Problem 11-12 Thermodynamics of the cell

Standard potential of the galvanic cell

$$\ominus\ \mathrm{Ag(s)}\ |\ \mathrm{AgI(s)}\ |\ \mathrm{AgI}\ (\textit{saturated solution})\ |\ \mathrm{Hg_2I_2\,(s)}\ |\ \mathrm{Hg}(\ell)\ \oplus$$

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 kJ mol^{-1}, calculate the enthalpy of Hg_2I_2 formation at 25 °C.

[$\Delta_f H^\ominus$ (Hg_2I_2) = –98.3 kJ mol^{-1}]

Solution:

Left ⊖: $Ag + I^- \rightarrow AgI\ (s) + e$	$\Delta G^\ominus(Ag\|I^-\|AgI) = -\boldsymbol{F}\cdot E^\ominus(Ag\|I^-\|\ AgI)$	(z = 1)
Right ⊕: $\frac{1}{2}\ Hg_2I_2 + e \rightarrow Hg\ (\ell) + I^-$	$\Delta G^\ominus(Hg_2I_2\|I^-\|Hg) = -\boldsymbol{F}\cdot E^\ominus(\ Hg_2I_2\|I^-\|Hg)$	(z = 1)
$\frac{1}{2}\ Hg_2I_2 + Ag \rightarrow Hg\ (\ell) + AgI\ (s)$	$\Delta_r G^\ominus = -\ \boldsymbol{F}\ E^\ominus$	

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

$T_1 = 298.15$ K $E_1^\ominus = 0.1928$ V

$T_2 = 313.15$ K $E_2^\ominus = 0.1955$ V

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

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

$$\Delta_r H_1^\ominus = \Delta_r G_1^\ominus + T_1 \cdot \Delta_r S^\ominus = -\ \boldsymbol{F}\ E_1^\ominus + T_1 \cdot \boldsymbol{F} \cdot (\frac{dE^\ominus}{dT}) = 96485.3 \cdot (-0.1928 + 298.15 \cdot 1.867 \cdot 10^{-4})$$

$$= -13231.55\ \mathrm{J\ mol^{-1}}$$

$$\Delta_r H_1^\ominus = \Delta_f H^\ominus(AgI) - \tfrac{1}{2}\ \Delta_f H^\ominus(Hg_2I_2)$$

$$\Delta_f H^\ominus(Hg_2I_2) = 2\ (\Delta_f H^\ominus(AgI) - \Delta_r H_1^\ominus) = 2 \cdot (-62.38 - (-13.232)) = -98.296\ \mathrm{kJ\ mol^{-1}}$$