Marks 6

- The solubility product constant of AgCl is $K_{sp} = 1.8 \times 10^{-10}$ 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:
  (a) an Ag electrode immersed in a saturated solution of AgCl.

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

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

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

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

$$E = E° - \frac{0.0592}{n}\log Q$$

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

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

Answer: $E = +0.52$ **V**

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

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

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

The electrode potential is now,

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

Answer: $E° = +0.24$ **V**

ANSWER CONTINUES ON THE NEXT PAGE

Each of these half-cells is connected to a standard Cu^{2+}(1 M)/Cu(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 Cu^{2+} (1 M)/Cu(s) half cell, the reduction potential is $E°$ = +0.34 V.

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

$Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$	E = -0.34 V
$Ag^+(s) + e^- \rightarrow Ag(s)$ ($[Ag^+(aq)] = 1.3 \times 10^{-5}$ M)	E = +0.52 V
$Cu(s) + 2Ag^+(aq) \rightarrow Cu^{2+}(aq) + 2Ag(s)$	E = (-0.34)+(+0.52) = +0.18 V

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

$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$	E = +0.34 V
$Ag(s) \rightarrow Ag^+(s) + e^-$ ($[Ag^+(aq)] = 3.6 \times 10^{-10}$ M)	E = -0.24 V
$Cu^{2+}(aq) + 2Ag(s) \rightarrow Cu(s) + 2Ag^+(aq)$	E = (+0.34)+(-0.24) = +0.10 V

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