

ELECTROLYSIS

Electrolysis and Electrolytic Cells

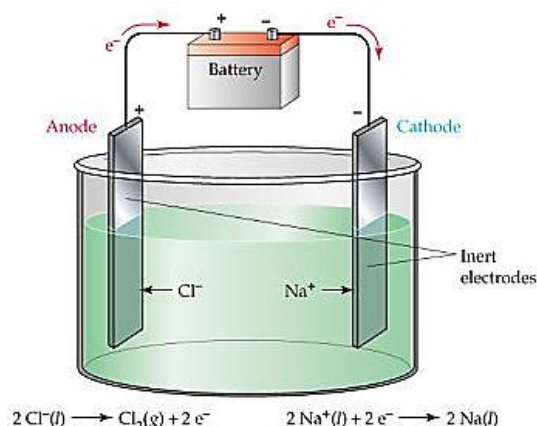
A voltaic cell uses a spontaneous redox reaction to generate an electric current. It is also possible to do the opposite. When an external source of direct current is applied to an electrochemical cell, a reaction that is nonspontaneous can be made to proceed. A nonspontaneous reaction will have an overall standard reduction potential that is negative ($E^0 < 0$). **Electrolysis** is the process in which electrical energy is used to cause a nonspontaneous chemical reaction to occur. Electrolysis is responsible for the appearance of many everyday objects such as gold-plated or silver-plated jewellery and chrome-plated car bumpers.

An **electrolytic cell** is the apparatus used for carrying out an electrolysis reaction. In an electrolytic cell, electric current is applied to provide a source of electrons for driving the reaction in a nonspontaneous direction. In a voltaic cell, the reaction goes in a direction that releases electrons spontaneously. In an electrolytic cell, the input of electrons from an external source forces the reaction to go in the opposite direction. There are many similarities between galvanic cells and electrolytic cells (for example oxidation occurs at the anode and reduction occurs at the cathode), however there are also some very important differences which are listed below.

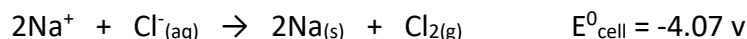
Electrolytic Cell Vs Galvanic Cell

Electrolytic Cell (s)	Galvanic Cell (s)
Electrical energy is transformed into chemical energy.	Chemical energy is transformed into electrical energy.
Anode is positive electrode & Cathode is negative electrode.	Anode is negative electrode & Cathode is positive electrode.
Both the electrodes can be fitted in the same cell .	The electrodes are fitted in different cell .

Electrolysis of molten Sodium Chloride



In the diagram above on the right, sodium ions are being reduced to sodium metal, and the chloride ions are being oxidised to chlorine gas. The overall reaction is



The E^0_{cell} for this combination of half reactions is very negative indicating that a voltage of just over 4.07 volts would be needed to force this reaction to occur. How far over 4.07 v would depend on the efficiencies within the circuit itself – normally we say “just over” the numerical value.

The opposite of this reaction - sodium metal releasing electrons to Chlorine gas, to form sodium chloride, has an E^0 of +4.07 volts, indicating a combination of sodium metal and chlorine gas would be very dangerous reaction if a lot of energy would be released in a very short time.

There are several application of electrolysis which are commercially important

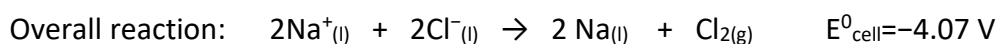
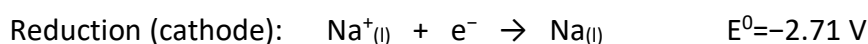
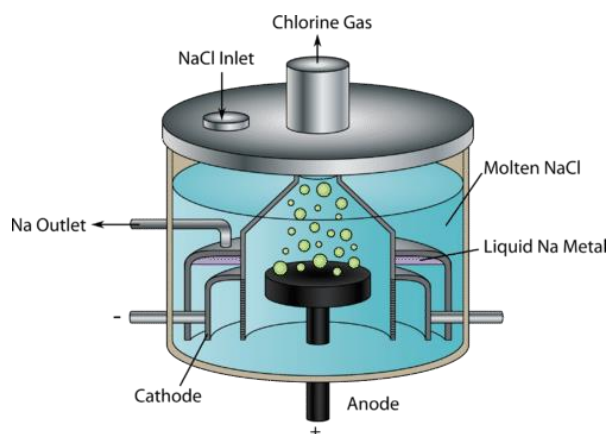
Electrolysis of Molten Compounds

Molten simply means a solid ionic compound melted to a liquid. As a liquid the ions are no longer in their lattice structure and can move in response to an electric field (ie conduct a current). Electrolysis is common for some molten ionic compounds as in their molten form the only ions present are the ions of

the ionic substance. For example, molten sodium chloride contains only sodium ions and chloride ions, and molten copper sulphate contains only copper (II) ions and Sulphate ions. Since there are only two ions in the electrolysis cell, the possible reactions are very easy to predict. One of the ions (the metallic ion) will undergo reduction to a metal, and the non-metal ion will undergo oxidation.

An example is molten (liquid) sodium chloride can be electrolysed to produce sodium metal and chlorine gas. The electrolytic cell used in the process is called a Down's cell (see Figure below).

In a Down's cell, the liquid sodium ions are reduced at the cathode to liquid sodium metal. At the anode, liquid chloride ions are oxidized to chlorine gas. The reactions and cell potentials are shown below:



The battery must supply over 4 volts to carry out this electrolysis. This reaction is one way to produce chlorine gas and is the only way to obtain pure sodium metal. Chlorine gas is widely used in cleaning, disinfecting, and in swimming pools.

Electrolysis of Aqueous solutions (inert electrodes)

In Electrolysis, an aqueous solution is simply an ionic compound dissolved in water. Technically there are other aqueous solutions involving polar covalent compounds (such as sugar dissolved in water), but these do not conduct electricity so cannot be used for electrolysis... so we will ignore these.

If an aqueous solution is used for electrolysis, the water is also a possible reactant in the electrolytic process as well as the metallic and non-metallic ions. This can make predicting the oxidant and the reductant more difficult than in a molten solution.

The general rule to apply in the electrolysis of aqueous solution is that the oxidation and reduction half reactions which combine to give the least negative (or largest) E^0_{cell} , are the oxidation and reduction reactions which will occur preferentially. Let's look at how this works in an example... the electrolysis of aqueous NaCl ($\text{NaCl}_{(aq)}$).

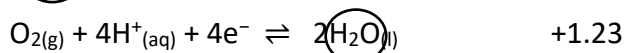
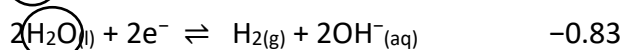
Step 1:

List the possible reactants = Na^+ , Cl^- , H_2O

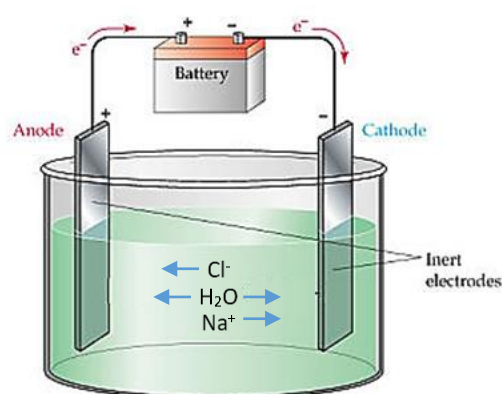
Step 2:

Identify reactions for these reactants in the table of standard electrode potentials, and write them down.

Na^+ , Cl^- , H_2O

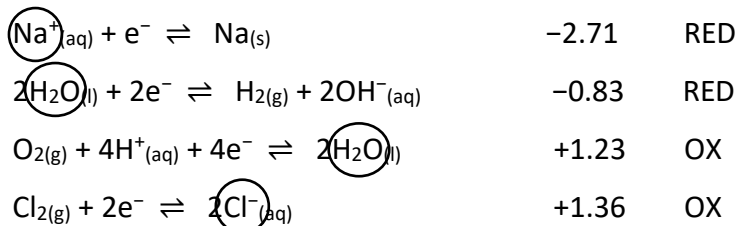


Electrolysis of aqueous Sodium Chloride



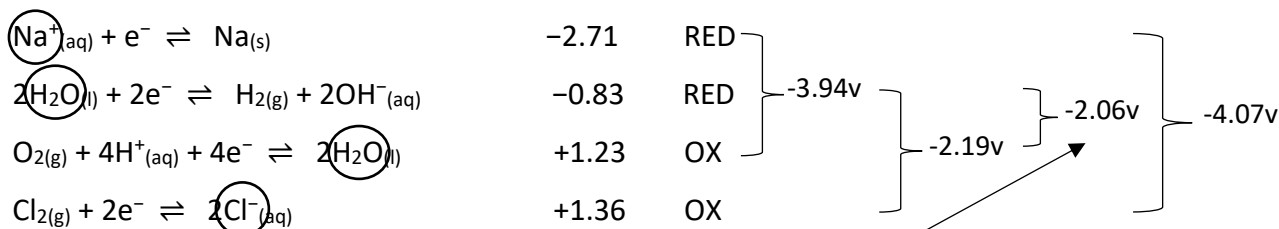
Step 3:

Label the reactions as Oxidation or Reduction – oxidation goes from right to left, Oxidation as left to right.



Step 4:

Determine the E^0_{cell} for each combination (RED + OX) of half reactions.



Step 5:

The least negative E^0_{cell} will be the preferred cell reaction.



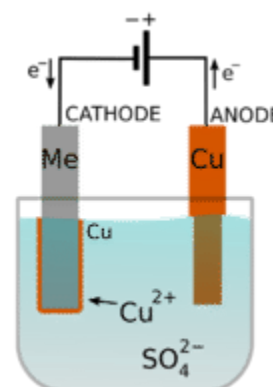
Assuming a voltage of just over 2.06 volts, and less than 2.19 volts is applied, to an aqueous solution of sodium chloride, the reaction will be reduction of water to hydrogen gas at the cathode, and the oxidation of water to Oxygen gas at the anode. If a significantly higher voltage is applied (but still less than 3.94 v) then the oxidation of chloride ions to chlorine gas at the anode will also occur.

HOWEVER – the assumptions above are entirely dependent on the E^0 values being correct, which is only true if the solutions are at 1M and 25°C and 1 atm pressure. If a very concentrated solution of Sodium chloride solution was used (say concentrated seawater), the reduction of chloride ions is actually the preferred reaction. This is also a commercial way of producing sodium hydroxide solution – can you figure out how (see question 2 below)?

Electroplating

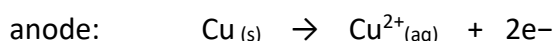
Electroplating is an application of electrolysis where the aim is to produce a coating of a metal onto the cathode. Many decorative objects like jewellery are manufactured with the aid of an electrolytic process. Electroplating is a process in which a metal ion is reduced in an electrolytic cell and the solid metal is deposited onto a surface. The figure below shows a cell in which copper metal is to be plated onto a second metal.

The cell consists of a solution of copper sulfate and a strip of copper which acts as the anode. The metal (Me) is the cathode. The anode is connected to the positive electrode of a

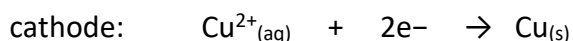


battery, while the metal is connected to the negative electrode. The copper anode is being oxidised, and the copper ions in solution are being reduced. For this reason electroplating requires very little voltage as the reduction and oxidation half reactions have the same E^0 values

When the circuit is connected, copper metal from the anode is oxidized, allowing copper ions to enter the solution.



Meanwhile copper ions from the solution are reduced to copper metal on the surface of the cathode (the second metal):



The copper anode is being oxidised, and the copper ions in solution are being reduced. For this reason electroplating requires very little voltage as the reduction and oxidation half reactions have the same E^0 values. The concentration of copper ions in the solution is effectively constant. This is because the electroplating process transfers metal from the anode to the cathode of the cell. Other metals commonly plated onto objects include chromium, gold, silver, and platinum.

One specific application of this is the purification of copper metal. When copper is extracted from ores it is reasonably pure (~99% or more), like most metals. However to be used as electrical wiring the copper must be very pure – and this is achieved by electroplating. The “nearly pure” copper is used as the anode, and pure copper (>99.9%) deposits at the cathode – similar to the diagram earlier except the Me cathode is a pure copper cathode. The impurities within the anode (“nearly pure” copper) either sink to the bottom of the electrolytic cell, or dissolve into the solution – depending on their E^0 value.

Checking for understanding:

1. For the electrolysis of aqueous Copper sulphate, determine:

- | | |
|--|--|
| (a) The ions present in the solution | (b) products at the cathode and anode |
| (b) draw the electrolytic cell with labels | (c) Overall cell equation for the preferred reaction |
| (b) The preferred cell reaction | (d) Minimum voltage at 1M concentrations |

2. If a very concentrated solution of sodium chloride underwent electrolysis at a voltage of 2.5 volts, what would be the products at the anode and cathode?

3. How would the minimum cell voltage and possible preferred reaction change if the concentrations of the aqueous solution was less than 1.0 M. Apply your logic to the electrolysis of both Sodium Chloride and Copper Sulphate.

4. Consider the electroplating of copper using “nearly pure” copper as an anode. What is the minimum voltage for this reaction to occur? List two metals which would dissolve in the