

### 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

$$E^{\ominus}(T) = 0.5999 - 4.034 \cdot 10^{-8} \cdot T - \frac{85.25}{T^2} \quad [\text{V}, \text{K}] .$$

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:

$$E^{\ominus}(\text{CuCl} | \text{Cu} | \text{Cl}^-) = +0.137 \text{ V}$$

$$E^{\ominus}(\text{Ni}(\text{OH})_2 | \text{Ni} | \text{OH}^-) = -0.720 \text{ V}$$

$$E^{\ominus}(\text{Cu}^{2+} | \text{Cu}) = +0.337 \text{ V}$$

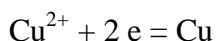
$$E^{\ominus}(\text{Ni}^{2+} | \text{Ni}) = -0.250 \text{ V}$$

$$E^{\ominus}(\text{Cl}_2 | \text{Cl}^-) = 1.36 \text{ V}$$

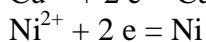
$$E^{\ominus}(\text{O}_2 | \text{OH}^-) = +0.401 \text{ V}$$

$$[\text{CuCl}_2 + \text{Ni} = \text{Cu} + \text{NiCl}_2 \quad (E^{\ominus} = E^{\ominus}(\text{Cu}^{2+} | \text{Cu}) - E^{\ominus}(\text{Ni}^{2+} | \text{Ni}) > 0), \Delta_r H^{\ominus} = -115.45 \text{ kJ mol}^{-1}]$$

Solution:

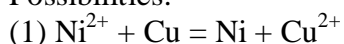


$$E^{\ominus}(\text{Cu}^{2+} | \text{Cu}) = +0.337 \text{ V}$$

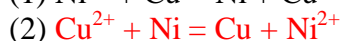


$$E^{\ominus}(\text{Ni}^{2+} | \text{Ni}) = -0.250 \text{ V}$$

Possibilities:



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



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

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

$$\begin{aligned} \Delta_r H^{\ominus} &= \Delta_r G^{\ominus} + T \Delta_r S^{\ominus} = \Delta_r G^{\ominus} + T \left( -\frac{\partial \Delta_r G^{\ominus}}{\partial T} \right)_p = -z F E^{\ominus} + T \cdot z F \left( -\frac{\partial E^{\ominus}}{\partial T} \right)_p \\ &= -2 \cdot F \cdot \left( 0.5999 - 4.034 \cdot 10^{-8} \cdot T - \frac{85.25}{T^2} \right) + 2 \cdot F \cdot \left( +4.034 \cdot 10^{-8} \cdot T + T \cdot (-2) \cdot \frac{85.25}{T^3} \right) \\ &= -2 \cdot F \cdot \left( 0.5999 - 3 \cdot \frac{85.25}{T^2} \right) = -2 \cdot 96485.3 \cdot 0.597239 \end{aligned}$$

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