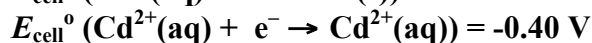
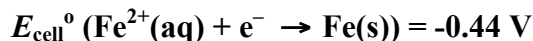


- An electrochemical cell consists of 1.0 L half-cells of Fe/Fe²⁺ and Cd/Cd²⁺ with the following initial concentrations: [Fe²⁺] = 0.800 M, [Cd²⁺] = 0.200 M.

Marks
8

What is the initial E_{cell} at 25 °C?

From the reduction potential table,



The Fe²⁺/Fe half cell has the more negative reduction potential so it is the half cell that is turned around to act as the oxidation half cell: $E_{\text{cell}}^{\circ} (\text{Fe}(\text{s}) \rightarrow \text{Fe}^{2+}(\text{aq}) + \text{e}^{-}) = +0.44 \text{ V}$

In combination with the Cd²⁺/Cd reduction half cell, this gives an overall reaction and cell potential of:



For this reaction with [Fe²⁺(aq)] = 0.800 M and [Cd²⁺(aq)] = 0.200 M:

$$Q = \frac{[\text{Fe}^{2+}(\text{aq})]}{[\text{Cd}^{2+}(\text{aq})]} = \frac{0.800}{0.200}$$

For the 2e⁻ reaction, the Nernst equation gives the cell potential as:

$$\begin{aligned} E_{\text{cell}} &= E^{\circ} - \frac{RT}{nF} \ln Q \\ &= (0.04 \text{ V}) - \frac{(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(298 \text{ K})}{(2 \times 96485 \text{ C mol}^{-1})} \ln \frac{0.800}{0.200} = +0.02 \text{ V} \end{aligned}$$

Answer: +0.02 V

What is E_{cell} when [Cd²⁺] reaches 0.15 M?

[Cd²⁺(aq)] has decreased from 0.200 M to 0.15 M: a change of 0.05 M. [Fe²⁺(aq)] will increase by the same amount: [Fe²⁺(aq)] = (0.800 + 0.05) M = 0.85 M. Using the Nernst equation again gives:

$$\begin{aligned} E_{\text{cell}} &= E^{\circ} - \frac{RT}{nF} \ln Q \\ &= (0.04 \text{ V}) - \frac{(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(298 \text{ K})}{(2 \times 96485 \text{ C mol}^{-1})} \ln \frac{0.85}{0.15} = +0.02 \text{ V} \end{aligned}$$

Answer: +0.02 V

ANSWER CONTINUES ON THE NEXT PAGE

What is $[\text{Cd}^{2+}]$ when E_{cell} reaches 0.015 V?

$$E_{\text{cell}} = (0.04 \text{ V}) - \frac{(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(298 \text{ K})}{(2 \times 96485 \text{ C mol}^{-1})} \ln \frac{[\text{Fe}^{2+}(\text{aq})]}{[\text{Cd}^{2+}(\text{aq})]} = +0.015 \text{ V}$$

so:

$$\frac{[\text{Fe}^{2+}(\text{aq})]}{[\text{Cd}^{2+}(\text{aq})]} = 7.0$$

If the change from the initial concentrations is x , $[\text{Cd}^{2+}(\text{aq})] = (0.200 - x) \text{ M}$ and $[\text{Fe}^{2+}(\text{aq})] = (0.800 + x) \text{ M}$:

$$\frac{0.800 - x}{0.200 + x} = 7.0 \quad x = -0.075 \text{ M}$$

So that $[\text{Cd}^{2+}(\text{aq})] = (0.200 - 0.075) \text{ M} = 0.125 \text{ M}$.

Answer: **0.125 M**

What are the equilibrium concentrations of both ions?

Using $E^{\circ} = \frac{RT}{nF} \ln K = 0.04 \text{ V}$ gives $K = 22.5$

so:

$$\frac{[\text{Fe}^{2+}(\text{aq})]}{[\text{Cd}^{2+}(\text{aq})]} = 22.5$$

If the change from the initial concentrations is x , $[\text{Cd}^{2+}(\text{aq})] = (0.200 - x) \text{ M}$ and $[\text{Fe}^{2+}(\text{aq})] = (0.800 + x) \text{ M}$:

$$\frac{0.800 - x}{0.200 + x} = 22.5 \quad x = 0.158 \text{ M}$$

So that $[\text{Cd}^{2+}(\text{aq})] = (0.200 - 0.158) \text{ M} = 0.042 \text{ M}$ and $[\text{Fe}^{2+}(\text{aq})] = (0.800 + 0.158) \text{ M} = 0.958 \text{ M}$

$[\text{Cd}^{2+}] = 0.042 \text{ M}$

$[\text{Fe}^{2+}] = 0.958 \text{ M}$