Worksheet – Electrolytic Cells

Electrolytic cells are non-spontaneous. They require a power supply to proceed. Oxidation still takes place at the anode and reduction at the cathode, but the flow of electrons comes from a power supply.

Use the following half-reactions to set up a standard galvanic and an electrolytic cell.

\[ \text{Pb}^{2+} + 2e^- \rightarrow \text{Pb} \text{ (s)} \quad \xi^o = 0.34 \text{ V} \]
\[ \text{Cu}^+ + e^- \rightarrow \text{Cu} \text{ (s)} \quad \xi^o = 0.52 \text{ V} \]

Galvanic cell

\[ \text{Pb} \rightarrow \text{Pb}^{2+} + 2e^- \quad 2(\text{Cu}^+ + e^- \rightarrow \text{Cu}) \]
\[ \xi^o = 1.52 - 0.34 = 1.18 \text{ V} \]

Electrolytic cell

\[ \text{Cu} \rightarrow \text{Cu}^+ + e^- \quad \text{Pb}^{2+} + 2e^- \rightarrow \text{Pb} \]
\[ \xi^o = 0.34 - 0.52 = -0.18 \text{ V} \]

Label the electrodes, solutions, flow of electrons, flow of ions half-reactions and cell potential in each diagram.

1. Calculate the \( \Delta G^o \) and \( K \) (at 298 K) for the cell in which \( \text{Pb}^{2+} \) is reduced and \( \text{Cu} \) is oxidized.

\[
\Delta G^o = nRT \xi^o = -2 \times 298 \times 0.18 = 34.7 \text{ kJ}
\]

\[
\ln K = \frac{-34.7}{298} = 8.27 \times 10^{-7}
\]

2. Calculate the potential of the galvanic cell (298 K) when the \([\text{Cu}^+]\) is 15 times greater than the \([\text{Pb}^{2+}]\).

\[
Q = \frac{[\text{Pb}^{2+}]}{[\text{Cu}^+]} = \left(\frac{1}{15}\right)^2 = 0.00444
\]

\[
\xi = \frac{RT}{nF} \ln Q = 0.18 - (8.314 \times 10^{-3})(298) \ln 0.00444
\]

\[
\xi = 0.25 \text{ V}
\]
The electrons for the half-reaction in the electrolytic cell are provided by the power supply. The rate of delivery of charge is given by its \textbf{amperage} (A), which has the units of charge (coulombs) per second.

\text{amperage (C/s) x time (s) = coulombs}
\text{coulombs ÷ 96,500 C/mol e}^{-} (F) = \text{moles of e}^{-}
\text{moles of e}^{-} ÷ n (\text{mol e}^{-}/\text{mol product}) = \text{moles of product}
\text{moles of product x molar mass (g product/mol prod) = grams of product}

3. Determine the number of grams of Pb deposited at the cathode if the electrolytic cell is run at 5 amps for 1 minute (\text{mw Pb} = 207.2 \text{ g/mol})

\[
\frac{5 \text{ A}}{\frac{1 \text{ min}}{1 \text{ min}}} \times \frac{60 \text{ sec}}{1 \text{ min}} \times \frac{1 \text{ mol e}^{-}}{1 \text{ mol Pb}} \times 207.2 \text{ g Pb} = 322 \text{ g Pb}
\]

4. Sketch a cell for the electroplating of a copper medal with gold, for Lindsey Vonn's Olympic victory in the downhill in Vancouver. You will need only one compartment, a battery, a bar of gold and the copper medal.

Which metal will be your anode, your cathode? What solution will you need? How will you hook up your battery? Indicate the flow of electrons, and the reactions at the anode and cathode.

5. How long must a current of 2.5 amps be applied to the solution of Au\textsuperscript{+} ions to plate out 3 grams of gold on the metal? (\text{mw Au} = 197.0).

\[
3 \text{ g Au} \times \frac{1 \text{ mol Au}}{197 \text{ g Au}} \times \frac{1 \text{ mol e}^{-}}{1 \text{ mol Au}} \times \frac{96,500 \text{ C}}{1 \text{ mol e}^{-}} = 1470 \text{ C} \times \frac{1 \text{ min}}{2.5 \text{ C}} = 588 \text{ s} \times \frac{1 \text{ min}}{60 \text{ s}} = 9.8 \text{ min}
\]
6. An aqueous solution of a platinum chloride salt is electrolyzed by passing a current of 2.50 amperes for 2.00 hours. As a result, 9.09 g of metallic platinum are deposited at the cathode. (mw Pt = 195 g/mol)

What is the formula of the platinum salt?

\[
\frac{2.5 \text{CU}}{5} \times 2 \text{hr} \times \frac{60 \text{min}}{1 \text{hr}} \times \frac{60 \text{s}}{1 \text{min}} = 18000 \text{C} \times \frac{1 \text{mole}}{96500 \text{C}} = 0.187 \text{mole}
\]

\[
9.09 \text{g Pt} \times \frac{1 \text{mole}}{195 \text{g Pt}} = 0.0466 \text{mole Pt}
\]

\[
\frac{0.187 \text{mole}}{0.0466 \text{mole Pt}} = 4
\]

\[
\text{Pt}^{4+} + 1 \text{m}
\]