	0.0256	36.0	0.0369	12.8	0.0476	30.0	0.0769
20.1	0.0285						

No measurements of the solubilities of the trihydrate are recorded in the literature; those of the dihydrate have been determined by Hauser and Wirth (*J. pr. Chem.*, 1909, **79**, 358), who found 0.0312 g. of MnC_2O_4 per 100 g. of solution at 25°, and by Chatterjee and Dhar (*J. Physical Chem.*, 1924, **28**, 1009) at 36° and 93°. These authors found 0.0377 at 36° and 0.0813 at 93° (results re-calculated to g. per 100 g. of solution); thus their value at 36° is 2.1% higher than ours. However, it would seem not improbable that the cause of the discrepancy is the presence of a small amount of trihydrate in the dihydrate which they prepared by precipitation at 30°, since at this temperature the precipitate obtained consists at first of a mixture of the two hydrates; the fact that their product gave analytical results in agreement with the formula $\text{MnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ is not significant in this connexion, since, on drying the sample for analysis, the change into dihydrate would be completed. On the other hand, at 93° any trihydrate present at the beginning of the solubility determinations would very rapidly change into dihydrate, so that the value obtained at this temperature would not be too high from this cause; moreover, when the solubility curve of the dihydrate is extrapolated to 93°, by a formula analogous to Ramsay and Young's vapour-pressure formula, a value is obtained in agreement with the result of Chatterjee and Dhar.

In connexion with measurements of the rate of change of the trihydrate into the dihydrate, it is of interest to know the (hypothetical) equilibrium temperature for the system trihydrate-dihydrate-saturated solution.

An estimate of this temperature can be made by extrapolating the solubility curves below 0° by means of the Ramsay and Young relationship

$$T_1/T_2 = T_1'/T_2' + c(T_1 - T_1')$$

where T_1 and T_1' are, respectively, the absolute temperatures at which the trihydrate has the same solubility as the dihydrate at T_2 and T_2' , and c is a constant. On plotting T_1/T_2 against $(T_1 - T_1')$, a straight line is obtained, giving $c = -0.002301$; the transition temperature T_0 is then given by the formula

$$T_0 = \{T_1'(cT_2' - 1) + T_2'\}/cT_2'.$$

In this way, the transition temperature is found to be -40.6° .

Alternatively, the solubility curves may be extrapolated by means of a formula of the type

$$\log_{10} s = A - B/T - C \log_{10} T$$

(the form of which results from the assumption that both the heat of solution and the van 't Hoff factor i remain sensibly constant over the temperature range considered), where A , B , and C are constants, and T is the absolute temperature corresponding to the solubility s . In this case, the transition temperature is calculated from the equation

$$0 = (A - A') - (B - B')/T_0 - (C - C') \log_{10} T_0,$$

where A' , etc., refer to the trihydrate, and A , etc., to the dihydrate. The solubility parameters obtained from the curves were:

Trihydrate: $A' = -26.8626$; $B' = -222.82$; $C' = -10.080$.

Dihydrate: $A = -8.9868$; $B = +201.42$; $C = -3.2944$.

The discrepancy between values of s calculated from these figures and the experimental curves is nowhere greater than $0.004s$. The transition temperature obtained in this way is -41.7° ; and therefore it would seem probable that it lies in the neighbourhood of -41° .

Determinations of the Densities of the Hydrates at 0° .—The density of each of the hydrates was determined as follows: A calibrated specific gravity bottle was filled at 0° with a saturated solution, together with a quantity of the crystals, and weighed. The total manganous oxalate content of the bulb was found by titration with $N/10$ -potassium permanganate. The amount of manganous oxalate in solution was calculated from a knowledge of the concentration and density of the saturated solution, and the weight of the hydrate was thus obtained by difference. These data, together with the weight of the bulb filled with saturated solution, determine the density.

Density of dihydrate at 0°	= 2.2946	}
„ saturated solution at 0°	= 1.0001	}
„ trihydrate at 0°	= 1.9930	}
„ saturated solution at 0°	= 1.0002	}

A check on the accuracy of these results was obtained by measuring in a calibrated dilatometer the change in volume at 0° corresponding to the decomposition of trihydrate into dihydrate. Allowance was made for the difference in solubility of the two hydrates at 0° (Found: -0.0173 c.c. per g. of $\text{MnC}_2\text{O}_4 \cdot 3\text{H}_2\text{O}$. Calc. from the densities: -0.0176 c.c.).

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[Received, July 28th, 1926.]
