

Marks
6

- The solubility product constant of AgCl is $K_{sp} = 1.8 \times 10^{-10} \text{ M}^2$. Using the relevant electrode potentials found on the data page, calculate the reduction potential at 298 K of a half-cell formed by:
 - an Ag electrode immersed in a saturated solution of AgCl.

The standard electrode potential for $\text{Ag}^+(\text{aq}) + \text{e}^- \rightarrow \text{Ag}(\text{s})$ is $E^\circ = +0.80 \text{ V}$. This refers to the potential with $[\text{Ag}^+(\text{aq})] = 1 \text{ M}$.

For the dissolution of $\text{AgCl}(\text{s}) \rightleftharpoons \text{Ag}^+(\text{aq}) + \text{Cl}^-(\text{aq})$, $K_{sp} = [\text{Ag}^+(\text{aq})][\text{Cl}^-(\text{aq})]$. As $[\text{Ag}^+(\text{aq})] = [\text{Cl}^-(\text{aq})]$,

$$[\text{Ag}^+(\text{aq})] = \sqrt{K_{sp}} = \sqrt{1.8 \times 10^{-10}} = 1.3 \times 10^{-5} \text{ M}$$

Using the Nernst equation, the cell potential at 298 K (25 °C) is,

$$E = E^\circ - \frac{0.0592}{n} \log Q$$

The $\text{Ag}^+(\text{aq}) + \text{e}^- \rightarrow \text{Ag}(\text{s})$ half cell involves one electron and so $n = 1$. The reaction quotient is $\frac{1}{[\text{Ag}^+(\text{aq})]}$. Hence,

$$E = (+0.80) - \frac{0.0592}{1} \log \left(\frac{1}{1.3 \times 10^{-5}} \right) = +0.52 \text{ V}$$

Answer: $E = +0.52 \text{ V}$

- an Ag electrode immersed in a 0.5 M solution of KCl containing some AgCl precipitate.

$[\text{Cl}^-(\text{aq})] = 0.5 \text{ M}$ and as $K_{sp} = [\text{Ag}^+(\text{aq})][\text{Cl}^-(\text{aq})]$,

$$[\text{Ag}^+(\text{aq})] = \frac{K_{sp}}{[\text{Cl}^-(\text{aq})]} = \frac{1.8 \times 10^{-10} \text{ M}^2}{0.5 \text{ M}} = 3.6 \times 10^{-10} \text{ M}$$

The electrode potential is now,

$$E = (+0.80) - \frac{0.0592}{1} \log \left(\frac{1}{3.6 \times 10^{-10}} \right) = +0.24 \text{ V}$$

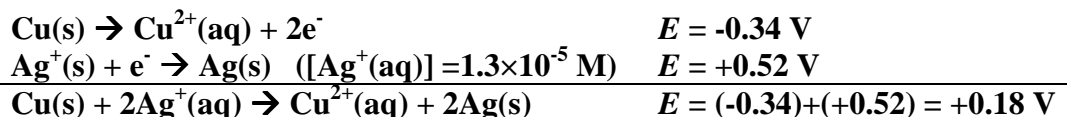
Answer: $E^\circ = +0.24 \text{ V}$

ANSWER CONTINUES ON THE NEXT PAGE

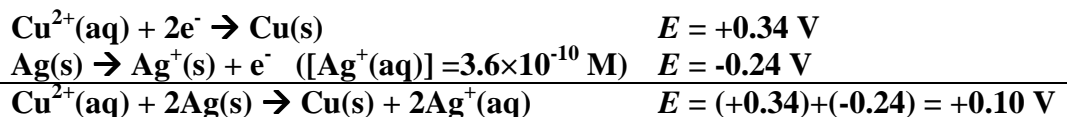
Each of these half-cells is connected to a standard $\text{Cu}^{2+}(1\text{ M})/\text{Cu}(\text{s})$ half-cell. In which half-cell, (a) or (b), will clear evidence of a reaction be seen? Describe the change(s) observed.

For the $\text{Cu}^{2+}(1\text{ M})/\text{Cu}(\text{s})$ half cell, the reduction potential is $E^\circ = +0.34\text{ V}$.

If the half cell is combined with half cell (a), the former has the least positive cell potential and is reversed:



If the half cell is combined with half cell (b), the latter has the least positive cell potential and is reversed:



Although both reactions have $E > 0\text{ V}$ and so are spontaneous, only the second reaction will give clear evidence of a reaction. The $\text{Ag}^+(\text{aq})$ ions produced will react with the excess $\text{Cl}^-(\text{aq})$ present to give a white precipitate of AgCl around the electrode