269. *Heats of Formation of the Hydrates of Manganous Oxalate.*

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Manganous oxalate forms a trihydrate unstable in contact with water at all temperatures, and a stable dihydrate. In connexion with some kinetic experiments, a knowledge of the heats of dissociation of the hydrates to the anhydrous salt was required. No previous thermal measurements on these hydrates have been recorded, and no vapour-pressure data exist for the dihydrate; moreover, it was found that equilibrium in a tensimeter containing dihydrate and anhydrous salt was approached so slowly that sufficiently reliable vapour-pressure measurements could not be made. Calorimetric measurements with an accuracy of about 1% are now recorded.

The method adopted was measurement of the heats of solution of the anhydrous salt and the two hydrates in $6N$-nitric acid, which dissolves the solids very rapidly. The required heat of formation (Q) from the anhydrous salt and liquid water is found from the sum $Q = Q_d + Q_a - Q_h$, according to the scheme :

$$\begin{tikzcd}
\begin{array}{c} MnC_2O_4 + nH_2O \\ + \{HNO_3 \text{ in } (a - n) \text{ mols. } H_2O\} \end{array} \arrow[r, "Q"] \arrow[d, "Q_d"] & \begin{array}{c} MnC_2O_4,nH_2O \\ + \{HNO_3 \text{ in } (a - n) \text{ mols. } H_2O\} \end{array} \arrow[d, "Q_h"] \\
\begin{array}{c} MnC_2O_4 \\ + \{HNO_3 \text{ in } a \text{ mols. } H_2O\} \end{array} \arrow[r, "Q_a"] & \left\{\begin{array}{c} MnC_2O_4 \text{ and } HNO_3 \\ \text{in } a \text{ mols. } H_2O \end{array}\right\}
\end{tikzcd}$$

Q_a and Q_h are the measured heats of solution of the anhydrous salt and the hydrate ($n = 2$ or 3), the final solution being always the same, containing an arbitrary amount of nitric acid and a mols. of water. Q_d is the heat of dilution of the nitric acid solution from $(a - n)$ to a mols. of water; under the conditions of the experiment, this is almost negligible within the accuracy aimed at : it has been calculated from the data given by Julius Thomsen ("Thermochemistry," London, 1908, p. 78).

The calorimeter was constructed from a Dewar vessel with a hollow double-walled copper cover dipping into the water in a large water-jacket. It was calibrated electrically with a Weston milliammeter specially checked by the makers to an absolute accuracy of 0·25%.

The two hydrates were prepared as previously described (Chamberlain, Hume, and Topley, J., 1926, 2620) and the anhydrous salt by dehydration at 120° in an atmosphere of nitrogen. With the trihydrate it was found best to use slightly damp crystals (with about 1% of uncombined water), because decomposition starts so rapidly when the crystals are completely dried; the damp crystals were analysed, and account taken of the extra water. The quantity of manganous oxalate in saturated solution in this small amount of extra water is negligible in view of the low solubility.

Results.—The following results were obtained for the heats of solution, calculated for 1 g.-mol. of the solid, at 16—19°.

MnC_2O_4 : + 2716, + 2754; mean heat of solution = 2735.

$MnC_2O_4,2H_2O$: − 3505, − 3514, − 3517, − 3497, − 3502, − 3514; mean heat of solution = − 3508.

$$Q_d = +4.$$

$MnC_2O_4,3H_2O$: − 5035, − 5090, − 5048; mean heat of solution = − 5058.

$$Q_d = +6{\cdot}6.$$

From these results we have :

$$MnC_2O_4 + 2H_2O\ \text{(liquid)} = MnC_2O_4,2H_2O + 6247\ \text{calories},$$
$$MnC_2O_4 + 3H_2O\ \text{(liquid)} = MnC_2O_4,3H_2O + 7800\ \text{calories}.$$

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