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Marks • A galvanic cell is made of a Zn^{2+}/Zn half cell with $[Zn^{2+}] = 2.0$ M and an Ag⁺/Ag half cell with $[Ag^{+}] = 0.050$ M. Calculate the electromotive force of the cell at 25 °C.

The standard reduction reactions and potentials for the two half cells are:

$$Zn^{2+}(aq) + 2e^{-} \rightarrow Zn(s) \qquad E^{\circ} = -0.76 V$$

Ag⁺(aq) + e⁻ \rightarrow Ag(s)
$$E^{\circ} = +0.80 V$$

The least positive (Zn^{2+}/Zn) couple is reversed giving the overall reaction:

$$Zn(s) + 2Ag^{+}(aq) \rightarrow Zn^{2+}(aq) + 2Ag(s)$$
 $E^{\circ} = (+0.76 \text{ V}) + (0.80) = 1.56 \text{ V}$

As non-standard concentrations are used, the cell potential is calculated using the Nernst equation. The reaction involves the transfer of $2e^{-1}$ so with n = 2 this becomes:

$$E = E^{\circ} - \frac{RT}{nF} \ln Q = E^{\circ} - \frac{RT}{nF} \ln \left(\frac{[\text{Zn}^{2+}(\text{aq})]}{[\text{Ag}^{+}(\text{aq})]^{2}} \right)$$

= (+1.56 V) - $-\frac{(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(298 \text{ K})}{(2 \times 96485 \text{ C mol}^{-1})} \ln \left(\frac{2.0}{0.050^{2}} \right) = +1.47 \text{ V}$
Answer: +1.47 V

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

The equilibrium constant is related to the standard cell potential:

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

Hence,

$$\ln K = E^{\circ} \times \frac{nF}{RT} = (1.56 \text{ V}) \times \frac{(2 \times 96485 \text{ C mol}^{-1})}{(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(298 \text{ K})} = 121.5$$
$$K = 5.9 \times 10^{52}$$

Answer: $K = 5.9 \times 10^{52}$

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

Using
$$\Delta G^{\circ} = nFE^{\circ}$$
:
 $\Delta G^{\circ} = -(2 \times 96485 \text{ C mol}^{-1}) \times (+1.56 \text{ V}) = -301 \text{ kJ mol}^{-1}$
Answer: -301 kJ mol⁻¹

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

As E > 0, $\Delta G^{\circ} < 0$ and K is very large: the reaction is spontaneous.

Express the overall reaction in the shorthand voltaic cell notation.

$Zn(s) | Zn^{2+}(aq) (2.0 M) | | Ag^{+}(aq) (0.050 M) | Ag(s)$