Electrolysis
Topic 4 – Chemical Changes

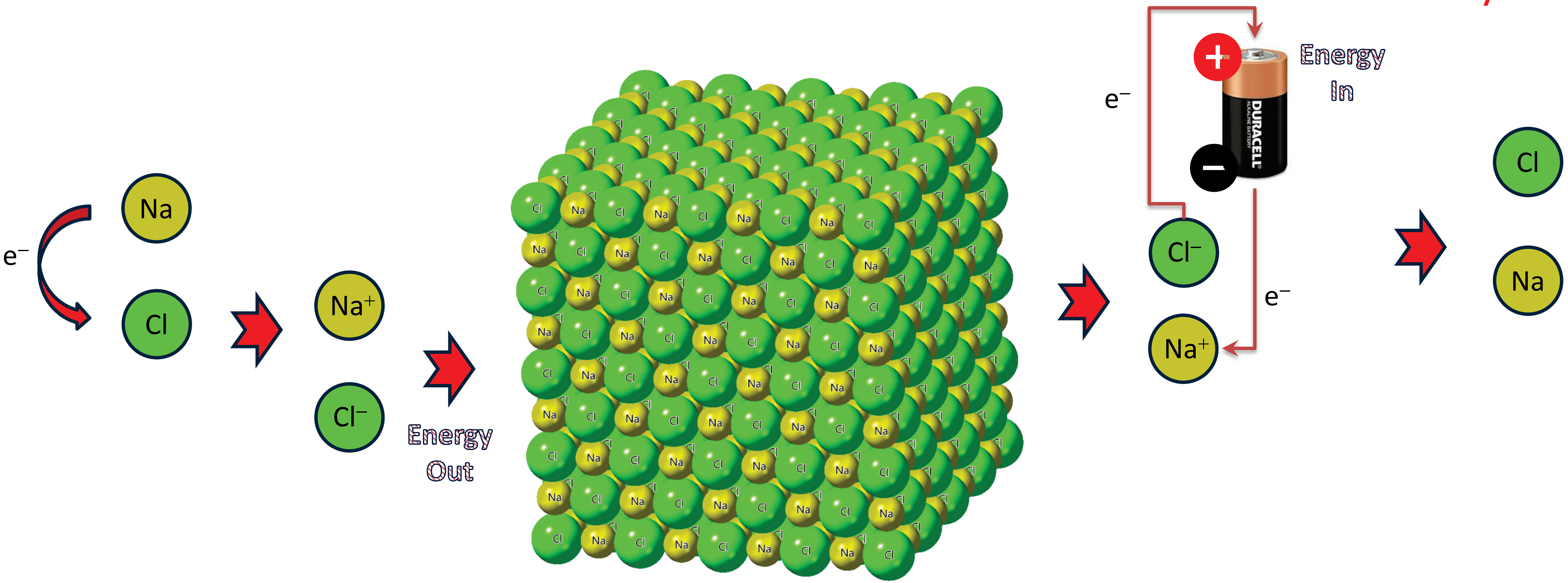
Dr Mark S. D. Read
School of Chemistry

Nuclear Education and Research Centre
www.chem.bham.ac.uk

Electrolysis

Electrolysis: ‘Splitting Up’ using Electricity

Electrolysis:



e^-

Na

Cl

Na^+

Cl^-

Energy Out

e^-

Energy In

Cl^-

Na^+

e^-

Cl

Na

Electrolysis

Electrolysis: ‘Splitting Up’ using Electricity

Electrolysis:

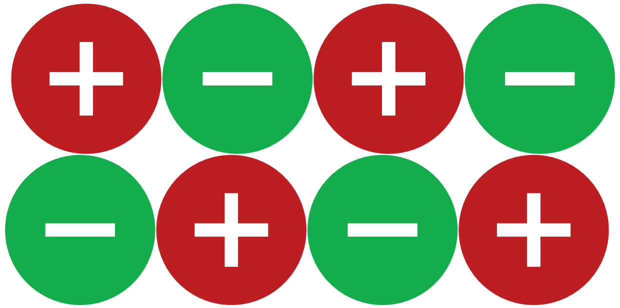
> “The process of using electricity to break down an ionic compound into its elements”

- ○ An electric current is passed through a molten or aqueous ionic substance
- ○ When molten or in solution, ions are mobile – allowing them to move to electrodes
- ○ +’ve Ions (cations) move to the cathode (–’ve electrode) and gain e^-’s (reduction)
- ○ –’ve Ions (anions) move to the anode (+’ve electrode) and lose e^-’s (oxidation)
- ○ This overall process splits the compound into simpler substances or elements

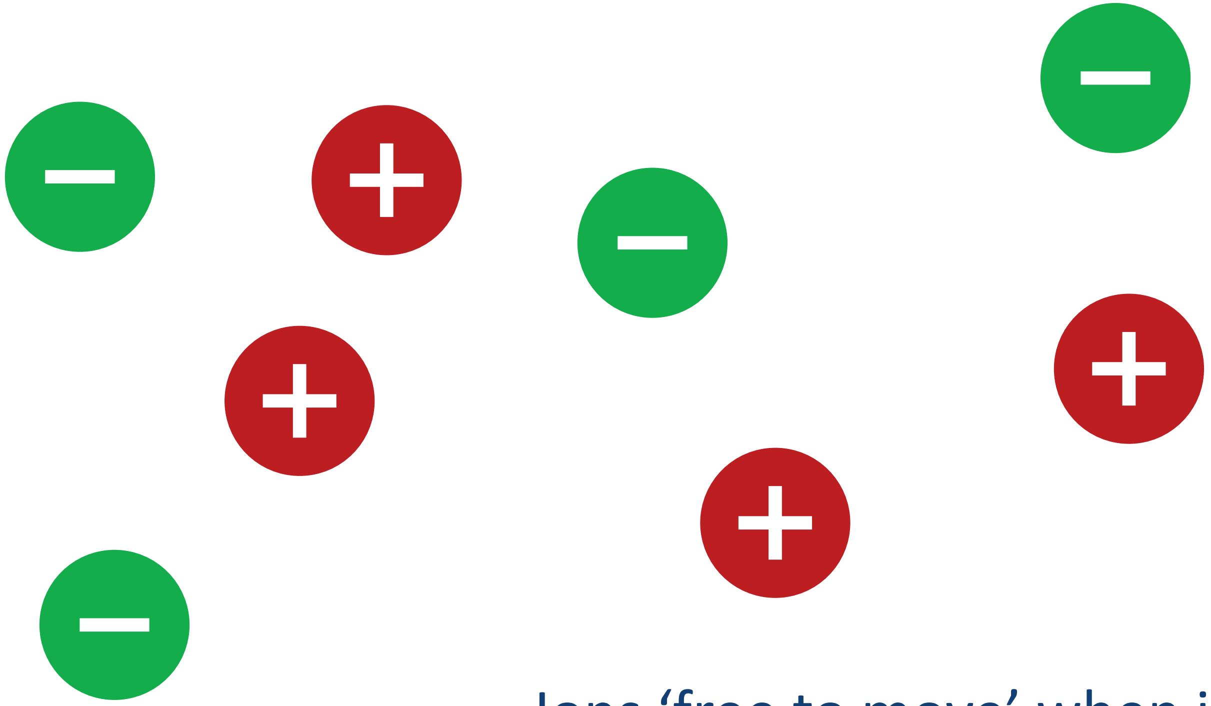
Electrolysis

Electrolysis: ‘Splitting Up’ using Electricity

During electrolysis, an electric current is passed through an **electrolyte**.
The electrolyte is a **molten** or **dissolved** ionic compound.
It must be molten or dissolved so that the ions are **free to move**.



Ions ‘trapped’ in ionic lattice



Ions ‘free to move’ when in molten liquid or dissolved!

Electrolysis

Electrolysis: ‘Splitting Up’ using Electricity

Ions move towards the electrodes, where they react and the compound **decomposes**.

Positive Ions in the electrolyte move towards the Negative electrode (Cathode)
and gain electrons (they are reduced) [OILRIG]

Negative Ions in the electrolyte move towards the Positive electrode (Anode)
and lose electrons (they are oxidised) [OILRIG]

This creates a ‘flow of charge’ through the electrolyte as ions travel to electrodes

As ions gain or lose electrons:
they form the uncharged element and are discharged from the electrolyte

Electrolysis

Electrolysis of Molten Ionic Solids Forms Elements

Ionic Solids:

can't be electrolysed because ions in fixed positions and can't move!

Molten Ionic Compounds:

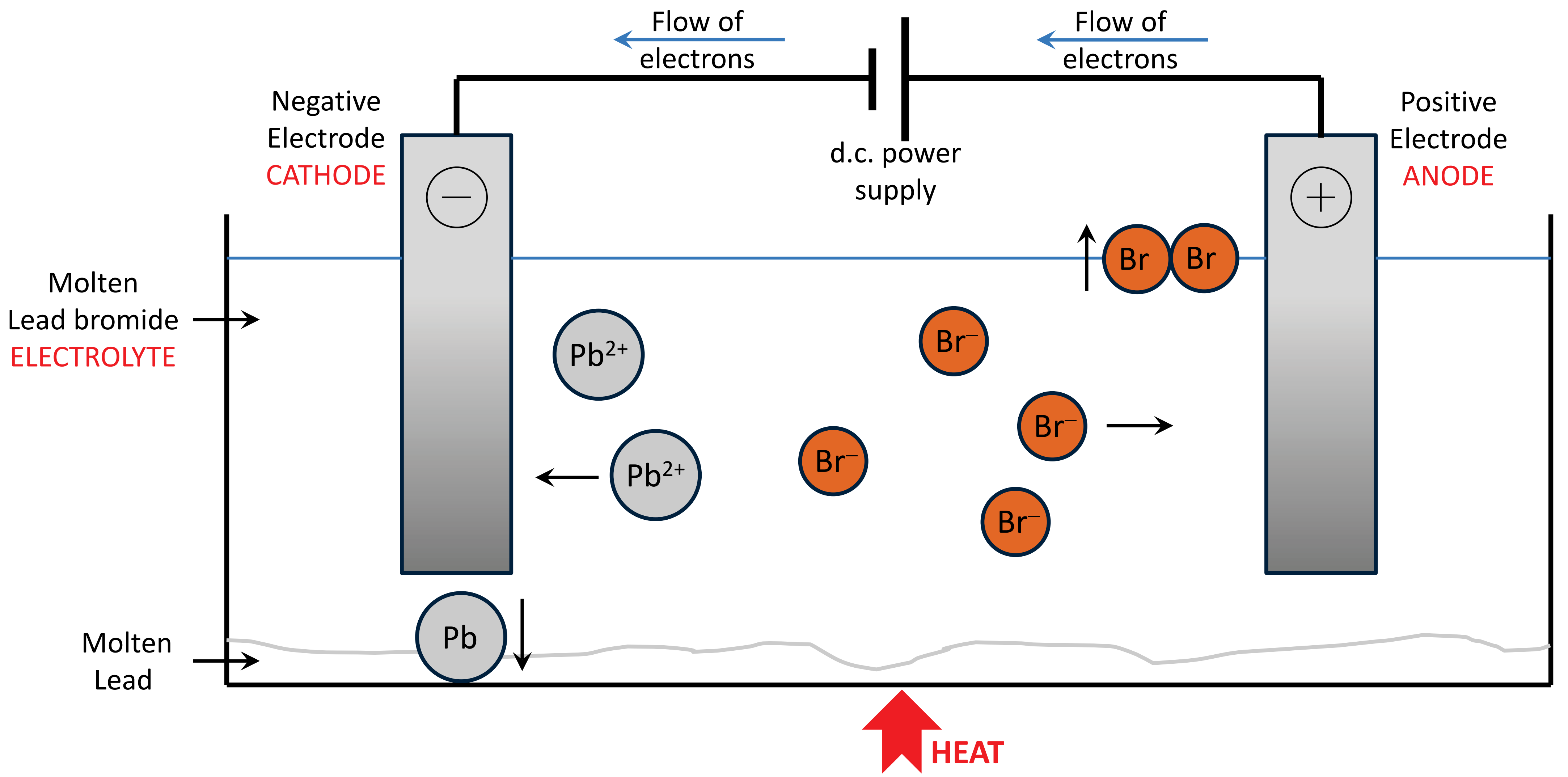
can be electrolysed because ions can move freely and conduct electricity

Molten Ionic Compounds are always broken up into their elements.

e.g. electrolysis of molten lead bromide ($PbBr_2$)

Electrolysis

Electrolysis of Molten Ionic Solids Forms Elements



Electrolysis

Electrolysis of Molten Ionic Solids Forms Elements

Electrodes should be made of an inert material so they do not react with the electrolyte.

Positive metal ions are reduced to the element at the cathode:

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

Negative non-metal ions are oxidised to the element at the anode:

$$\boxed{2Br^{-} \rightarrow Br_2 + 2e^{-}}$$

Both of these equations are ‘half equations’

Electrolysis

Electrolysis: Metals can be Extracted From Their Ores Using Electrolysis

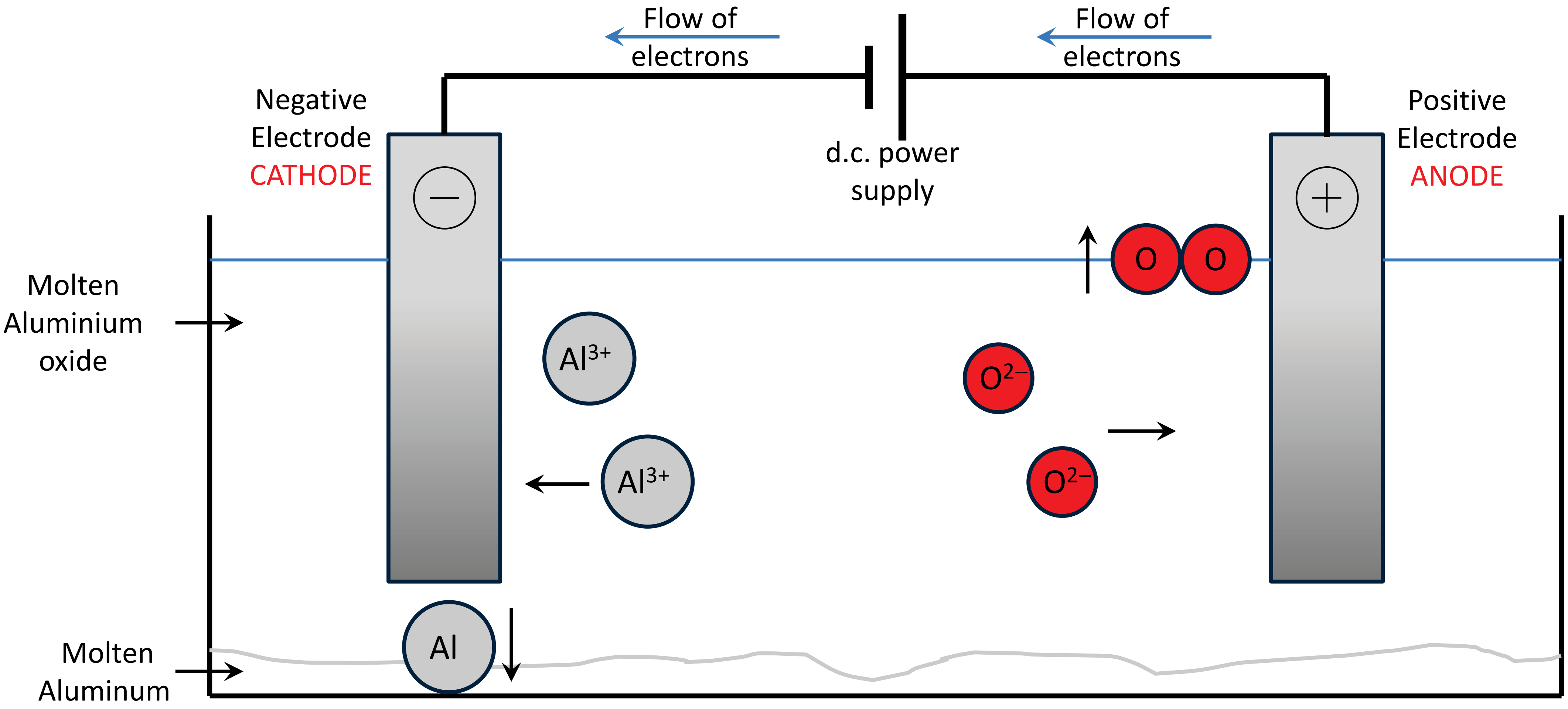
If a metal is too reactive to be reduced with carbon, or reacts with carbon:

Electrolysis can be used to extract it. BUT extraction via this method is very expensive as a lot of energy is required to melt the ore and produce the required current.

1. Aluminium is extracted from the ore bauxite by electrolysis. Bauxite contains aluminium oxide, Al_2O_3
2. Al_2O_3 has a very high melting temperature, so is mixed with cryolite to lower the m.p.
3. The molten mixture contains free ions – so it will conduct electricity.
4. Positive Al^{3+} ions are attracted to the negative electrode, each picking up $3e^-$ and turn into neutral Al atoms. These sink to the bottom of the electrolysis tank.
5. Negative O^{2-} ions are attracted to the positive electrode, each loosing $2e^-$ to become neutral O atoms which combine to form O_2 molecules.

Electrolysis

Electrolysis: Extraction of Al from Bauxite



Anode made of Carbon and needs to be replaced regularly as it reacts with O_2 to produce CO_2!

Electrolysis

Electrolysis: Extraction of Al from Bauxite

Positive metal Al^{3+} ions are reduced to the element at the cathode: aluminium is produced

$$\boxed{\mathrm{Al^{3+} + 3e^- \rightarrow Al}}$$

Negative non-metal O^{2-} ions are oxidised to the element at the anode: oxygen is produced

$$\boxed{\mathrm{2O^{2-} \rightarrow O_2 + 4e^-}}$$

Overall Equation combine these ‘half equations’

$$\left.\begin{array}{lll} \mathrm{Al^{3+} + 3e^- \rightarrow Al} & \times 4 & \mathrm{4Al^{3+} + 12e^- \rightarrow 4Al} \\ \mathrm{2O^{2-} \rightarrow O_2 + 4e^-} & \times 3 & \mathrm{6O^{2-} \rightarrow 3O_2 + 12e^-} \end{array}\right\} \qquad \mathrm{4Al^{3+} + 6O^{2-} + \cancel{12}e^- \rightarrow 4Al + 3O_2 + \cancel{12}e^-}$$

$$\boxed{\begin{array}{c} \text{aluminium oxide} \rightarrow \text{aluminium + oxygen} \\ \mathrm{2\,Al_2O_{3\,(l)} \rightarrow 4\,Al_{\,(l)} + 3\,O_{2\,(g)}} \end{array}}$$

Electrolysis

Electrolysis of Aqueous Solutions

When conducting electrolysis on an aqueous solution – have to factor in the ions in water!

It May be Easier to Discharge Ions from Water than the Solute!

1. In aqueous solutions, as well as the ions from ionic compounds, there will be hydrogen ions (H^+) and hydroxide ions (OH^-) from the water: $H_2O_{(l)} \leftrightarrows H^+_{(aq)} + OH^-_{(aq)}$
2. Which ions are discharged at the electrodes when the solution is electrolysed will depend on the relative reactivity of all the ions in the solution.

Electrolysis of Aqueous Solutions

Cathode Reactions

During electrolysis of aqueous solutions, +'ve Ions (cations) move to the cathode (–'ve electrode) where they are reduced (they gain electrons)

If more than one type of +'ve Ion is present,

the ion that is easier to reduce will be discharged

The ion lower in the reactivity series is discharged first:

e.g. Copper is less reactive than hydrogen,

Electrolysis of Aqueous Solutions

Cathode Reactions

e.g. Copper is less reactive than hydrogen, so:

$$Cu^{2+} + 2\,e^{-} \rightarrow Cu$$ (solid copper)

Happens more easily than

$$2\,H^{+} + 2\,e^{-} \rightarrow H_2$$ (hydrogen gas)

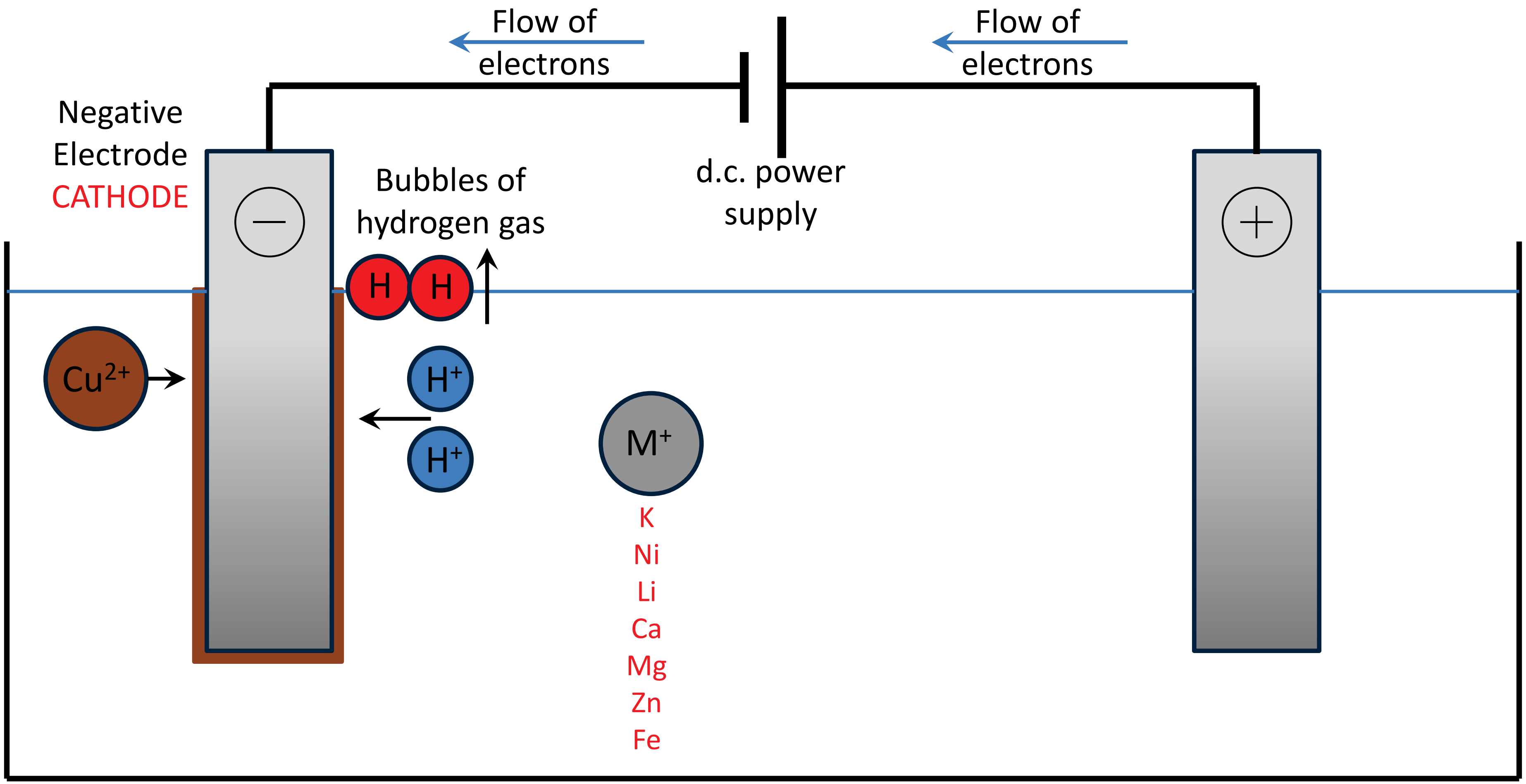
Therefore Cu^{2+} ions are discharged in preference to H^{+} ions

Because Cu is below H in the reactivity series, Cu^{2+} ions accept e^{-}'s more readily than H^{+} ions

- Copper metal is produced at the cathode
- Hydrogen is not produced (its ions are not discharged when copper ions are present)

Electrolysis of Aqueous Solutions

Anode Reactions



$H_{2(g)}$ ↑ UNLESS M less reactive (i.e. Cu)

K > Ni > Li > Ca> Mg > C > Zn > Fe > H > Cu

Electrolysis of Aqueous Solutions

Anode Reactions

During electrolysis of aqueous solutions, –'ve Ions (anions) move to the anode (+'ve electrode) where they are oxidised (they loose electrons)

However, not all anions are equally easy to oxidise!

The anode discharges the ion that is easiest to oxidise

If halide ions (Cl^-, Br^- and I^-) are present in the solution,
they are discharged before hydroxide ions (OH^-) because:

Halide ions require less energy to lose electrons

Their oxidation reactions are more favourable than oxidising hydroxide to oxygen.

Electrolysis of Aqueous Solutions

Anode Reactions

E.g. **Oxidation of chloride ions (Cl⁻)**

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

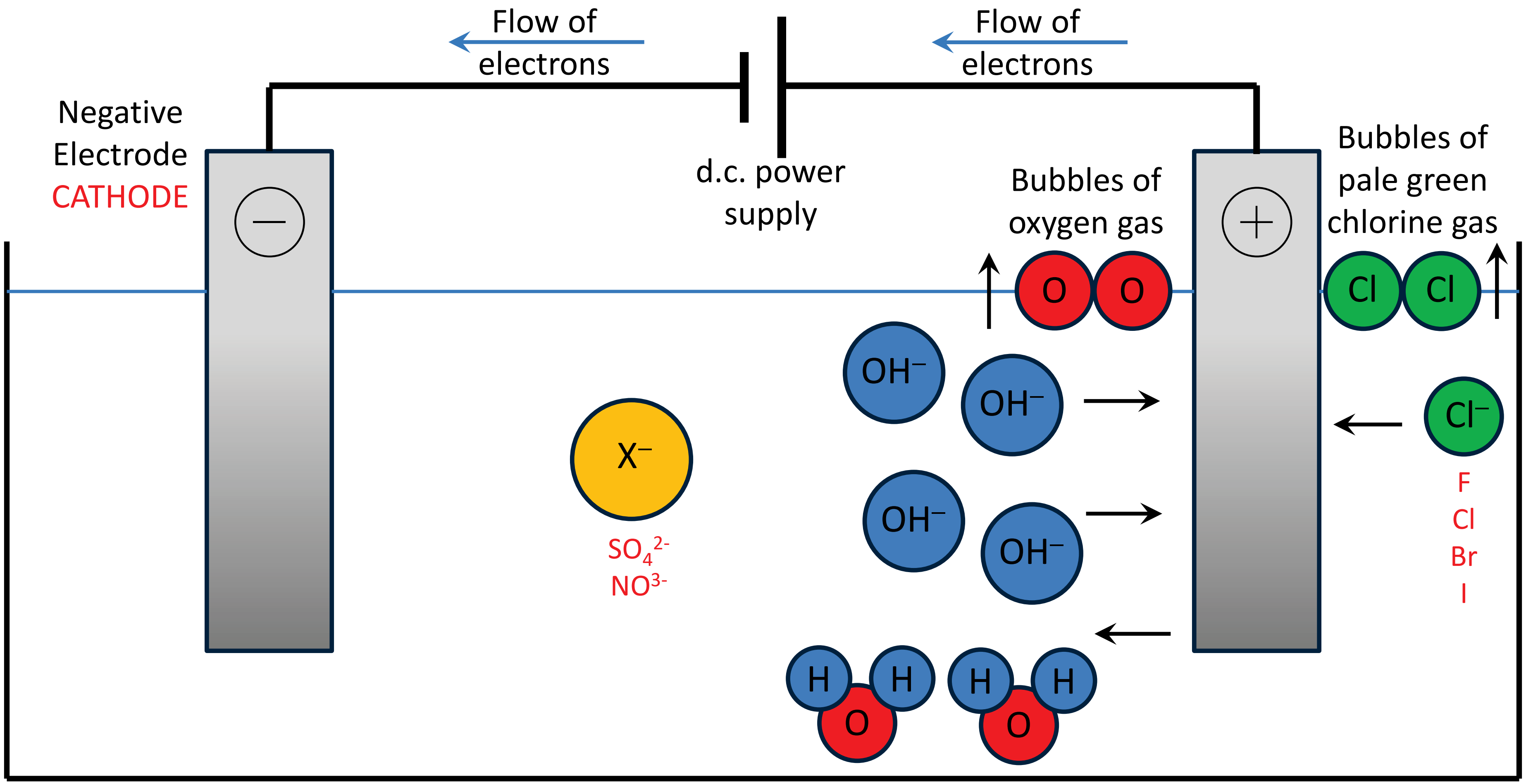
Hydroxide oxidation (only happens if there are no halides!)

$$4\,OH^- \rightarrow O_2 + 2\,H_2O + 4\,e^-$$

The hydroxide reaction needs more energy, so it only happens when no halides are available!

Electrolysis of Aqueous Solutions

Anode Reactions



$O_{2(g)}$ ↑ UNLESS X is a Halogen (Group 7)
F, Cl, Br or I

Electrolysis

Electrolysis of Aqueous Solutions

Cathode

- At the cathode, if H^+ ions and metal ions are present, hydrogen gas will be produced if the metal ions form an elemental metal that is more reactive than hydrogen (e.g. Na^+)
- If the metal ions form an elemental metal that is less reactive than hydrogen (e.g. Cu^{2+}), a solid layer of the pure metal will be produced instead, which will coat the cathode.

Anode

- At the anode, if OH^- ions and halide ions (Cl^-, Br^-, I^-) are present, molecules of halide gas will be produced (Cl_2, Br_2, I_2)
- If no halide ions are present, then the OH^- ions from the water will be discharged and oxygen gas (and water) will be formed.

Electrolysis

Example 1: Electrolysis of Copper Sulfate Solution

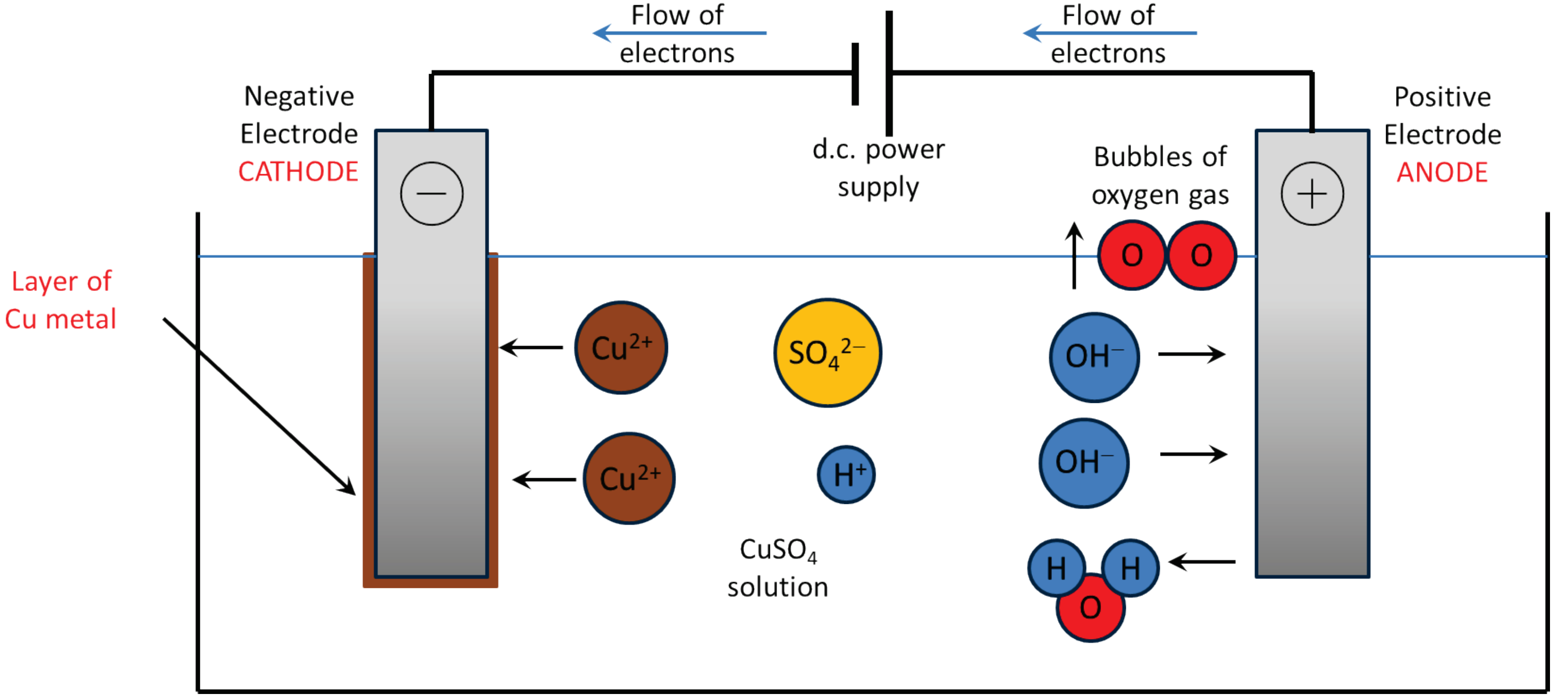
A solution of copper (II) sulfate ($CuSO_4$) contains 4 different ions: Cu^{2+}, SO_4^{2-}, H^+ and OH^-

Copper metal is less reactive than hydrogen, so at the cathode, Cu coats the electrode

$$Cu^{2+} + 2e^- \rightarrow Cu$$

No halide ions are present, so oxygen and water are produced at the anode

$$4OH^- \rightarrow O_2 + 2H_2O + 4e^-$$



Electrolysis

Example 2: Electrolysis of Sodium Chloride Solution

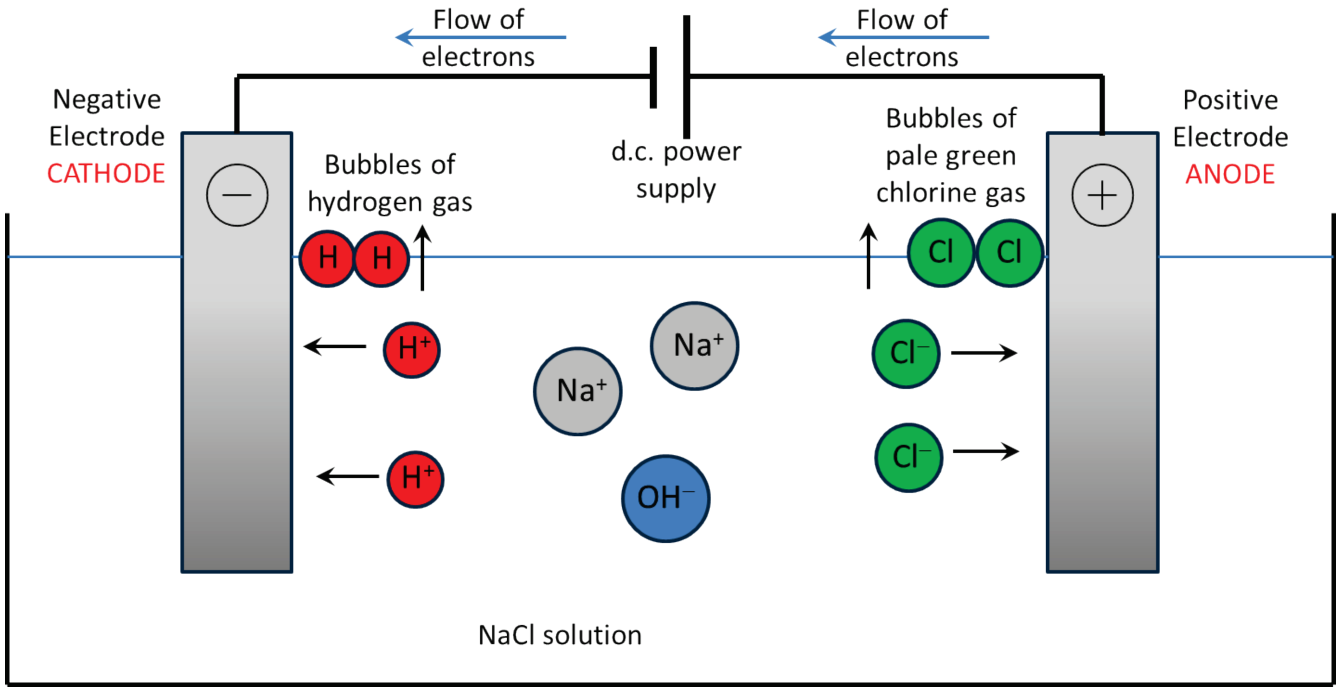
A solution of sodium chloride (NaCl) contains 4 different ions: Na^+, Cl^-, H^+ and OH^-

Sodium metal is MORE reactive than hydrogen, so at the cathode, Hydrogen gas produced

$$2H^+ + 2e^- \rightarrow H_2$$

Chloride ions are present, so chlorine gas is produced at the anode

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



Electrolysis

Electrolysis of Aqueous Solutions

Testing gaseous products

- Chlorine bleaches damp litmus paper, turning it white
- Hydrogen makes a “squeaky pop” with a lighted splint
- Oxygen will relight a glowing splint

Electrolysis

The Half Equations – Ensure the Electrons Balance

Half equations show reactions at the electrodes (ions or atoms gaining or losing electrons)

Half equations for the reactions at both electrodes combine to give the ionic equation for the overall reaction. N.B. number of electrons shown in each half equation must be the same.

For the electrolysis of aqueous sodium chloride solution, the half equations are:

–'ve Cathode: $2H^+ + 2e^- \rightarrow H_2$

+'ve Anode: $2Cl^- \rightarrow Cl_2 + 2e^-$

Combine to give the ionic equation: $2H^+ + 2Cl^- \rightarrow H_2 + Cl_2$

Remember, if no halide ions present in aqueous solution, OH^- ions are discharged at the Anode: $4OH^- \rightarrow O_2 + 2H_2O + 4e^-$

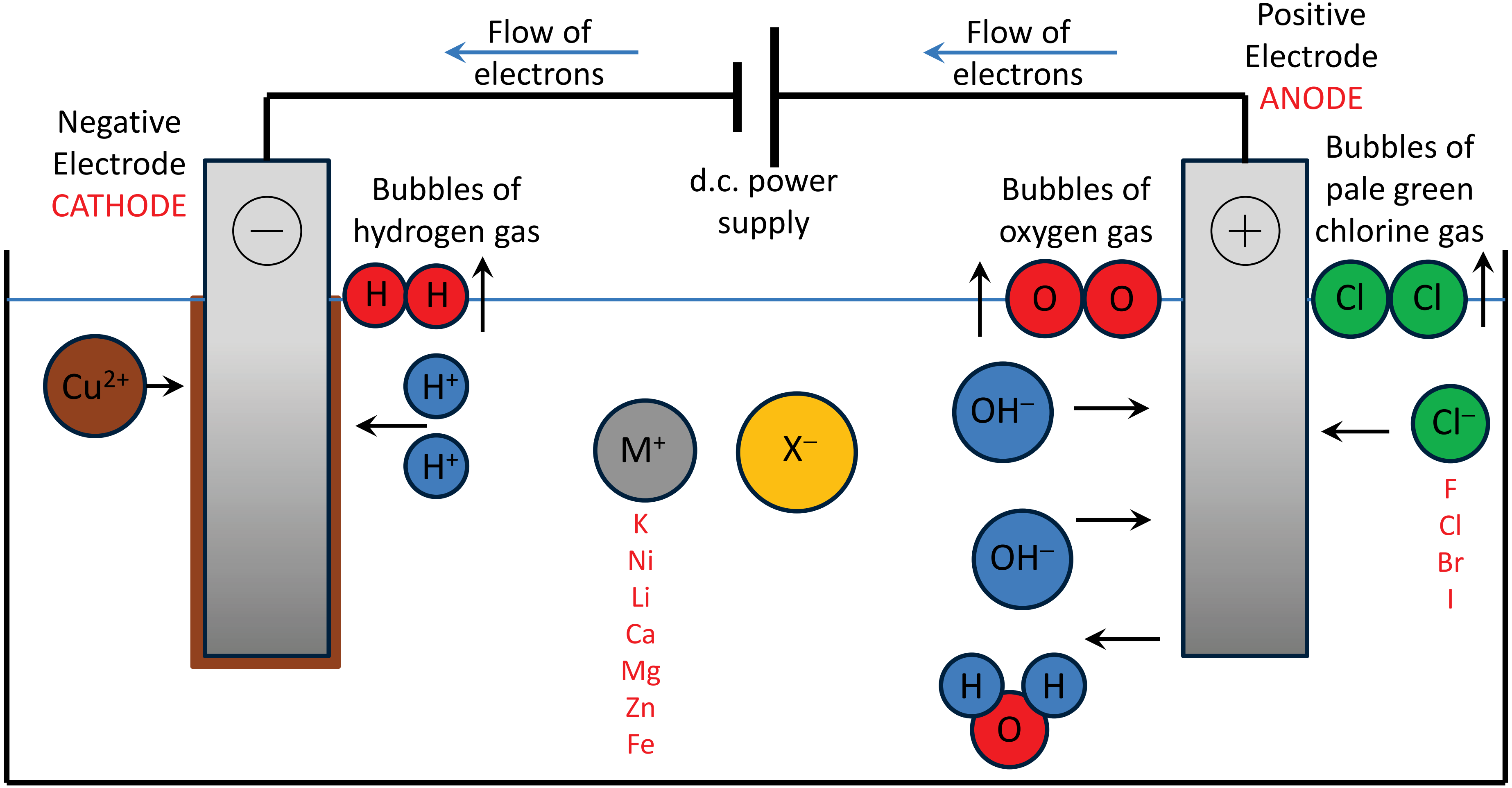
Electrolysis

The Reactivity Series of Metals

Potassium	K	VERY Reactive
Sodium	Na	
Lithium	Li	
Calcium	Ca	
Magnesium	Mg	Fairly Reactive
Carbon	C	
Zinc	Zn	
Iron	Fe	
Hydrogen	H	Not Very Reactive
Copper	Cu	

Electrolysis

Essential Summary – Aqueous Solutions



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