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Note

STANDARD ENTHALPY OF FORMATION OF $Cd_3(OH)_5NO_3$

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A new cadmium hydroxide nitrate, $Cd_3(OH)_5NO_3$, has recently been prepared by an interdiffusion method. Its X-ray powder pattern was indexed and its thermal decomposition has been investigated [1]. This paper concerns the determination of its enthalpy of formation which is based on its enthalpy of solution and also on that of cadmium oxide, CdO, in 2 mol dm^{-3} HNO_3(aq). These were measured using a Calvet microcalorimeter, the design of which has been described elsewhere [2]. The general procedure and the calibration have been published [3]. The masses of $Cd_3(OH)_5NO_3$ and CdO were about 7 and 5.5 mg, respectively, and the molality of the final solution was adjusted to 7.162×10^{-3} mol kg^{-1}.

The enthalpy of formation of $Cd_3(OH)_5NO_3$ was determined from the enthalpy of the following reactions

$$Cd_3(OH)_5NO_3(cr) + [786HNO_3 + 20310H_2O](sln) \rightarrow [3Cd(NO_3)_2 + 781HNO_3 + 20315H_2O](sln) \qquad \Delta_r H_1^{\ominus} \qquad (1)$$

$$3CdO(cr) + [786HNO_3 + 20310H_2O](sln) \rightarrow [3Cd(NO_3)_2 + 780HNO_3 + 20313H_2O](sln) \qquad \Delta_r H_2^{\ominus} \qquad (2)$$

$$2H_2O(l) + [3Cd(NO_3)_2 + 780HNO_3 + 20313H_2O](sln) \rightarrow [3Cd(NO_3)_2 + 780HNO_3 + 20315H_2O](sln) \qquad \Delta_r H_3^{\ominus} \qquad (3)$$

$$HNO_3(l) + [3Cd(NO_3)_2 + 780HNO_3 + 20315H_2O](sln) \rightarrow [3Cd(NO_3)_2 + 781HNO_3 + 20315H_2O](sln) \qquad \Delta_r H_4^{\ominus} \qquad (4)$$

$$3CdO(cr) + HNO_3(l) + 2H_2O(l) \rightarrow Cd_3(OH)_5NO_3(cr) \qquad \Delta_r H_5^{\ominus} \qquad (5)$$

If $\Delta_f H^{\ominus}_{CdO(cr)}$, $\Delta_f H^{\ominus}_{HNO_3(l)}$ and $\Delta_f H^{\ominus}_{H_2O(l)}$ are the standard enthalpies of formation of CdO(cr), HNO_3(l) and H_2O(l) respectively, the standard enthalpy of formation of $Cd_3(OH)_5NO_3$ can be calculated from the following equation

$$\Delta_f H^{\ominus}_{Cd_3(OH)_5NO_3(cr)} = \Delta_r H_2^{\ominus} + \Delta_r H_3^{\ominus} + \Delta_r H_4^{\ominus} - \Delta_r H_1^{\ominus} + 3\Delta_f H^{\ominus}_{CdO(cr)} + 2\Delta_f H^{\ominus}_{H_2O(l)} + \Delta_f H^{\ominus}_{HNO_3(l)} \qquad (6)$$

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The mean values of $\Delta_r H_1^\ominus$ and $\Delta_r H_2^\ominus$ obtained from ten calorimetric measurements of each parameter are -203.34 ± 0.54 and -299.9 ± 2.4 kJ mol^{-1} respectively, the uncertainties being twice the standard deviation of the means. $\Delta_r H_3^\ominus$ and $\Delta_r H_4^\ominus$ were calculated from data in thermodynamic tables [4]. Taking account of the very low molality of $Cd(NO_3)_2$ in the solutions, it was assumed that the variations in the partial molar enthalpy of this salt in reactions (3) and (4) are negligible in comparison with the precision of $\Delta_r H_1^\ominus$ and $\Delta_r H_2^\ominus$. So $\Delta_r H_3^\ominus$ and $\Delta_r H_4^\ominus$ are considered to be equal to the standard enthalpies, $\Delta_r H_6^\ominus$ and $\Delta_r H_7^\ominus$, of the reactions

$$2H_2O(l) + [780HNO_3 + 20313H_2O](sln) \rightarrow [780HNO_3 + 20315H_2O](sln) \qquad \Delta_r H_6^\ominus \qquad (7)$$

$$HNO_3(l) + [780HNO_3 + 20315H_2O](sln) \rightarrow [781HNO_3 + 20315H_2O](sln) \qquad \Delta_r H_7^\ominus \qquad (8)$$

$\Delta_r H_6^\ominus$ is negligible and $\Delta_r H_7^\ominus$ was calculated to be $-32\,740 \pm 175$ J mol^{-1}. The standard molar enthalpies of formation of CdO, $HNO_3(l)$ and $H_2O(l)$ were taken from the literature, $\Delta_f H^\ominus_{CdO(cr)} = -259.40 \pm 1.67$ kJ mol^{-1} [5], $\Delta_f H^\ominus_{HNO_3(l)} = -173.78 \pm 0.04$ kJ mol^{-1} [4] and $\Delta_f H^\ominus_{H_2O(l)} = -285.83 \pm 0.04$ kJ mol^{-1} [6]. From eqn. (6), the standard enthalpy of formation of $Cd_3(OH)_5NO_3$ was calculated to be $\Delta_f H^\ominus_{Cd_3(OH)_5NO_3(cr)} = -1652.94 \pm 5.69$ kJ mol^{-1}.

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