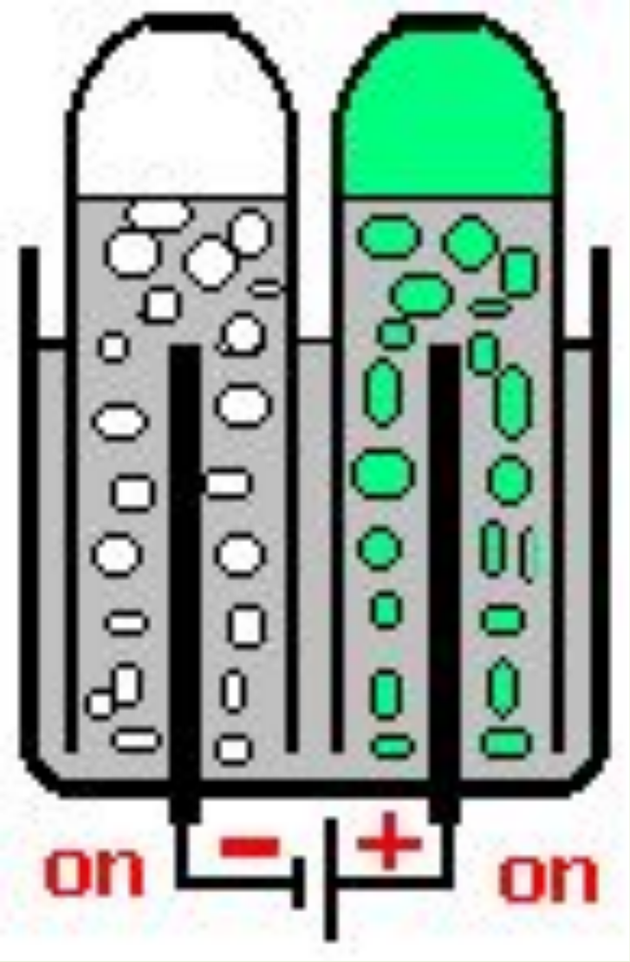


LECTURE 12

ELECTROLYSIS

25.04.2017

Learning Objectives:

- Definition an electrolysis
- Learn to predict products of electrolysis: molten compounds and aqueous solutions
- Describe the electrolysis of an aqueous solution
- Describe the electrolysis of a molten ionic compounds
- Write half equations for the discharge of ions at the anode and the cathode,
- Laws of electrolysis – Faraday's laws

GLOSSARY

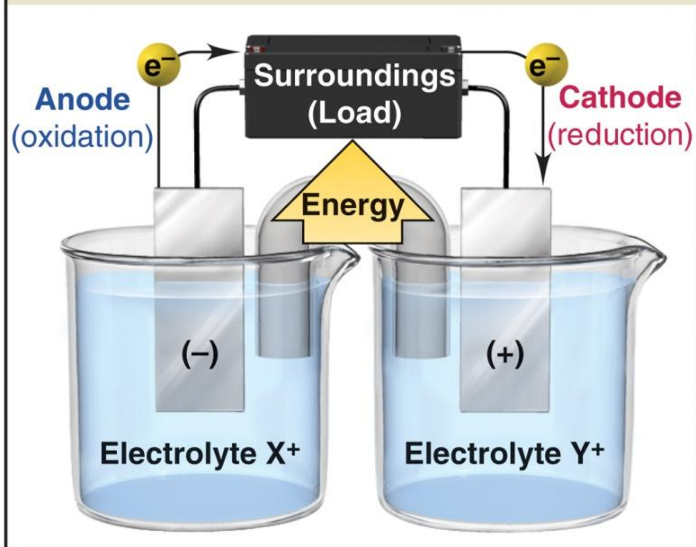
- An electrolyte is an ionic compound which, when molten or in aqueous solution, conducts an electric current and is decomposed in the process.
- An electrode is a rod or plate where electricity enters or leaves an electrolyte during electrolysis. Reactions occur at the electrodes (and not inside the electrolyte). (inert/reactive)
- The anode is the positive electrode connected to the positive terminal of the d.c. power source. Oxidation occurs at the anode.
- The cathode is the negative electrode connected to the negative terminal of the d.c. power source. Reduction occurs at the cathode.
- An anion is an ion with a negative charge. During electrolysis, it is attracted to the anode.
- A cation is an ion with a positive charge. During electrolysis, it is attracted to the cathode.
- In electrolysis, a compound in the molten state or in aqueous solution, conducts electricity and is decomposed by it.

Sir Humphry Davy
(1778 – 1829)

A

VOLTAIC CELL
Energy is *released* from a spontaneous redox reaction.

System does work on surroundings.



Oxidation half-reaction
$X \longrightarrow X^+ + e^-$

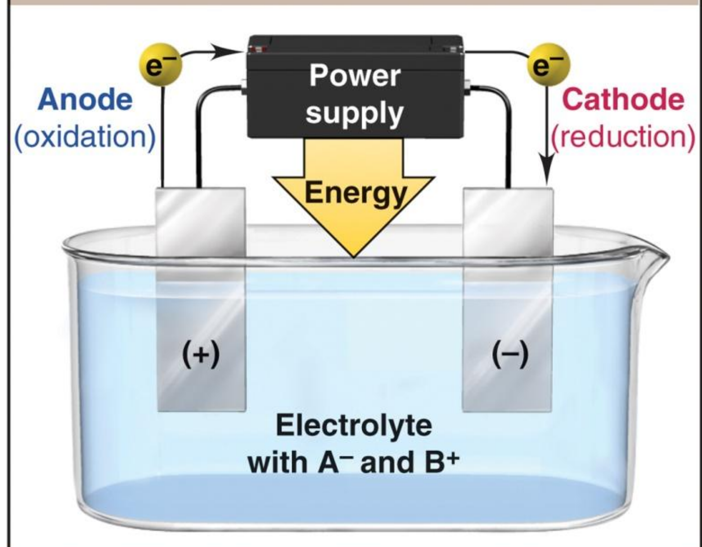
Reduction half-reaction
$e^- + Y^+ \longrightarrow Y$

Overall (cell) reaction
$\mathbf{X + Y^+ \longrightarrow X^+ + Y;\ \Delta G < 0}$

B

ELECTROLYTIC CELL
Energy is *absorbed* to drive a nonspontaneous redox reaction.

Surroundings (power supply) do work on system (cell).



Oxidation half-reaction
$A^- \longrightarrow A + e^-$

Reduction half-reaction
$e^- + B^+ \longrightarrow B$

Overall (cell) reaction
$\mathbf{A^- + B^+ \longrightarrow A + B;\ \Delta G > 0}$

Майкл
ФАРАДЕЙ
(1791 -1867)

The term **electrolysis** was introduced by Michael Faraday: "**Lysis**" means loosening in Greek, thus electrolysis means "**loosening by electricity**".

Electrolytes are substances able to conduct electricity in molten state or liquid state and undergo chemical change.

Electrolysis is a process where the electrolytes are broken down into its constituent elements by passing electricity through it.

Introducing Electrolysis

<u>**Electrolysis**</u> **is the redox decomposition of an ionic compounds by passing electricity through molten compounds or aqueous solutions of compounds.**

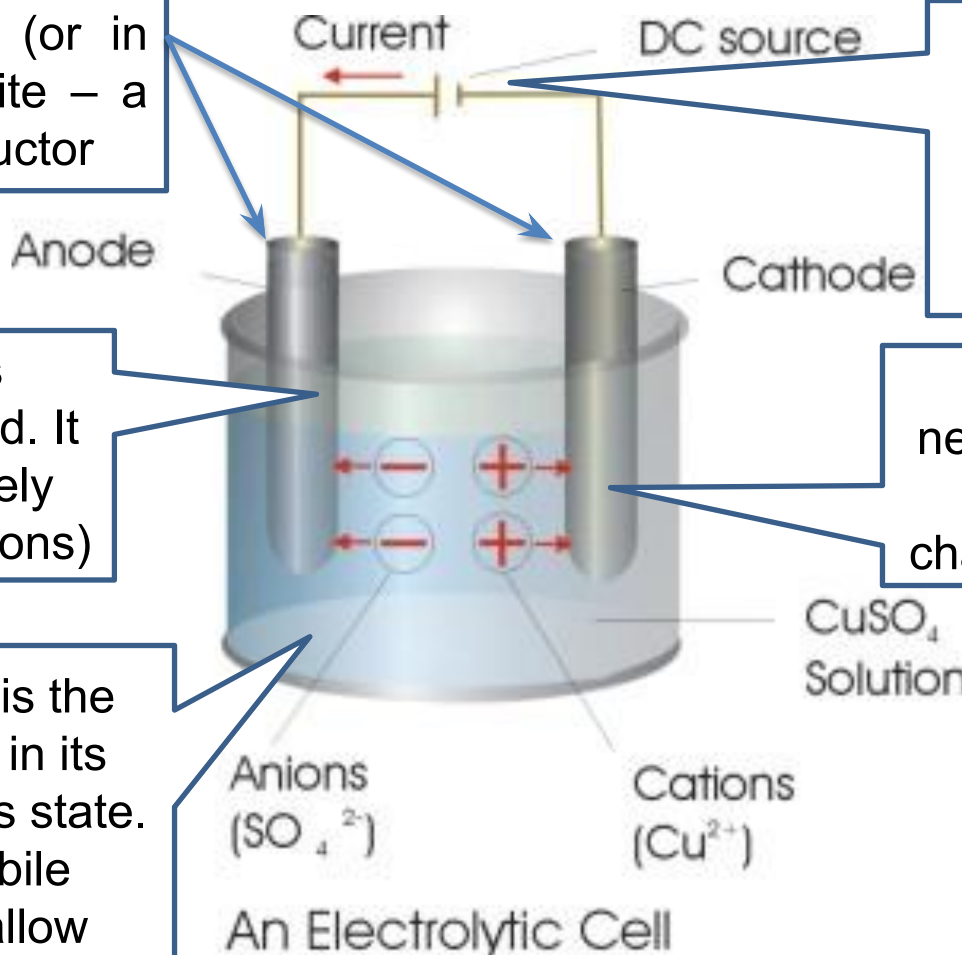
Electricity is used to produce chemical changes.

The apparatus used for electrolysis is called an electrolytic cell. *<u>An electrolytic cell</u>* is an electrochemical cell in which an electric current drives an otherwise non-spontaneous reaction.

The electrolytic cell

These are known as <u>electrodes</u>. They are usually a metallic (or in the case of graphite – a non-metallic) conductor

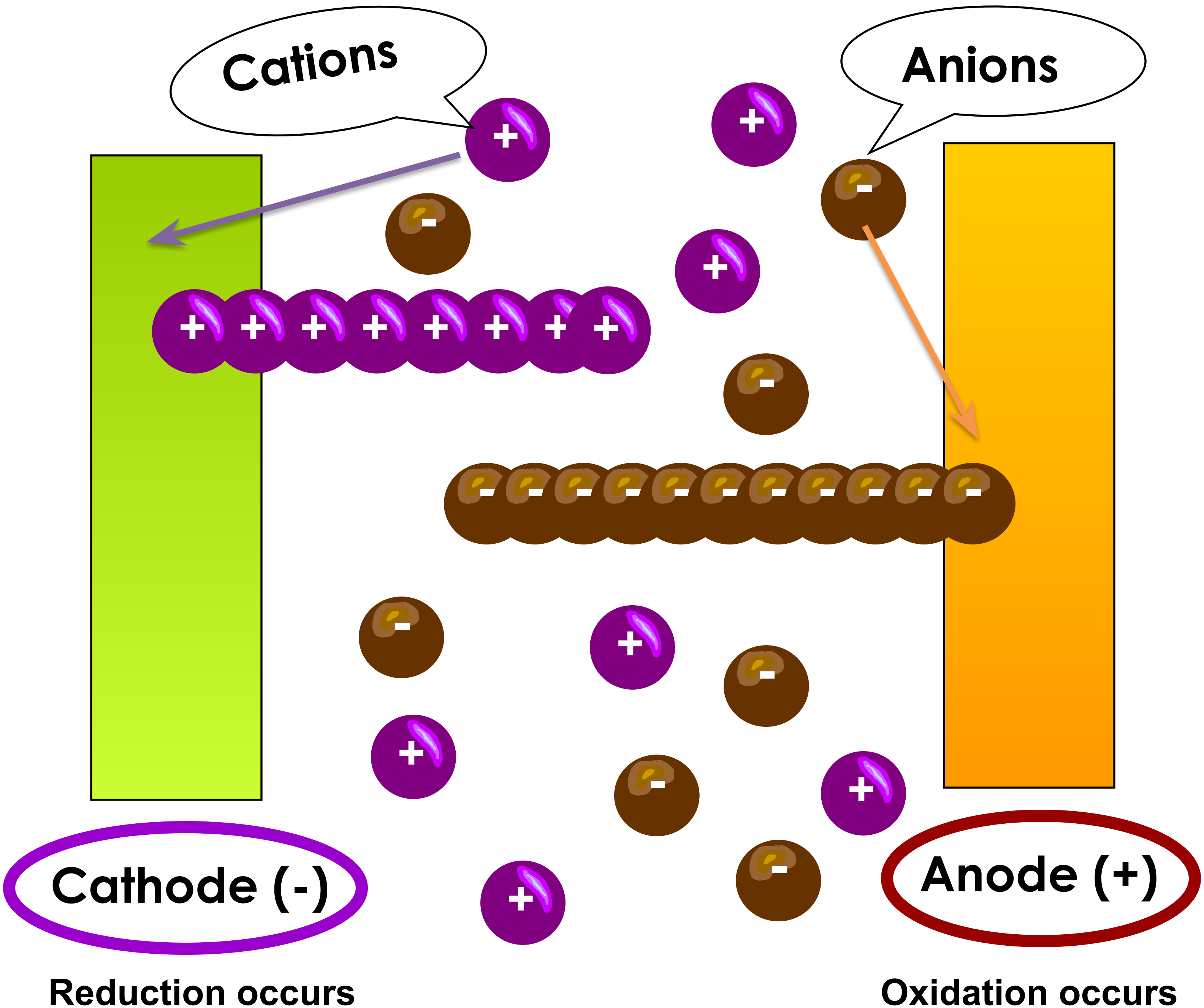
The **<u>power source</u>** provides electrical current that gives the electrodes their respective charges



The **<u>anode</u>** is positively charged. It attracts negatively charged ions (anions)

The **<u>cathode</u>** is negatively charged. It attracts positively charged ions (cations)

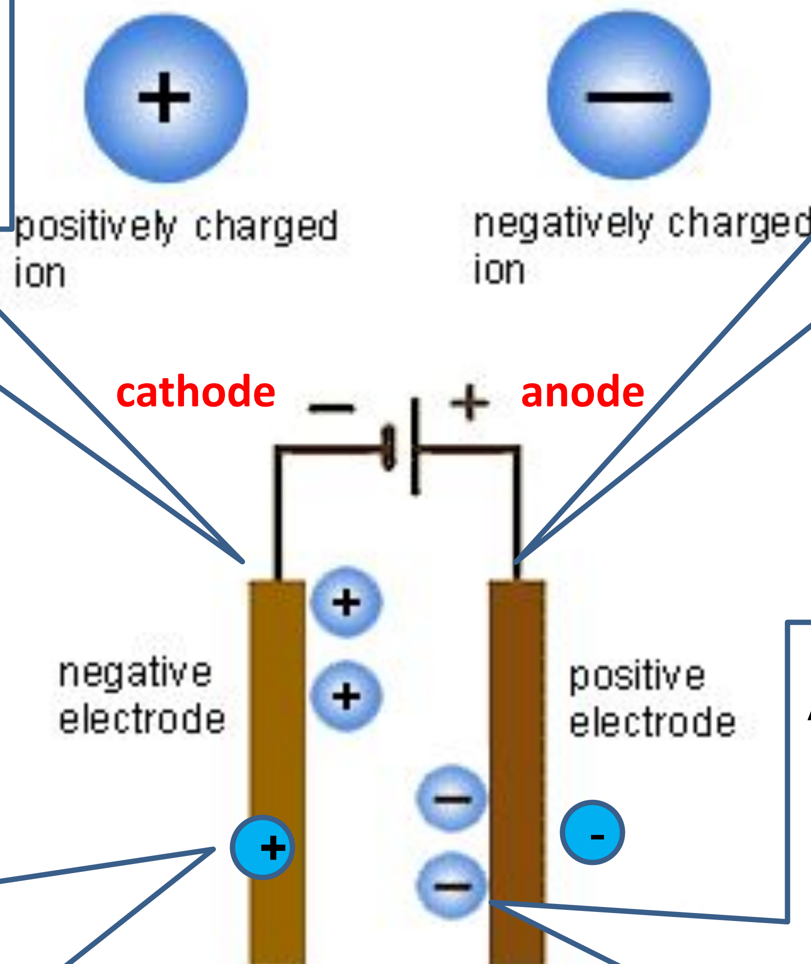
The **<u>electrolyte</u>** is the ionic compound in its molten or aqueous state. It provides mobile electrons that allow electrical conduction


Cations
Anions
Cathode (-)
Anode (+)
Reduction occurs
Oxidation occurs

How electrolysis works?

These electrons then provide the negative charge for the negative electrode (cathode)

The electrons from the anions then move along the circuit through the power source to the negative electrode



The cations move towards this negatively charged electrode (cathode).
In doing so, they gain electrons to become an electrically neutral element:

$Y^{n+} + ne^{-} \rightarrow Y$

Anions move towards the positive electrode (anode).
In doing so, they lose electrons to become a neutral element:

$nX^{n-} - ne^{-} \rightarrow X_n$

How do you know which ions will be discharged?

The selection of ions to be discharged during electrolysis is based on:

<u>Factors affecting products of electrolysis:</u>

- Type of electrolyte (molten or solution)
- The electrochemical series
- Molarity / Concentration of Solution
- Type of Electrodes (inert or active)

Types of Electrolysis

Electrolytes can be either

Molten or Solution

- Pure
- Ionic compound
- Liquid form

Molten electrolysis

$$K_xA_y \rightarrow xK^{+n} + yA^{-m}$$

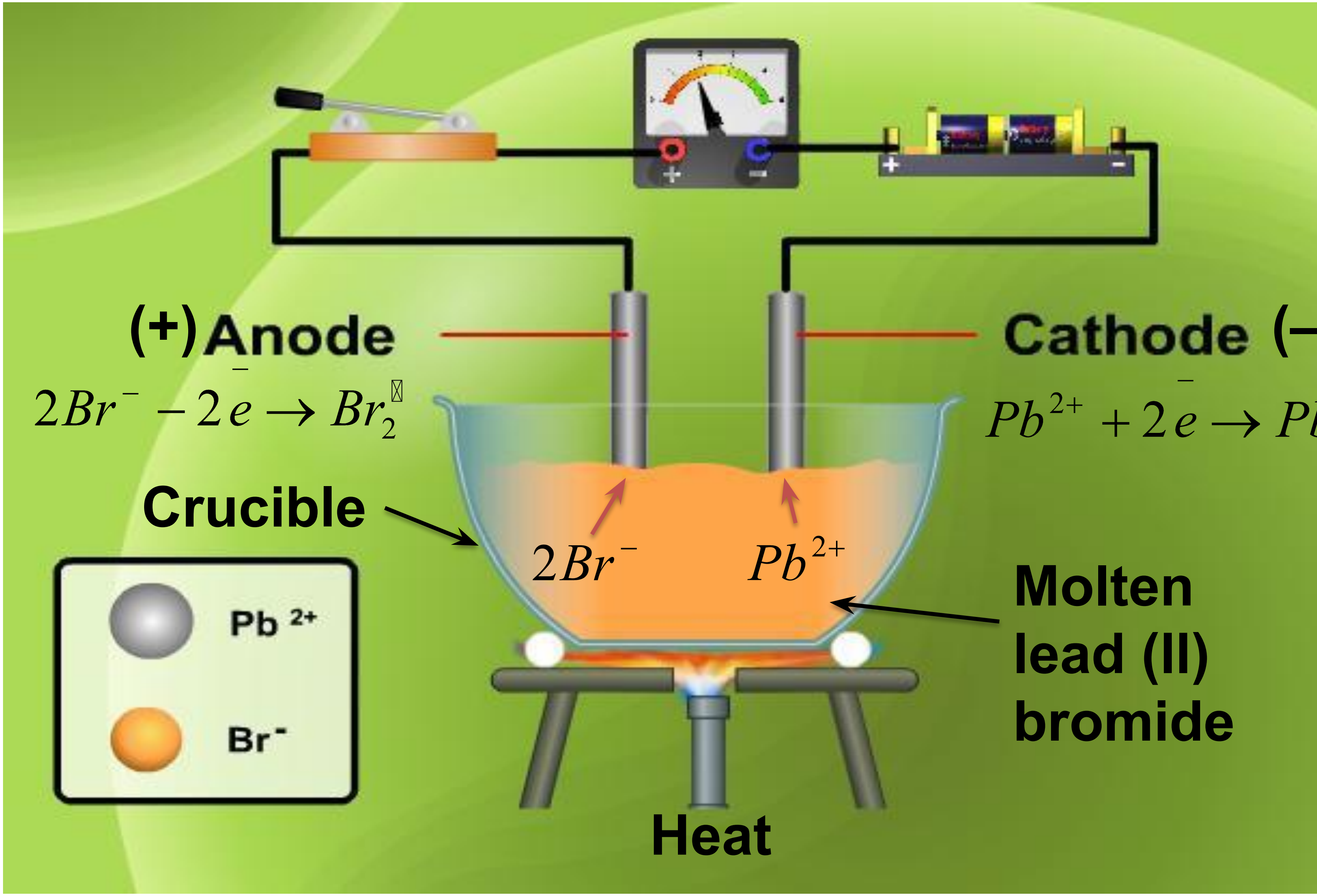
- Impure
- Mixture of ionic compounds

Solution electrolysis

$$K_xA_y \rightarrow xK^{+n} + yA^{-m}$$

$$HOH \rightarrow H^+ + OH^-$$

Electrolysis of molten lead (II) bromide



At the anode … brown gas … Br_2

$$2Br^- - 2\bar{e} \rightarrow Br_2 \uparrow$$

At the cathode … silvery liquid… Pb

$$Pb^{2+} + 2\bar{e} \rightarrow Pb$$

Combining the two half equations, we get the overall equation that represent the electrolysis of molten lead (II) bromide:

$$PbBr_2 \rightarrow Pb^{2+} + 2Br^-$$

(–) Cathode:

$$Pb^{2+} + 2\overset{-}{e} \rightarrow Pb$$

(+) Anode:

$$2Br^- - 2\overset{-}{e} \rightarrow Br_2 \uparrow$$

$$PbBr_{2\ (molten)} \rightarrow Pb_s + Br_{2\ (gas)} \uparrow$$

Electrolysis of alkaline (NaOH) molten

$$NaOH \rightarrow Na^{+} + OH^{-}$$

(–) Cathode:

$$Na^{+} + 1\bar{e} \rightarrow Na^{\square}$$

(+) Anode:

$$OH^{-} - 1\bar{e} \rightarrow OH^{\square}$$

$$4OH^{\square} \rightarrow 2H_2O + O_2 \uparrow$$

$$4NaOH_{(molten)} \rightarrow 4Na^{\square} + 2H_2O + O_2 \uparrow$$

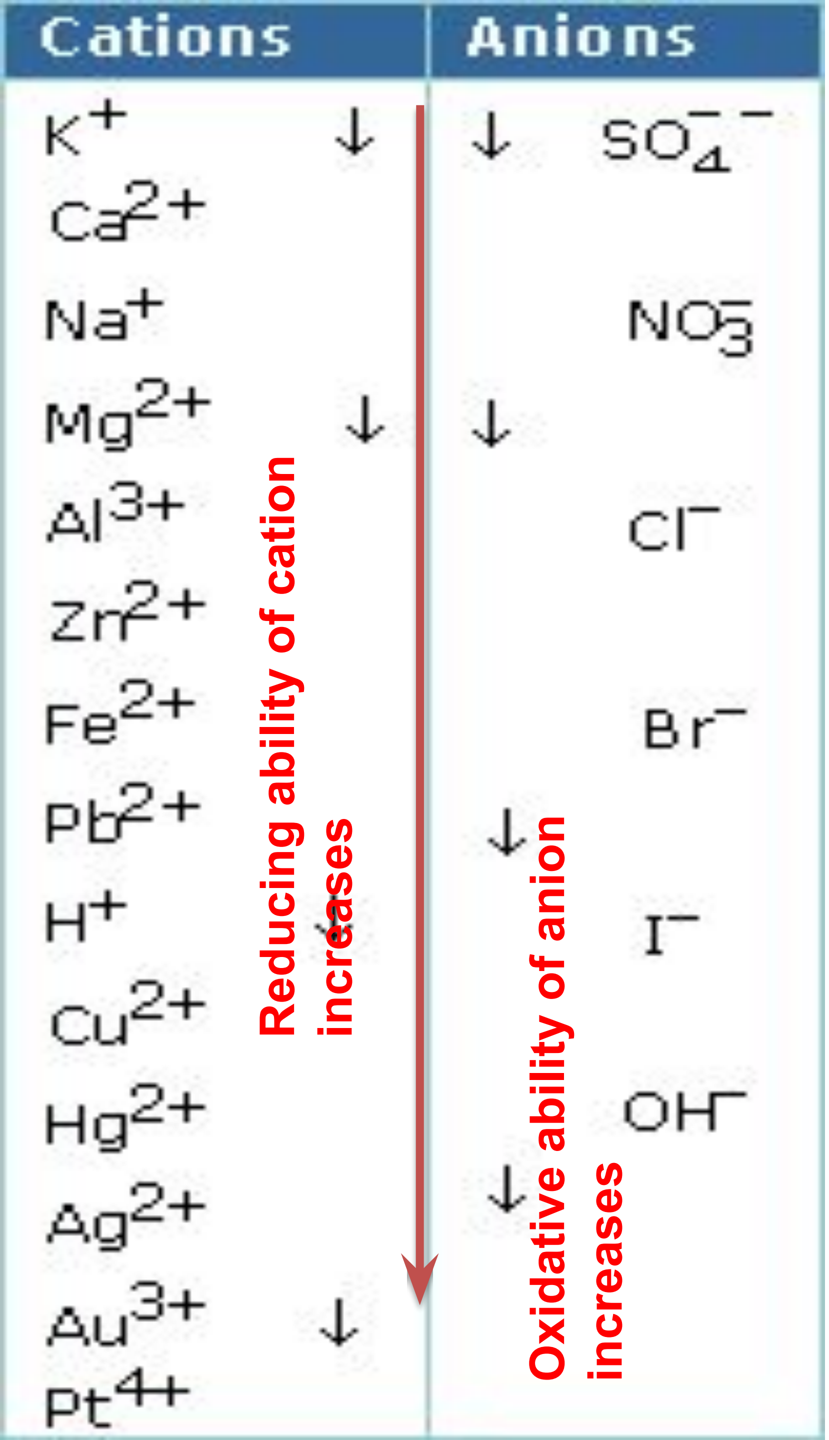
Electrolysis of solution

$$K_xA_y \rightarrow xK^{+n} + yA^{-m}$$

$$HOH \rightarrow H^+ + OH^-$$

The selection of ions to be discharged during electrolysis of solution is based on:

Factors	Ions will be discharged
Position of ions in the electrochemical series	The ions that are **LOWER in the ELECTROCHEMICAL SERIES** will be selectively discharged.
Concentration of ions in the electrolytes	The particular ions with **HIGHER CONCENTRATION** will be selectively discharged
Types of electrodes used in the electrolysis	**ACTIVE ELECTRODES occur in electrolysis and ionises (form ions)**



What is the electrochemical series?

This is a list of elements in order of their ability to be reduced.

For cations, the higher the element in the series, the less likely it is that this will gain electrons (that is be reduced).

For anions, the higher it is on the series the less likely will it lose electrons (that is be oxidized)

RULES FOR IONIC SOLUTIONS

+ ANODE: the anion which is stronger reducing agent (low value of standard potential) is liberated first at the anode

- CATHODE: the ion which is stronger oxidizing agent (high value of standard potential) is discharged first at the cathode

if anions are halogens i.e.

chloride Cl^-, bromide Br^- and iodide I^- the **halogen is produced**: $2I^- - 2e \rightarrow I_2^0 \uparrow$

if – ions are not halogens eg sulphate SO_4^{2-}, nitrate NO^{3-}, carbonate CO_3^{2-} and other, **oxygen is produced**, because OH^- ion of water is electrolysed:

$$OH^- - 1\bar{e} \rightarrow OH^0$$

$$4OH^0 \rightarrow 2H_2O + O_2 \uparrow$$

if cations (metals) are more reactive than hydrogen (before H atom in ecs):

K, Na, Ca, Mg, Zn, Fe ...... H_2

then **hydrogen** is produced:

$$2H^+ + 2\bar{e} \rightarrow H_2^0 \uparrow$$

if cations (metals) are less reactive than hydrogen (after H atom in ecs): **Cu, Ag, Au, Pt**

then the **metal is produced**:

$$Me^{+n} + n\bar{e} \rightarrow Me^0$$

Electrolysis of sodium chloride (brine)solution

$$NaCl \rightarrow Na^{+} + Cl^{-}$$

$$HOH \rightarrow H^{+} + OH^{-}$$

(–) Cathode:

(+) Anode:

$$Na^{+} \xrightarrow{NaOH} OH^{-}$$

$$2H^{+} + 2\bar{e} \rightarrow \underline{H_2} \uparrow$$

$$2Cl^{-} - 2\bar{e} \rightarrow \underline{Cl_2} \uparrow$$

$$2NaCl + 2H_2O \rightarrow H_2 \uparrow + Cl_2 \uparrow + 2NaOH$$

Electrolysis of copper sulfate solution

$$CuSO_4 \rightarrow Cu^{2+} + SO_4^{2-}$$

$$HOH \rightarrow H^+ + OH^-$$

(–) Cathode:

(+) Anode:

$E_{Cu^{2+}} = +0,34\ V$ $\quad Cu^{2+} + 2\bar{e} \rightarrow \underline{Cu^0}$

SO_4^{2-}

$E_{H^+} = 0\ V$ $\quad H^+$

H_2SO_4

$OH^- - 1\bar{e} \rightarrow OH^0$

$4OH^0 \rightarrow 2H_2O + \underline{O_2} \uparrow$

$$2CuSO_4 + 2H_2O \rightarrow 2Cu^0 + O_2 \uparrow + 2H_2SO_4$$

Output current (W, %) at the cathode

These cations are not reduced from the solution
W = 0%

These cations are reduced from the solution with hydrogen ions
W < 50%

These cations are total reduced from the solution
W = 100%

Types of electrodes

Inert electrodes do not actually participate in electrolysis but just provide electrical current (graphite, platinum, mercury)

Active electrodes actually participate in electrolysis while providing electrical current. Usually made of the metal that corresponds to the metallic ion in the electrolyte: Zn, Cu, Al, Cr, Ni

Faraday's laws of Electrolysis

Michael Faraday, on the basis of his research, investigated electrolysis quantitatively. He found that, during electrolysis, the quantities of substances liberated at electrodes depend upon the following three factors.

i. The quantity of current passed.
ii. Time duration of passing the current at a uniform rate.
iii. Charge on the ions being deposited.

Faraday's law of electrolysis states that:

- ***Faraday's 1st law***: The mass of a substance produced at an electrode during electrolysis is proportional to the number of moles of electrons (the quantity of electricity) transferred at that electrode.

$$m_{El} = \frac{q \cdot Eq_{(El)}}{F} \quad \Rightarrow \quad m_{El} = \frac{I \cdot t \cdot Eq_{(El)}}{96500}$$

$$q = I \cdot t$$

Faraday's law of electrolysis states that:

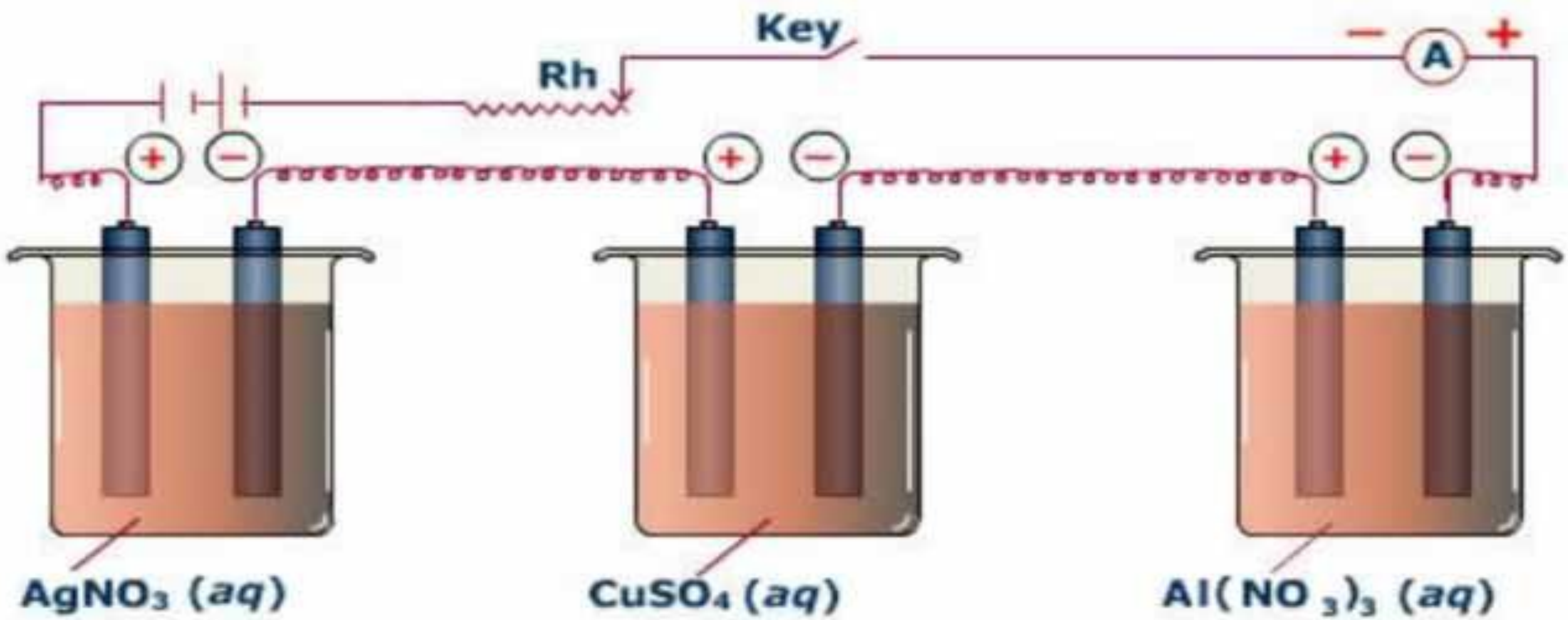
- ***Faraday's 2nd law***: The mass of a substance deposited or liberated at any electrode on passing a certain amount of charge is directly proportional to its chemical equivalent weight:

$$\frac{m_1}{m_2} = \frac{Eq^1}{Eq^2} \quad or \quad \frac{m_{El}}{V_{gas}} = \frac{Eq_{(El)}}{E_{V(gas)}}$$

$$E_{V(H_2)} = 11{,}2 mol / L$$

$$E_{V(O_2)} = 5{,}6 mol / L$$

Consider three different electrolytes, $AgNO_3$, $CuSO_4$ and $Al(NO_3)_3$ in their aqueous solutions, connected in series.



$$m_{Ag} = \frac{108}{1} = 108g \qquad m_{Cu} = \frac{63,5}{2} = 31,75g \qquad m_{Al} = \frac{27}{3} = 9g$$

Same quantity of electricity is passed through them, then the mass of Ag, Cu and Al, deposited on their respective electrodes would be directly proportional to their chemical equivalent masses

Some important uses of electrolysis:

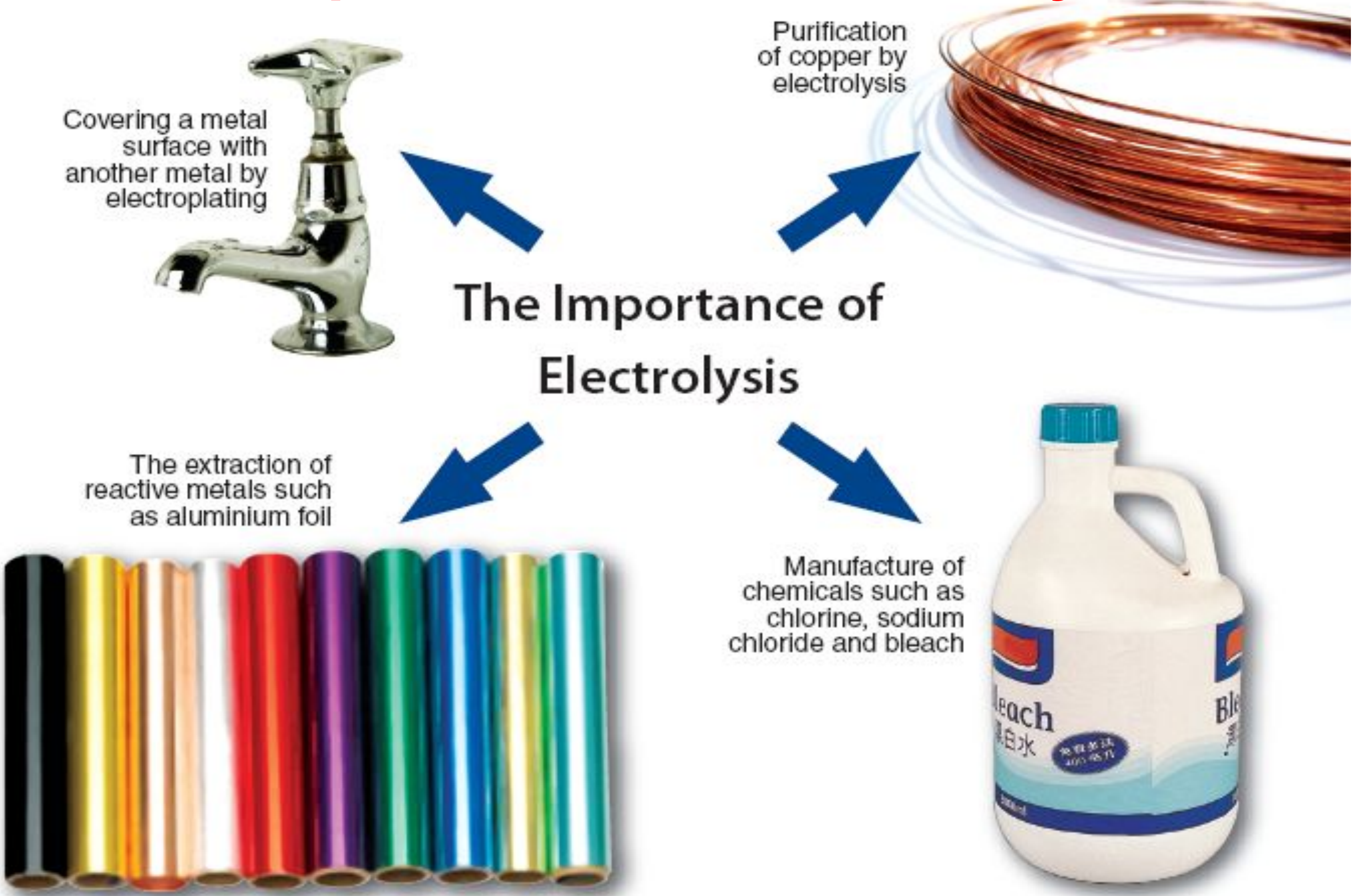
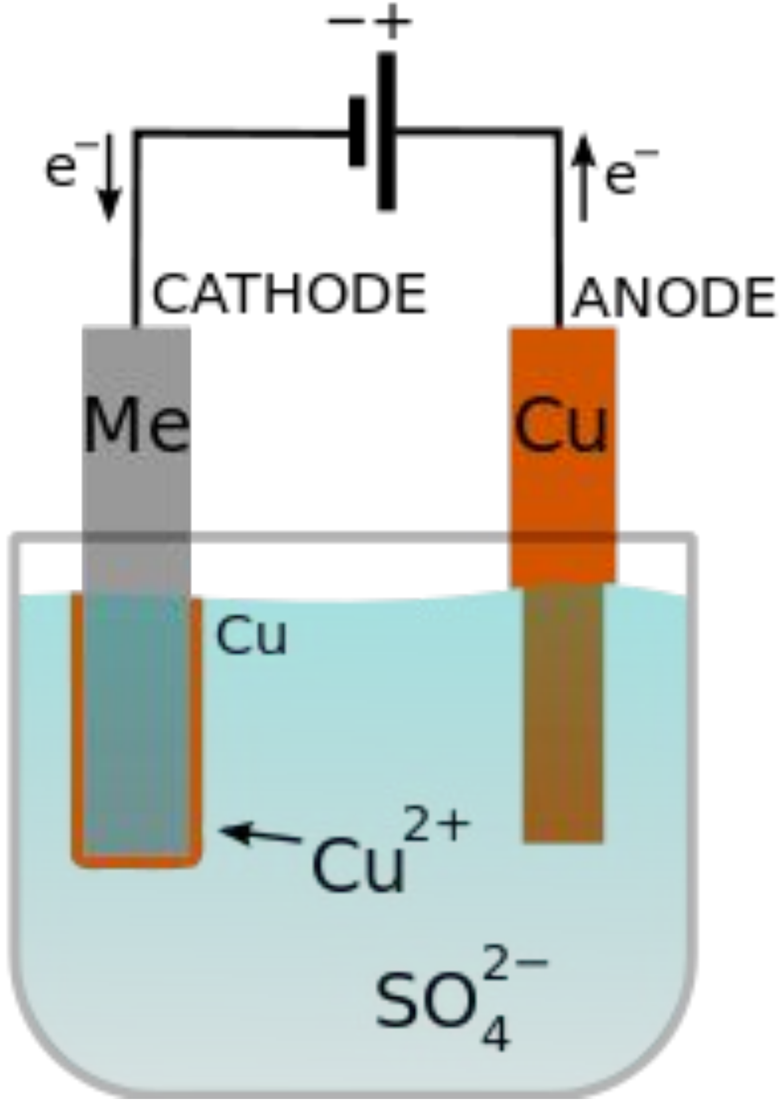


Figure 20.1 Some applications of electrolysis in daily life

ELECTROPLATING

An electrolytic process of Formation of a thin protective coating of a non-reactive or superior metal on an article made of a more reactive or inferior metal.



Purpose:

- To protect the article from rusting
- To make the article look better
- Most commonly used metals for electroplating: Copper, Chromium, Silver, Tin
- The anode usually is made of the plating metal. The object to be plated is the cathode.

Electrometallurgy:

Electrometallurgy is the process of extraction of metal from ore by electrolysis.

Manufacture of metals: The metals like sodium, potassium, magnesium, calcium aluminum, etc., are obtained by electrolytes of fused electrolytes.

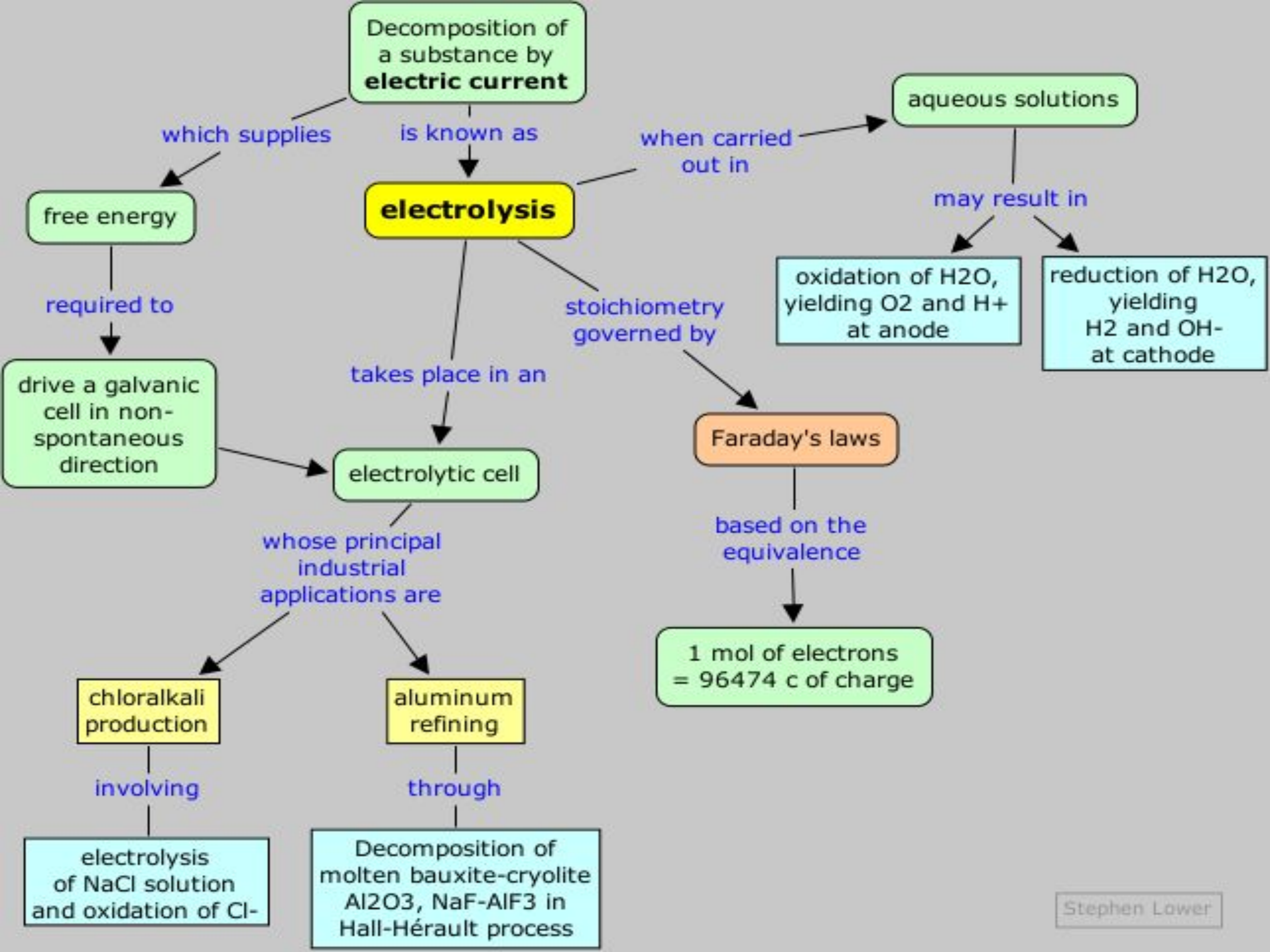
Manufacture of non-metals: Non-metals like hydrogen, fluorine, chlorine are obtained by electrolysis.

Electro-refining of metals: This is the process of refining the metal. i.e. removing impurity from metal by the use of electrolysis method. The metals like copper, silver, gold, aluminum, tin, etc., are refined by electrolysis.

Manufacture of compounds: Compounds like NaOH, KOH, Na_2CO_3 $KClO_3$, white lead, $KMnO_4$, etc., are manufactured by electrolysis.

Electroplating: The process of coating an inferior metal with a superior metal by electrolysis is known as electroplating. The aims of electroplating are:

- To prevent the inferior metal from corrosion.
- To make it more attractive in appearance.


Decomposition of a substance by **electric current**
which supplies
is known as
when carried out in
aqueous solutions
free energy
electrolysis
may result in
oxidation of H2O, yielding O2 and H+ at anode
reduction of H2O, yielding H2 and OH- at cathode
required to
stoichiometry governed by
takes place in an
drive a galvanic cell in non-spontaneous direction
Faraday's laws
electrolytic cell
based on the equivalence
whose principal industrial applications are
1 mol of electrons = 96474 c of charge
chloralkali production
aluminum refining
involving
through
electrolysis of NaCl solution and oxidation of Cl-
Decomposition of molten bauxite-cryolite Al2O3, NaF-AlF3 in Hall-Hérault process
Stephen Lower