

Note

STANDARD ENTHALPY OF FORMATION OF $\text{Cd}_3(\text{OH})_5\text{NO}_3$

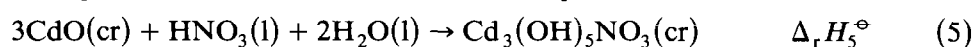
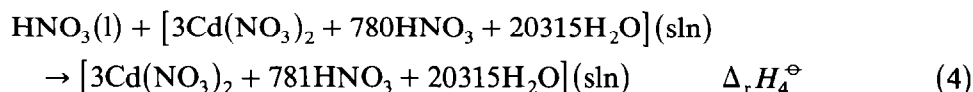
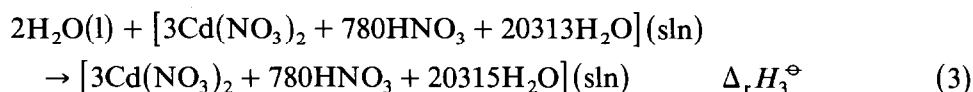
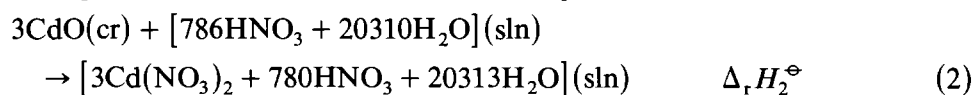
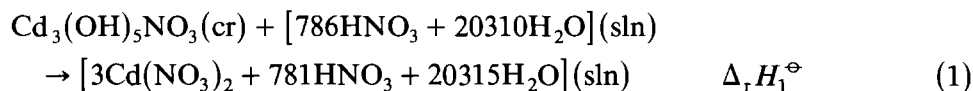
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A new cadmium hydroxide nitrate, $\text{Cd}_3(\text{OH})_5\text{NO}_3$, has recently been prepared by an interdiffusion method. Its X-ray powder pattern was indexed and its thermal decomposition has been investigated [1]. This paper concerns the determination 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} $\text{HNO}_3(\text{aq})$. 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 $\text{Cd}_3(\text{OH})_5\text{NO}_3$ and CdO were about 7 and 5.5 mg, respectively, and the molality of the final solution was adjusted to $7.162 \times 10^{-3} \text{ mol kg}^{-1}$.

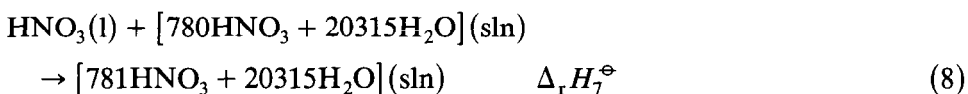
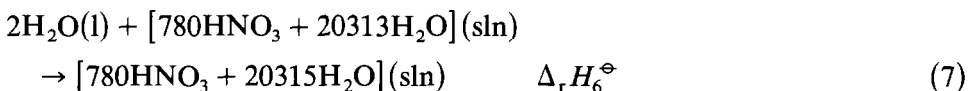
The enthalpy of formation of $\text{Cd}_3(\text{OH})_5\text{NO}_3$ was determined from the enthalpy of the following reactions



If $\Delta_f H_{\text{CdO}(\text{cr})}^\ominus$, $\Delta_f H_{\text{HNO}_3(\text{l})}^\ominus$ and $\Delta_f H_{\text{H}_2\text{O}(\text{l})}^\ominus$ are the standard enthalpies of formation of $\text{CdO}(\text{cr})$, $\text{HNO}_3(\text{l})$ and $\text{H}_2\text{O}(\text{l})$ respectively, the standard enthalpy of formation of $\text{Cd}_3(\text{OH})_5\text{NO}_3$ can be calculated from the following equation

$$\Delta_f H_{\text{Cd}_3(\text{OH})_5\text{NO}_3(\text{cr})}^\ominus = \Delta_r H_2^\ominus + \Delta_r H_3^\ominus + \Delta_r H_4^\ominus - \Delta_r H_1^\ominus + 3\Delta_f H_{\text{CdO}(\text{cr})}^\ominus + 2\Delta_f H_{\text{H}_2\text{O}(\text{l})}^\ominus + \Delta_f H_{\text{HNO}_3(\text{l})}^\ominus \quad (6)$$

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(NO₃)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



$\Delta_r H_6^\ominus$ 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, HNO₃(l) and H₂O(l) were taken from the literature, $\Delta_f H_{\text{CdO}(\text{cr})}^\ominus = -259.40 \pm 1.67$ kJ mol⁻¹ [5], $\Delta_f H_{\text{HNO}_3(\text{l})}^\ominus = -173.78 \pm 0.04$ kJ mol⁻¹ [4] and $\Delta_f H_{\text{H}_2\text{O}(\text{l})}^\ominus = -285.83 \pm 0.04$ kJ mol⁻¹ [6]. From eqn. (6), the standard enthalpy of formation of Cd₃(OH)₅NO₃ was calculated to be $\Delta_f H_{\text{Cd}_3(\text{OH})_5\text{NO}_3(\text{cr})}^\ominus = -1652.94 \pm 5.69$ kJ mol⁻¹.

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