ELECTROLYTIC CELLS

Predicting the equation for electrolytic cells is dependant on the type of electrolyte and electrode used.

**Molten Electrolyte**

When a molten Electrolyte is used there are only two chemicals in the cell therefore the reactions are easy to predict.

**Example 1:** A cell which contains molten Sodium Chloride. Only Na⁺ and Cl⁻ are present.

\[
\begin{align*}
\text{Cl}_2 + 2e^- & \rightarrow 2\text{Cl}^- \\
\text{Na}^+ + e^- & \rightarrow \text{Na}
\end{align*}
\]

**Aqueous Electrolyte**

There are two different types of cells with an Aqueous Electrolyte

**Inert Electrodes**

Inert electrodes are those that do not react such as carbon, platinum and graphite. Remember the following:

1. Circle all chemicals present. Be careful to ensure you consider the chemicals form such as ions.
2. The chemicals on the left hand side are considered first. The one highest up will be involved in the reaction. It will go forward. It is reduction and occurs at the cathode.
3. The chemicals on the right hand side are then considered. The equation closest to the reduction reaction will occur. It will go backwards.

**Example 1:** Predict the reactions occurring in an electrolytic cell with CuSO₄ and graphite electrodes

\[
\begin{align*}
\text{O}_2(g) + 4\text{H}^+ + 4e^- & \leftrightarrow 2\text{H}_2\text{O} \\
\text{Cu}^{2+} + 2e^- & \leftrightarrow \text{Cu} \\
\text{SO}_4^{2-} (\text{aq}) + 4\text{H}^+ + 2e^- & \leftrightarrow \text{SO}_2 + 2\text{H}_2\text{O} \\
2\text{H}_2\text{O} (1) + 2e^- & \leftrightarrow \text{H}_2 + 2\text{OH}^- 
\end{align*}
\]

The reaction will involve the top equation and the one with the copper ions

**Active Electrodes**

Consider the same cell as used in the previous example but this time copper electrodes are used.

\[
\begin{align*}
\text{O}_2 + 4\text{H}^+ + 4e^- & \leftrightarrow 2\text{H}_2\text{O} \\
\rightarrow \text{Cu}^{2+} + 2e^- & \leftrightarrow \text{Cu(s)} \\
\text{SO}_4^{2-} + 4\text{H}^+ + 2e^- & \leftrightarrow \text{SO}_2 + 2\text{H}_2\text{O} \\
2\text{H}_2\text{O} + 2e^- & \leftrightarrow \text{H}_2 + 2\text{OH}^- 
\end{align*}
\]

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The top reaction on the left hand side involves copper ions. The one on the right hand side that is closest involves copper solid. Both copper reactions are going to be involved in the reaction.

Mixture of Aqueous solutions with inert electrodes

Consider a cell containing a mixture of solutions as Cu$^{2+}$, Ni$^{2+}$ and Al$^{3+}$ with inert electrodes. What is the reaction at the cathode?

\[
\begin{align*}
\text{Cu}^{2+} + 2e^- & \leftrightarrow \text{Cu} \\
\text{Ni}^{2+} + 2e^- & \leftrightarrow \text{Ni} \\
2\text{H}_2\text{O}(l) + 2e^- & \leftrightarrow \text{H}_2(g) + 2\text{OH}^- \\
\text{Al}^{3+}(aq) + 3e^- & \leftrightarrow \text{Al}(s)
\end{align*}
\]

The reaction that is highest up on the right hand side is the Copper and therefore will be involved in the reaction.