Marks 6

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

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

$$Ni^{2+}(aq) + 2e^{-} \rightarrow Ni(s) \qquad E° = -0.24 \text{ V}$$
$$Ag^{+}(aq) + e^{-} \rightarrow Ag(s) \qquad E° = +0.80 \text{ V}$$

The Ni^{2+}(aq) / Ni(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

$$2Ag^{+}(aq) + Ni(s) \rightarrow 2Ag(s) + Ni^{2+}(aq) \qquad E° = (+0.80 \text{ V}) + (+0.24 \text{ V}) = 1.04 \text{ V}$$

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

$$E = E° - \frac{RT}{nF} \ln Q$$

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

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

$$E° = \frac{RT}{nF} \ln K$$

Hence, with $E°$ = 1.04 V and n = 2:

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

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, $\Delta G°$, is related to the standard electrode potential, $E°$:

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

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

$$\Delta G° = -RTlnK$$
$$= -(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K}) \times (1.51 \times 10^{35}) = -201 \text{ kJ mol}^{-1}$$

Answer: **-201 kJ mol^{-1}**

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

- **$E° > 0$ so the reaction is spontaneous.**
- **$\Delta G° < 0$ 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.

$Ni(s) | Ni^{2+}(aq) || Ag^{+}(aq) | Ag(s)$