**Electrolytic Cell (Electrolysis) Basics**

**Electrolysis** is a process that produces a non-spontaneous redox reaction by the passage of electrical energy from a power supply through a conducting liquid (electrolyte).

An **electrolytic cell** is an electrochemical cell where electrolysis occurs.

* During electrolysis, a reaction occurs at both electrodes and the energy for this is provided by the power source.
* The electrode connected to the negative terminal of the power supply is the negative electrode; the electrode connected to the positive terminal of the power supply is the positive electrode.
* During electrolysis, reduction occurs at the negative electrode and oxidation occurs at the positive electrode (this is the opposite of a galvanic cell).
* As with all electrochemical cells, the electrode where oxidation occurs is called the anode, and the electrode where reduction occurs is called the cathode.
* Unlike galvanic cells, there is no need to locate the electrodes in separate containers because a non-spontaneous reaction is involved.
* The products need to be kept apart as they are formed because they react spontaneously if in contact with each other and reform the original reactants.

**Predicting the redox reaction during the electrolysis of aqueous solutions**

In aqueous solutions, there is a mixture of at least two oxidising agents and two reducing agents. If non-inert electrodes are used, then even more possibilities may exist.

Which oxidising agent and which reducing agent will react?

Although electrolytic products depend on several factors, the following procedure is useful.

1. List the species present, including all metals that are used as electrodes.

2. Write the reduction half-equations involving these species in descending order of E. (or refer to the reduction potentials table)

3. Circle the species present in the electrolytic cell that could participate.

4. Select the oxidising agent with the highest EO(the strongest oxidising agent). This will be reduced at the cathode since it requires less energy for reduction than an oxidising agent with a lower Eo.

5. Select the reducing agent with the lowest E (the strongest reducing agent). This will be oxidised at the anode since it requires less energy for oxidation than a reducing agent with a higher Eo.

6. Write the overall equation, and calculate the EMF (it should be negative)

**Electrolytic Cell Examples**

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| http://schoolbag.info/chemistry/mcat_2/mcat_2.files/image653.jpg | **Electrolysis of Molten Ionic Compound (inert electrodes)**  Example: molten sodium chloride NaCl (l)  Anode: 2Cl- (l) 🡪Cl2 (g) + 2e- Eo = -1.36V  Cathode: Na+ (l) + e- 🡪 Na (l) Eo = -2.71V  Redox:  2Na+(l) + 2Cl-(g) 🡪 2Na(l) + Cl2  emf = -4.07V  Both ions are involved in the reaction |
| **Warning:** If conditions are not standard other reactions may occur, Cl2 (a toxic gas) is a common product at the anode. | **Electrolysis of an Aqueous Solution (inert electrodes)**  **Example: 1 mol L-1 sodium chloride solution**  **Anode**  Possible reducing agents: H2O(l), Cl-(aq)  2H2O(*l*)🡪 O2(g)+ 4H+(aq) + 4e- Eo = -1.23V   * O2(g) not Cl2(g) forms at the anode as H2O (l) is a stronger reducing agent than Cl -(aq)   **Cathode:**  Possible oxidising agents: H2O (l), Na+ (aq)    2H2O(*l*) + 2e− 🡪 H2(*g*) + 2OH-(*aq*) Eo = -0.83V   * H2(g) not Na(s) forms at the cathode as H2O(l) is a stronger oxidising agent than Na+(aq)   Redox:  2H2O(l) 🡪 O2(g) + 2H2(g) emf = -2.06V |
| Image result for electrolysis of copper sulfate | **Electrolysis of an Aqueous Solution (inert electrodes)**  **Example: 1 mol -1 copper (II) sulfate solution**  **Anode**  Possible reducing agents: H2O(l), SO4-(aq)  2H2O(*l*)🡪 O2(g)+ 4H+(aq) + 4e- Eo = -1.23V   * The SO42- ion is very stable in redox reactions as it is already highly oxidised.   **Cathode:**  Possible oxidising agents: H2O(l), Cu2+(aq)    Cu2+(aq) + 2e- 🡪 Cu(s) Eo = +0.34V   * Cu(s) is produced at the cathode as the Cu2+ ion is a stronger oxidising agent than H2O(aq)   **Redox:**  2Cu2+(aq) + 2H2O(*l*) **🡪** 2Cu(s) + O2(g)+ 4H+(aq) Eo = -0.89V |
| Image result for copper sulfate electrolysis | **Electrolysis of an Aqueous Solution (reactive electrodes)**  **Example: 1 mol -1 copper (II) sulfate solution**  **(with copper electrodes)**  **Anode**  Possible reducing agents: H2O(l), SO42-(aq), Cu(s)  Cu(s) 🡪 Cu2+  + 2e Eo = -0.34V   * Cu2+(aq) ions are produced at the anode as Cu(s) is a stronger reducing agent than H2O(aq) and SO42-   **Cathode:**  Possible oxidising agents: H2O(l), Cu2+(aq)    Cu2+(aq) + 2e- 🡪 Cu(s) Eo = +0.34V   * Cu(s) is produced at the cathode as the Cu2+ ion is a stronger oxidising agent than H2O(aq)   Cell emf = 0.00V (still not spontaneous) |
| **Industry Application (Electroplating)**   * **Coating a metallic object in a metallic layer** * **A sacrificial anode of the coating metal in an electrolyte of its ions, with the object to be coated placed as the cathode**   Image result for electroplating copper | **Industry Application (Electrorefining)**   * **Purifying and impure metal** * **Impure metal as the anode, collection plate as the cathode.** |

**Important**

The standard reduction potential tables are a very useful tool for predicting the products of an electrolysis reaction. It must be remembered, however, that it is based on standard conditions where the concentrations of dissolved species are 1 mol -1. If the concentrations of potential reactants are different from this, the observed results might be different from those predicted:

For Example:

The standard reduction potential tables predict that the electrolysis of a 1 mol-1 NaCl (aq) under standard conditions solution results in the formation of hydrogen and oxygen (as shown above). However, if conditions are not standard (such as a more concentrated NaCl solution), chlorine gas is produced at the anode rather than oxygen. The production of chlorine during the electrolysis of an aqueous NaCl solution is very common.

The overall reaction becomes:

2H2O(l) + 2Cl– (aq) 🡪 H2(g) + Cl2(g) + 2OH–(aq)