Marks 8

- An electrochemical cell is consists of 1.0 L half-cells of Fe/Fe^{2+} and Cd/Cd^{2+} with the following initial concentrations: $[Fe^{2+}]$ = 0.800 M, $[Cd^{2+}]$ = 0.200 M.

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

From the reduction potential table,

$$E_{cell}^{o}\ (Fe^{2+}(aq) + e^{-} \rightarrow Fe(s)) = -0.44\ V$$
$$E_{cell}^{o}\ (Cd^{2+}(aq) + e^{-} \rightarrow Cd^{2+}(aq)) = -0.40\ V$$

The Fe^{2+}/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_{cell}^{o} (Fe(s) → Fe^{2+}(aq) + e^{-}) = +0.44 V

In combination with the Cd^{2+}/Cd reduction half cell, this gives an overall reaction and cell potential of:

$$Fe(s) + Cd^{2+}(aq) \rightarrow Fe^{2+}(aq) + Cd(s) \qquad E^{o} = ((+0.44) + (-0.40))\ V = +0.04\ V$$

For this reaction with $[Fe^{2+}(aq)]$ = 0.800 M and $[Cd^{2+}(aq)]$ = 0.200 M:

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

For the $2e^{-}$ reaction, the Nernst equation gives the cell potential as:

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

Answer: **+0.02 V**

What is E_{cell} when $[Cd^{2+}]$ reaches 0.15 M?

$[Cd^{2+}(aq)]$ has decreased from 0.200 M to 0.15 M: a change of 0.05 M. $[Fe^{2+}(aq)]$ will increase by the same amount: $[Fe^{2+}(aq)]$ = (0.800 + 0.05) M = 0.85 M. Using the Nernst equation again gives:

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

Answer: **+0.02 V**

ANSWER CONTINUES ON THE NEXT PAGE

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

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

so:

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

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

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

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

Answer: **0.125 M**

What are the equilibrium concentrations of both ions?

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

so:

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

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

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

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

$[Cd^{2+}] = 0.042$ M	**$[Fe^{2+}] = 0.958$ M**