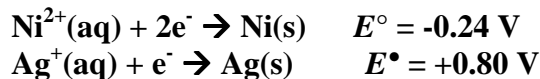
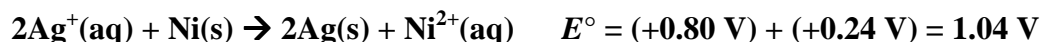


- A galvanic cell is made of a Ni^{2+}/Ni half cell with $[\text{Ni}^{2+}] = 1.00 \times 10^{-3} \text{ M}$ and a Ag^+/Ag half cell with $[\text{Ag}^+] = 5.00 \times 10^{-2} \text{ M}$. Calculate the electromotive force of the cell at 25°C .

The reduction potentials for the two half cells are (from the data sheet):



The $\text{Ni}^{2+}(\text{aq}) / \text{Ni}(\text{s})$ cell has the lower electrode potential and it is the one that is reversed. Hence, the cell reaction and the standard cell potential are



At non-standard concentrations, the electrode potential is given by the Nernst equation:

$$E = E^\circ - \frac{RT}{nF} \ln Q$$

For this two electron reduction, $n = 2$ and $Q = \frac{[\text{Ni}^{2+}(\text{aq})]}{[\text{Ag}^+(\text{aq})]^2}$

$[\text{Ni}^{2+}(\text{aq})] = 1.00 \times 10^{-3} \text{ M}$ and $[\text{Ag}^+(\text{aq})] = 5.00 \times 10^{-2} \text{ M}$. Hence, at $T = 25^\circ\text{C} = (25 + 273) \text{ K} = 298 \text{ K}$:

$$E = (1.04 \text{ V}) - \frac{(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(298 \text{ K})}{(2 \times 96485 \text{ C mol}^{-1})} \ln\left(\frac{1.00 \times 10^{-3}}{(5.00 \times 10^{-2})^2}\right) = 1.06 \text{ V}$$

Answer: **1.06 V**

Calculate the equilibrium constant of the reaction at 25°C .

The equilibrium constant is related to the standard electrode potential:

$$E^\circ = \frac{RT}{nF} \ln K$$

Hence, with $E^\circ = 1.04 \text{ V}$ and $n = 2$:

$$\ln K = E^\circ \times \frac{nF}{RT} = (1.04 \text{ V}) \times \frac{(2 \times 96485 \text{ C mol}^{-1})}{(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(298 \text{ K})} = 81.0$$

so,

$$K = 1.51 \times 10^{35}$$

Answer: **1.51×10^{35}**

ANSWER CONTINUES ON THE NEXT PAGE

Calculate the standard free energy change of the reaction at 25 °C.

The standard free energy change, ΔG° , is related to the standard electrode potential, E° :

$$\begin{aligned}\Delta G^\circ &= -nFE^\circ \\ &= -(2) \times (96485 \text{ C mol}^{-1}) \times (1.04 \text{ V}) = -201000 \text{ J mol}^{-1} = 201 \text{ kJ mol}^{-1}\end{aligned}$$

Alternatively, the free energy change is related to the equilibrium constant, K :

$$\begin{aligned}\Delta G^\circ &= -RT \ln K \\ &= -(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K}) \times (1.51 \times 10^{35}) = -201 \text{ kJ mol}^{-1}\end{aligned}$$

Answer: **-201 kJ mol⁻¹**

Indicate whether the reaction is spontaneous or not. Give reasons for your answer.

- $E^\circ > 0$ so the reaction is spontaneous.
- $\Delta G^\circ < 0$ so the reaction is spontaneous.
- K is much greater than 1 so the reaction is spontaneous.

Express the overall reaction in the shorthand voltaic cell notation.

