Problem 11-13 Thermodynamics of the cell

Temperature dependence of the potential of cell consisting of two metal wires, nickel and copper, immersed in a solution of cupric and nickel chloride, is expressed by the equation

$$E^{\ominus}(T) = 0.5999 - 4.034\cdot10^{-8}\cdot T - \frac{85.25}{T^2} \qquad \text{[V,K]} \ .$$

Write the equation occurring in this cell and calculate the reaction enthalpy at the temperature of 310 K. Further data needed for the calculation choose from the following values:

$E^{\ominus}(\mathrm{CuCl}\,|\,\mathrm{Cu/Cl^-}) = +0.137$ V
$E^{\ominus}(\mathrm{Cu^{2+}}|\mathrm{Cu}) = +\,0.337$ V
$E^{\ominus}(\mathrm{Cl_2}\,|\,\mathrm{Cl^-}) = 1.36$ V
$E^{\ominus}(\mathrm{Ni(OH)_2}\,|\,\mathrm{Ni/OH^-}) = -0.720$ V
$E^{\ominus}(\mathrm{Ni^{2+}}|\mathrm{Ni}) = -\,0.250$ V
$E^{\ominus}(\mathrm{O_2}\,|\,\mathrm{OH^-}) = +0.401$ V

[$\mathrm{CuCl_2 + Ni = Cu + NiCl_2}$ ($E^{\ominus} = E^{\ominus}(\mathrm{Cu^{2+}}|\mathrm{Cu}) - E^{\ominus}(\mathrm{Ni^{2+}}|\mathrm{Ni}) > 0$) , $\Delta_r H^{\ominus} = -\,115.45$ kJ mol^{-1}]

Solution:

$\mathrm{Cu^{2+}} + 2\,\mathrm{e} = \mathrm{Cu}$ $\quad E^{\ominus}(\mathrm{Cu^{2+}}|\mathrm{Cu}) = +\,0.337$ V
$\mathrm{Ni^{2+}} + 2\,\mathrm{e} = \mathrm{Ni}$ $\quad E^{\ominus}(\mathrm{Ni^{2+}}|\mathrm{Ni}) = -\,0.250$ V

Possibilities:

(1) $\mathrm{Ni^{2+}} + \mathrm{Cu} = \mathrm{Ni} + \mathrm{Cu^{2+}}$ $\quad E^{\ominus}(1) = E^{\ominus}(\mathrm{Ni^{2+}}|\mathrm{Ni}) - E^{\ominus}(\mathrm{Cu^{2+}}|\mathrm{Cu}) = -0.250 - 0.337 = -0.587$ V
(2) $\mathrm{Cu^{2+}} + \mathrm{Ni} = \mathrm{Cu} + \mathrm{Ni^{2+}}$ $\quad E^{\ominus}(2) = E^{\ominus}(\mathrm{Cu^{2+}}|\mathrm{Cu}) - E^{\ominus}(\mathrm{Ni^{2+}}|\mathrm{Ni}) = 0.337 - (-0.250) = 0.587$ V

$E^{\ominus}(2) = E^{\ominus}_{\mathrm{Cu^{2+}|Cu}} - E^{\ominus}_{\mathrm{Ni^{2+}|Ni}} > 0 \ \Rightarrow$ Reaction (2) is spontaneous

$$\Delta_r H^{\ominus} = \Delta_r G^{\ominus} + T\,\Delta_r S^{\ominus} = \Delta_r G^{\ominus} + T\left(-\frac{\partial \Delta_r G^{\ominus}}{\partial T}\right)_p = -z\,\boldsymbol{F}\,E^{\ominus} + T\cdot z\cdot\boldsymbol{F}\left(-\frac{\partial E^{\ominus}}{\partial T}\right)_p$$

$$= -\,2\cdot\boldsymbol{F}\cdot\left(0.5999 - 4.034\cdot10^{-8}\cdot T - \frac{85.25}{T^2}\right) + \ 2\cdot\boldsymbol{F}\cdot\left(+\,4.034\cdot10^{-8}\cdot T + T\cdot(-2)\cdot\frac{85.25}{T^3}\right)$$

$$= -\,2\cdot\boldsymbol{F}\cdot\left(0.5999 - 3\cdot\frac{85.25}{T^2}\right) = -\,2\cdot 96485.3\cdot 0.597239$$

$\Delta_r H^{\ominus} = -115249.5$ J mol^{-1}