Marks 5

- A galvanic cell consists of a Ni^{2+}/Ni half cell with $[Ni^{2+}] = 1.00$ M, and a Ag^{+}/Ag half cell with $[Ag^{+}] = 1.00$ M. Calculate the electromotive force of the cell at 25 °C.

As the concentrations of Ni^{2+} and Ag^{+} are both 1.00 M, the 'electromotive force' (i.e. the cell potential) refers to standard potentials. The two half-cell reactions and standard reduction potentials are:

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

The least positive (Ni^{2+}/Ni) cell is reversed – Ni is oxidized in this reaction and Cu^{2+} is reduced. This gives the overall reaction and potential:

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

Answer: +**1.04 V**

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

The equilibrium constant K and the standard cell potential are related by,

$$E° = \frac{RT}{nF} \ln K$$

The reaction involves two electrons, $n = 2$, and so at $T = 25$ °C,

$$+1.04 = \frac{8.314 \times (25+273)}{2 \times 96485} \ln K$$

$$\ln K = 81 \text{ or } K = e^{81} = 1.5 \times 10^{35}$$

Answer: **1.5×10^{35}**

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

The standard free energy change is directly related to the standard cell potential, $\Delta G° = -nFE°$,

$$\Delta G° = -2 \times 96485 \times 1.04 = -201 \text{ kJ mol}^{-1}$$

Alternatively, the standard free energy change is related to the equilibrium constant by $\Delta G° = -RT\ln K$,

$$\Delta G° = -(8.314) \times (25 + 273) \times \ln(1.5 \times 10^{35}) = -2.0 \times 10^{2} \text{ kJ mol}^{-1}$$

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

ANSWER CONTINUES ON THE NEXT PAGE

Is the reaction spontaneous? Give reasons for your answer.

As $E° > 0$, or, equivalently, as $\Delta G° < 0$, the reaction is spontaneous (2nd Law of Thermodynamics).

Express the overall reaction in the shorthand voltaic cell notation.

The oxidation half cell (the anode) is written on the left and the reduction half cell (the cathode) is written on the right. The two half-cells are connected by a salt bridge:

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