Chem12 Electrolysis : Notes - 50

Electrolysis is a process during which a non-spontaneous redox reaction occurs when electrical energy is supplied.

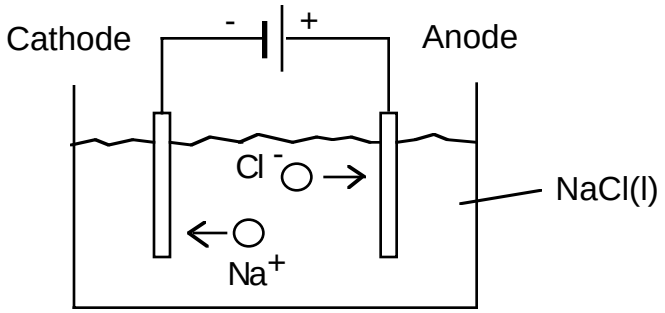
Electrolysis of molten NaCl

An example of this type of reaction is the electrolysis of molten sodium chloride. In this cell the anode is carbon and the cathode is iron. Both electrodes are inert in this case. (carbon and platinum are often used when inert electrodes are required)

The cathode reaction is $Na^+ + e^- \rightarrow Na(l)$ -2.71 volts

The anode reaction is $2Cl^- \rightarrow Cl_2(g) + 2e^-$ -1.36 volts

This redox cell has an overall voltage of -4.07 volts. This reaction is non-spontaneous. Electrical energy with a voltage of at least +4.07 volts must be supplied. This cell is used to produce sodium metal and chlorine gas. Sodium metal can be collected at the cathode and chlorine gas can be collected at the anode.



Reduction $Na^+ + e^- \rightarrow Na$

Oxidation $2Cl^- \rightarrow Cl_2 + 2e^-$

There are many practical problems that must be overcome in order to run this cell. The melting point of NaCl is 800°C and the sodium and chlorine must not come in contact or an explosion will occur.

Electrolysis of Aqueous Solutions

In the above cell, the operating temperature is very high. Electrolysis can occur in an aqueous solution at a much lower temperature. An

example of this type of reaction is the electrolysis of the aqueous salt CaI_2. In this cell, I^- or H_2O may be oxidized and Ca^{2+} or H_2O may be reduced. The electrodes are inert. The possible reactions are shown below.

anode	$2I^-(aq) \rightarrow I_2(s) + 2e^-$	-0.54 volts
	$2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$	-0.82 volts
cathode	$Ca^{2+}(aq) + 2e^- \rightarrow Ca(s)$	-2.87 volts
	$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$	-0.41 volts

For (almost) all electrolysis cells, the voltage required will be the **minimum** voltage. (It is a basic rule of nature to expend the least amount of energy possible in order to carry out a reaction). In the above cell the smallest voltage (in absolute terms) is -0.95 volts. So the anode reaction is the oxidation of iodine. The cathode reaction is the reduction of water. The minimum voltage required for input is + 0.95 volts.

Another way of looking at this is, I^- is more easily oxidized than H_2O so I^- will be oxidized. H_2O is more easily reduced than Ca^{2+}, so H_2O will be reduced.

There is an important exception to the above rule. If a dilute solution containing Cl^- or Br^- is being electrolyzed, then Cl_2 or Br_2 will form at the anode instead of O_2. This is due to the "overpotential effect".