C1 CHLOR-ALKALI

ELECTROLYSIS

CHEMICAL INDUSTRIES
RESOURCE PACK

Let's start at the very beginning...

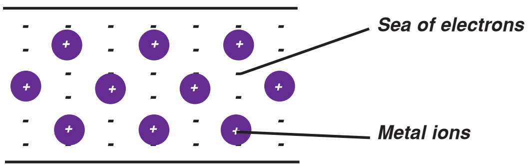
Electrolysis is a chemical decomposition reaction produced by passing an electric current through a solution containing ions.

Reduction is when an atom, ion or molecule gains electrons. Examples can be shown using half reactions: $Cl_2 + 2e^- \rightarrow 2Cl^-$ or $Mg^{2+} + 2e^- \rightarrow Mg(s)$

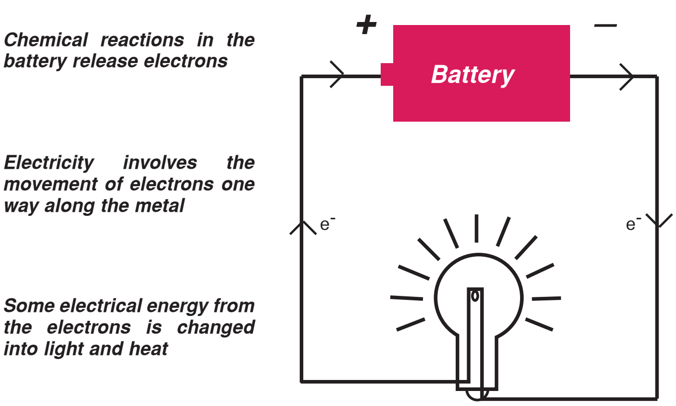
Oxidation is when an atom, ion or molecule gives off (loses) electrons, for example:
$Na(s) \rightarrow Na^+ + e^-$ or $S^{2-} \rightarrow S(s) + 2e^-$

A **redox** reaction is a reaction that involves electron transfer. One species is oxidised while another is reduced.

Charge can move within a conductor. Metals are good conductors because they have delocalised electrons which can move without chemically changing the metal. These electrons are already present in the metal.



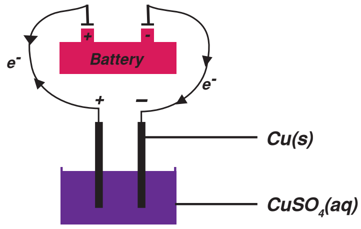
An **electrolyte** is a liquid that can conduct electricity. Electrons do not move freely through these liquids, rather it is charged ions present within the liquid that move. The effect is still moving charge. Many liquids with ions present are used as electrolytes. Some are pure liquid compounds and some are ions in solution.



A battery connected in a circuit sets up an electric field in the circuit which causes the electrons to move.

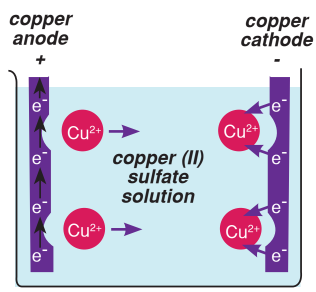
Purifying metals

Let us take two copper electrodes submerged in blue copper (II) sulfate solution and connect them to a battery. Copper sulfate is an electrolyte as it has ions (Cu^{2+} and SO_4^{2-}) which are free to move.

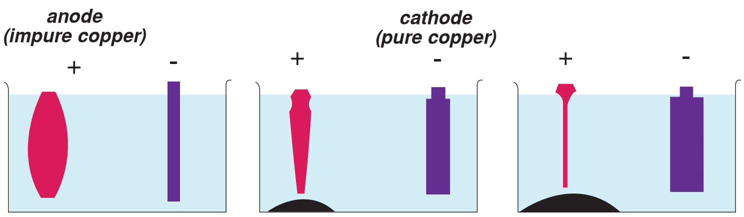


At the positive electrode (**anode**) copper atoms become copper ions and the released electrons move through the conductor towards the battery. Copper atoms are oxidised to form copper ions: $Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$. Oxidation occurs at the anode. Copper ions will go into solution at the anode.

Electrons moving to the negative electrode (**cathode**) combine with the positive copper ions from the solution to form copper atoms which then remain on the electrode. Copper ions are reduced to form copper atoms. $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$. Reduction occurs at the cathode. Copper metal will be formed at the cathode.

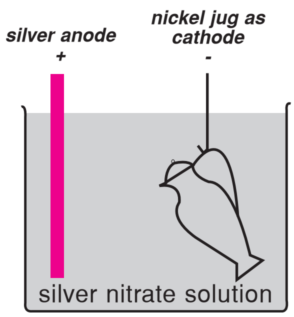


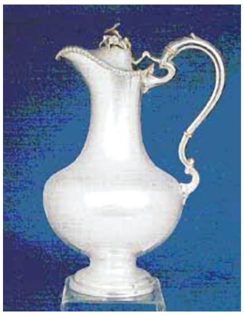
The result is that the anode decreases in mass as the copper goes into the solution. The cathode increases in mass. This can be used as a purification method as impurities will be exposed as the anode erodes, but will not be attracted to the cathode.



Electroplating

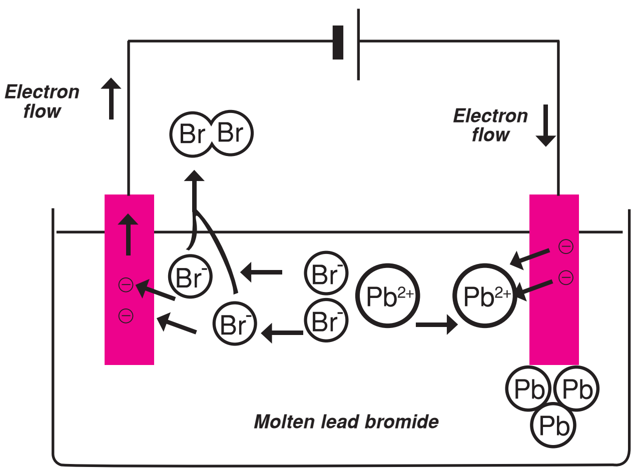
This is just a variation of the previous concept. If the anode is made of silver metal and the electrolyte contains silver ions (silver nitrate in this example), then the item used as a cathode will have a silver layer formed around it. Oxidation will take place at the anode: $Ag \rightarrow Ag^{+} + e^{-}$
Reduction will take place at the cathode:
$Ag^{+} + e^{-} \rightarrow Ag$





Decomposition using electrolysis

Let us set up a similar situation with graphite electrodes dipped in molten lead bromide ($PbBr_2$). (Graphite will conduct electricity but not take part in the reaction.) There are Pb^{2+} ions and Br^{-} ions present. The negative bromide ions will be attracted to the positive electrode. Here they will be oxidised (making this electrode the anode) into bromine atoms which will combine to form bromine gas. The positive lead ions will be attracted to the negative electrode where they will be reduced to form lead atoms. Brown bubbles are formed at the anode and the cathode is plated with lead.



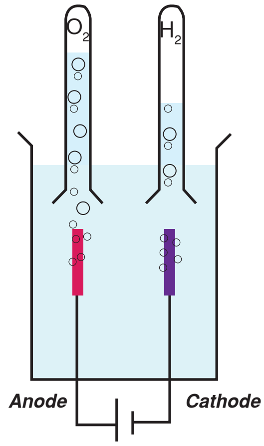
Two Br- ions each lose 1 electron to the anode... forming atoms of bromine gas.

Each Pb^{2+} ion gains 2 electrons from the cathode... ...to form a lead atom.

At the anode:
$Br^{-} \longrightarrow Br + e^{-}$

At the cathode:
$Pb^{2+} + 2e^{-} \longrightarrow Pb$

Water, which can break up into H^{+} ions and OH^{-} ions, can be decomposed in a similar manner:
The reaction that takes place at the anode is an oxidation reaction (loss of electrons): $4OH^{-} \rightarrow 2H_2O + O_2 + 4e^{-}$
The reaction that takes place at the cathode is a reduction reaction (gain of electrons): $2H^{+} + 2e^{-} \rightarrow H_2$
Therefore the net reaction is: $2H_2O\ (\ell) \rightarrow 2H_2(g) + O_2(g)$



Electrolysis of brine

Brine is sodium chloride (NaCl or table salt) solution and contains **Na^{+}** and **Cl^{-}**. Some **H^{+}** and **OH^{-}** ions are also present since water dissociates to a small extent. We find that some cations are better at accepting electrons than others, and that some anions lose their electrons easier than others. This is what happens in the electrolysis of brine:

1. Positive ions attracted to negative electrode. Negative ions attracted to positive electrode.
2. Hydrogen ions accept electrons more readily than sodium ions. Hydrogen is therefore reduced at the cathode to form hydrogen gas: $2H^{+} + 2e^{-} \rightarrow H_2$
3. Chloride ions lose electrons more readily than hydroxide ions. Chlorine is therefore oxidised at the anode to form chlorine gas: $2Cl^{-} \rightarrow Cl_2 + 2e^{-}$
4. Chlorine gas bubbles are formed at the anode and hydrogen gas bubbles are formed at the cathode. The remaining solution becomes alkaline due to the presence of sodium hydroxide.