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## Note

# STANDARD ENTHALPY OF FORMATION OF THE MONOCLINIC FORM OF $Cs_2CdI_4$

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Dicaesium cadmium tetraiodide $Cs_2CdI_4$ has two polymorphic forms at room temperature depending on its preparation [1,2]. When prepared from an aqueous equimolar solution of CsI and $CdI_2$, the monoclinic $\alpha$-phase is obtained with a $Sr_2GeS_4$-type structure. Above 400 K, it undergoes a phase transformation to an orthorhombic modification which is isotypic with $K_2SO_4$ [3,4]. In this paper the standard enthalpy of formation of $\alpha$-$Cs_2CdI_4$ is reported as calculated from the results of solution calorimetry.

Calorimetric measurements were made of the enthalpy of solution of $\alpha$-$Cs_2CdI_4$ in pure water and of CsI in an aqueous $CdI_2$ solution. The masses of $\alpha$-$Cs_2CdI_4$ and CsI dissolved were about 60 and 40 mg respectively, so that the molality of $Cs_2CdI_4$ was $1.163 \times 10^{-2}$ mol kg$^{-1}$ in the resulting solutions. The measurements were carried out at 298 K using a Calvet microcalorimeter, the design of which has been described [5]. The general procedure and the calibration have been published [6].

The enthalpy of formation of $\alpha$-$Cs_2CdI_4$ was calculated from the reaction enthalpies of the following reactions

$$\alpha\text{-}Cs_2CdI_4(cr) + 4780H_2O(l) = [Cs_2CdI_4 + 4780H_2O](sln) \qquad \Delta_r H_1^{\ominus} \tag{1}$$

$$Cs(cr) + \tfrac{1}{2}I_2(cr) = CsI(cr) \qquad \Delta_r H_2^{\ominus} \tag{2}$$

$$Cd(cr) + I_2(cr) = CdI_2(cr) \qquad \Delta_r H_3^{\ominus} \tag{3}$$

$$CdI_2(cr) + 4780H_2O(l) = [CdI_2 + 4780H_2O](sln) \qquad \Delta_r H_4^{\ominus} \tag{4}$$

$$2CsI(cr) + [CdI_2 + 4780H_2O](sln) = [Cs_2CdI_4 + 4780H_2O](sln) \qquad \Delta_r H_5^{\ominus} \tag{5}$$

The mean values of $\Delta_r H_1^{\ominus}$ and $\Delta_r H_5^{\ominus}$, obtained from eight calorimeter measurements of each quantity, are $89.33 \pm 0.88$ kJ mol$^{-1}$ and $62.78 \pm 0.60$ kJ mol$^{-1}$ respectively, the uncertainties being twice the standard deviation of the means. Values of $\Delta_r H_2^{\ominus}$, $\Delta_r H_3^{\ominus}$ and $\Delta_r H_4^{\ominus}$ were taken from the

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literature: $\Delta_r H_2^{\ominus} = -348.14 \pm 0.16$ kJ mol$^{-1}$ [7]; $\Delta_r H_3^{\ominus} = -204.18 \pm 3.35$ kJ mol$^{-1}$ [8]; $\Delta_r H_4^{\ominus} = 10.38 \pm 0.08$ kJ mol$^{-1}$ [9,10].

Based on the following equation

$$\Delta_f H^{\ominus}_{\alpha\text{-}Cs_2CdI_4(cr)} = 2\Delta_r H_2^{\ominus} + \Delta_r H_3^{\ominus} + \Delta_r H_4^{\ominus} + \Delta_r H_5^{\ominus} - \Delta_r H_1^{\ominus} \quad (6)$$

the enthalpy of formation of $\alpha$-$Cs_2CdI_4$ was calculated to be $\Delta_f H^{\ominus}_{\alpha\text{-}Cs_2CdI_4(cr)} = -916.63 \pm 3.53$ kJ mol$^{-1}$.

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