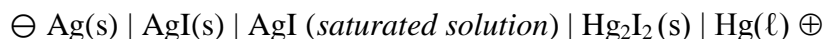


Problem 11-12 Thermodynamics of the cell

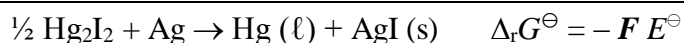
Standard potential of the galvanic cell



is a linear function of temperature. At the temperature of 25 °C the potential cell is 0.1928 V and at 40 °C it is 0.1956 V. If you know that the enthalpy of AgI formation is $-62.38 \text{ kJ mol}^{-1}$, calculate the enthalpy of Hg_2I_2 formation at 25 °C.

$$[\Delta_f H^\ominus (\text{Hg}_2\text{I}_2) = -98.3 \text{ kJ mol}^{-1}]$$

Solution:



$$E^\ominus = a + b T$$

$$T_1 = 298.15 \text{ K} \quad E_1^\ominus = 0.1928 \text{ V}$$

$$T_2 = 313.15 \text{ K} \quad E_2^\ominus = 0.1955 \text{ V}$$

$$\frac{dE^\ominus}{dT} = b = \frac{0.1956 - 0.1928}{313.15 - 298.15} = 1.867 \cdot 10^{-4} \text{ V K}^{-1}$$

$$\Delta_r S^\ominus = -\frac{d\Delta_r G^\ominus}{dT} = -(-z F \cdot \frac{dE^\ominus}{dT}) = 18.0138 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\begin{aligned} \Delta_r H_1^\ominus &= \Delta_r G_1^\ominus + T_1 \cdot \Delta_r S^\ominus = -F E_1^\ominus + T_1 \cdot F \cdot \left(\frac{dE^\ominus}{dT}\right) = 96485.3 \cdot (-0.1928 + 298.15 \cdot 1.867 \cdot 10^{-4}) \\ &= -13231.55 \text{ J mol}^{-1} \end{aligned}$$

$$\Delta_r H_1^\ominus = \Delta_f H^\ominus(\text{AgI}) - \frac{1}{2} \Delta_f H^\ominus(\text{Hg}_2\text{I}_2)$$

$$\Delta_f H^\ominus(\text{Hg}_2\text{I}_2) = 2 (\Delta_f H^\ominus(\text{AgI}) - \Delta_r H_1^\ominus) = 2 \cdot (-62.38 - (-13.232)) = -98.296 \text{ kJ mol}^{-1}$$