4 Electrolysis

Candidates should be able to:

(a) describe electrolysis as the conduction of electricity by an ionic compound (an electrolyte), when molten or dissolved in water, leading to the decomposition of the electrolyte

(b) describe electrolysis as evidence for the existence of ions which are held in a lattice when solid but which are free to move when molten or in solution

(c) describe, in terms of the mobility of ions present and the electrode products, the electrolysis of molten lead bromide, using inert electrodes

(d) predict the likely products of the electrolysis of a molten compound

(e) apply the idea of selective discharge (linked to the reactivity series for cations, see 9.2) to deduce the electrolysis products of aqueous solutions; describe the electrolysis of concentrated aqueous sodium chloride, aqueous copper(II) sulfate and dilute sulfuric acid using inert electrodes

(f) predict the likely products of the electrolysis of an aqueous electrolyte, given relevant information

(g) construct equations for the reactions occurring at each electrode (anode and cathode) during electrolysis

(h) describe the electrolysis of purified aluminium oxide dissolved in molten cryolite as the method of extraction of aluminium (see 9.5(a))

(i) describe the electrolysis of aqueous copper(II) sulfate with copper electrodes as a means of purifying copper

(j) describe the electroplating of metals, including copper plating, and recall one use of electroplating

(k) describe the production of electrical energy from simple cells (i.e. two electrodes in an electrolyte) linked to the reactivity series (see 9.2)

اَللّٰھُمَّ اِنِّیۡۤ اَسۡئَلُکَ عِلۡمًا نَّافِعًا وَّ عَمَلًا مُّتَقَبَّلًا (مشکوٰۃ)
وَّ رِزۡقًا طَیِّبًا ۝

6th September, 2021

اے اللہ میں تجھ سے نفع دینے والے علم، اور قبول ہونے والے عمل اور پاکیزہ رزق کا سوال کرتا ہوں۔ (آمین)

Electrolysis

Electrochemistry

Electro → Electricity

Chemistry → Chemical reaction or change

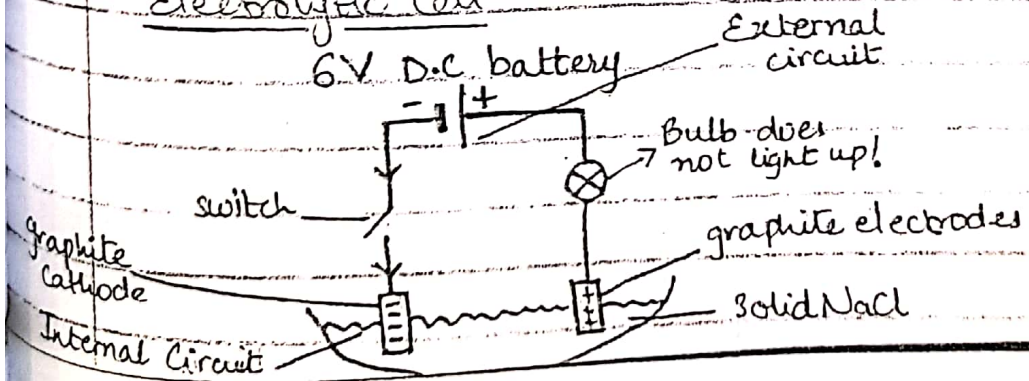
→ It is a branch of chemistry that deals with the conversion of electrical energy into chemical energy and chemical energy into electrical energy.

How? Device

Cell

- Electrolytic cell → Conversion of electrical energy into chemical energy.
  - an electrolytic cell, Electrical energy brings about a redox reaction
- Voltaic, Galvanic, Simple Chemical Cell → Conversion of chemical energy into electrical energy.
  - In a voltaic cell, a redox reaction produces electricity

Electrolytic Cell



→ Bulb does not light: solid NaCl is a non-conductor of electricity.

carbon in the form of graphite

→ Elements conduct electricity due to freely moving electrons
(metals)

→ If compounds conduct electricity they are ionic compounds & conduct electricity due to freely moving ions.

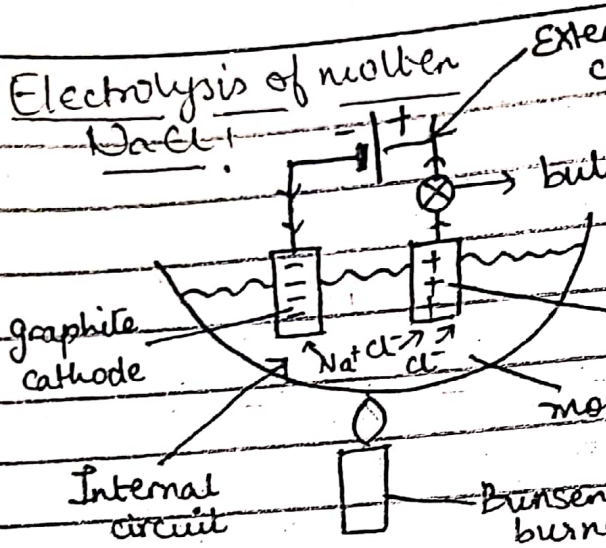
⊙⟹ Ionic compounds have ↑ m.p. because of strong electrostatic forces of attraction b/w oppoite ions which need large amounts of energy to breake.

→ External circuit – current flows due to the movement of electrons!

→ Internal circuit – current flows due to the movement of ions!
↓
Electrolyte

Electrolytic cell has a battery but voltaic cell does not have a battery.

Electrolysis of molten NaCl



⇒ We use china dish because it is made from refra material that ha a high mp & bp compounds have very high melti point. Beakers cannot be used because they can withstand such a high temperature.

Cathode (−)

$Na^+_{(l)} + 1e^- \longrightarrow Na_{(l)}$ (Reduction)

Anode (+)

$2Cl^-_{(l)} \longrightarrow Cl_{2(g)} + 2e^-$ (Oxidation)

Greenish yellow fumes of Cl_2 are seen at the anode.

Overall Equation

$2Na^+_{(l)} + 2Cl^-_{(l)} \longrightarrow 2Na_{(l)} + Cl_{2(g)}$

Electrolysis

Electro — Electricity

Lysis — break down

→ Decomposition of a compound (Electrolyte) into its comp by the passage of electricity is electrolysis.

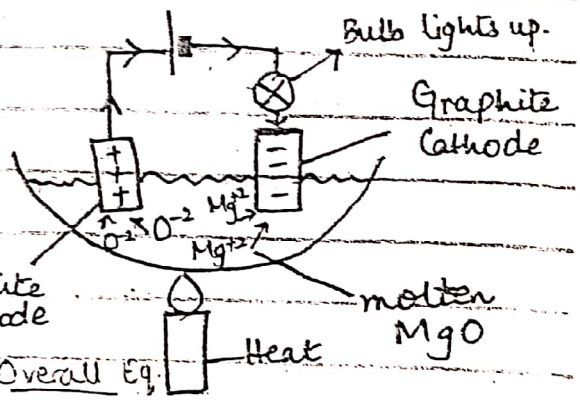
Electrolyte

→ Electrolytes are the molten or aqueous compounds which conduct electricity due to the presence of freely moving ions. Their examples are :-

① Ionic compounds in their molten and aqueous states.
② Acids and alkalis in their aqueous solutions.

Electrolyte	Conductors
→ Electrolytes are compounds	Conductors are elements.
→ " conduct electricity in their molten and aqueous state only.	" conduct electricity in their molten and solid states both.
→ Electrolytes have freely moving ions.	Conductors have freely moving electrons.
→ Electrolytes pass electricity by undergoing a chemical change.	Conductors pass electricity without undergoing a chemical change.

① Electrolysis of molten MgO



Cathode (−)

$Mg^{+2}_{(l)} + 2e^- \longrightarrow Mg_{(l)}$ (reduction)

Anode (+)

$2O^{-2}_{(l)} \longrightarrow O_{2(g)} + 4e^-$ (oxidation)

Overall Eq.

$2Mg^{+2}_{(l)} + 2O^{-2}_{(l)} \longrightarrow 2Mg_{(l)} + O_{2(g)}$

② Electrolysis of molten Al_2O_3 . .

Cathode (−)

$$Al^{+3}_{(l)} + 3\bar{e} \longrightarrow Al_{(l)}$$

Anode (+)

$$2O^{-2}_{(l)} \longrightarrow O_{2(g)} + 4\bar{e}$$

Overall Equation

$$4\,Al^{+3}_{(l)} + 6\,O^{-2}_{(l)} \longrightarrow 4\,Al_{(l)} + 3\,O_{2(g)}$$

Aqueous solution = A solution in which water is the solvent is an aq solution.

Electrolysis of aqueous solutions

Saturated solution
↓
solute can no longer dissolve in a given volume of solvent.

dilute solution (less amount of dissolved solute in a given volume of solvent).

concentrated solution (larger amount of dissolved solute in a given volume of solvent).

① Electrolysis of dilute aq NaCl.

next page! →

Electrolysis of dillute aq NaCl

$$Na^+Cl^-_{(s)} + H_2O_{(l)} \longrightarrow Na^+_{(aq)} + Cl^-_{(aq)}$$

$$H_2O_{(l)} \longrightarrow H^+_{(aq)} + OH^-_{(aq)}$$

6×10^8 molecules — 1 ion — 1 ion

Discharge Series

Cations

K^+
Na^+
Ca^{+2}
Mg^{+2}
Al^{+3}

Zn^{+2}
Fe^{+2}
Pb^{+2}
H^+
Cu^{+2}
Hg^{+2}
Ag^+
Au^{+3}
Pt^{+3}

Ability to discharge at the electrodes increases ↓

Anions

SO_4^{-2}	shoes
NO_3^{-1}	not
Cl^-	clothes
Br^-	bought
I^-	$
OH^-	Oh

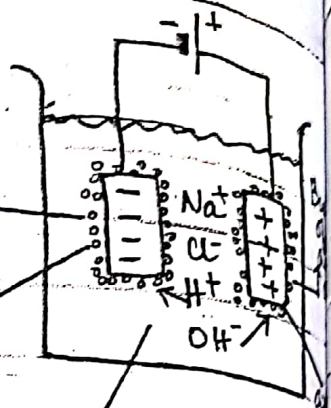
more reactive ← K — K^+ → less reactive

less reactive ← Pt — Pt^{+3} → more reactive

→ More reactive metals form less reactive ions while less reactive metals form more reactive ions.

Cathode (−) Na^+/H^+

$2H^+_{(aq)} + 2e^- \longrightarrow H_{2(g)}$



Anode (+) Cl^-/OH^-

$4OH^-_{(aq)} \longrightarrow O_{2(g)} + 2H_2O_{(l)} + 4e^-$

→ In carbon H_2O electrol not dilute H_2SO_4

Overall equation

$4H^+_{(aq)} + 4OH^-_{(aq)} \longrightarrow 2H_{2(g)} + O_{2(g)} + 2H_2O_{(l)}$

② Electrolysis of dilute aq $PbBr_2$

Cathode (−)

$2H^+_{(aq)} + 2e^- \longrightarrow H_{2(g)}$

Anode (+)

$4OH^-_{(aq)} \longrightarrow O_{2(g)} + 2H_2O_{(l)}$

Overall Equation

$4H^+_{(aq)} + 4OH^-_{(aq)} \longrightarrow 2H_{2(g)} + O_{2(g)} + 2H_2O_{(l)} + 4e^-$

③ Electrolysis of dilute aq $CuSO_4$

Cathode (−)

$Cu^{+2}_{(aq)} + 2e^- \longrightarrow Cu_{(s)}$

Anode (+)

$4OH^-_{(aq)} \longrightarrow O_{2(g)} + 2H_2O_{(l)} + 4e^-$

Overall Equation

$4OH^-_{(aq)} + 2Cu^{+2}_{(aq)} \longrightarrow 2Cu_{(s)} + O_{2(g)} + 2H_2O_{(l)}$

Observations at electrodes

- **Cathode**
  - → Deposition of pink solid
  - → Cathode increases in size
- **Anode**
  - → Bubbles are seen.
  - → Blue colour of the solution fades.

Nature of leftover solution

The nature of the left over solution will be acidic. This is due to the discharge of hydroxide ions at the anode which leaves behind excess of hydrogen ions in the solution

④ Electrolysis of dilute aq $AgNO_3$

Cathode (−)

$Ag^+_{(aq)} + 1e^- \longrightarrow Ag_{(s)}$

Anode (+)

$4OH^-_{(aq)} \longrightarrow O_{2(g)} + 2H_2O_{(l)} + 4e^-$

Overall Equation

$$4Ag^{+}_{(aq)} + 4OH^{-}_{(aq)} \longrightarrow 4Ag_{(s)} + O_{2(g)} + 2H_2O_{(l)}$$

Observation at electrodes

→ The cathode increases in size.
→ Bubbles are seen at the anode → oxygen released is insoluble in H
→ Deposition of a greyish solid at the cathode
silvery grey / silver / grey

Nature of left over solution

H+ ions are acidic

The left over solution will be acidic due to the discharge of hydroxide ions at the anode which leaves behind an excess of hydrogen ions in the solution

Factors affecting discharge of ions at electrode

① → Effect of concentration
② → Nature of electrode

Effect of concentration

→ In a concentrated aqueous solution, ions with greater concentration get preferential discharge even if they are above hydrogen and hydroxide ions in the discharge series but this prefrence is given only to those ions which are not above by more than two ions.

① Electrolysis of conc. aq NaCl or Electrolysis of dig NaCl

greater concentration

$NaCl_{(s)} + H_2O_{(l)} \longrightarrow Na^+_{(aq)} + Cl^-_{(aq)}$

$H_2O_{(l)} \longrightarrow H^+_{(aq)} + OH^-_{(aq)}$ — Lesser concentration

6×10^8 molecules 1 ion 1 ion

Cathode (−)

$2H^+_{(aq)} + 2e^- \longrightarrow H_{2(g)}$ (Reduction)

Anode (+)

$2Cl^-_{(aq)} \longrightarrow Cl_{2(g)} + 2e^-$ (Oxidation)

Overall Equation

$2H^+_{(aq)} + 2Cl^-_{(aq)} \longrightarrow H_{2(g)} + Cl_{2(g)}$

Nature of left over solution

The left over solution will be alkaline due to the discharge of hydrogen ions at the cathode which will leave behind an excess of hydroxide ions which are alkaline.

② Electrolysis of aq $ZnBr_2$

Cathode (−)

$$Zn^{+2}_{(aq)} + 2e^- \longrightarrow Zn_{(s)}$$

Anode (+)

$$2Br^-_{(aq)} \longrightarrow Br_{2(g)} + 2e^-$$

Overall Equation

$$Zn^{+2}_{(aq)} + 2Br^-_{(aq)} \longrightarrow Zn_{(s)} + Br_{2(g)}$$

Fumes are gases evolved from solution

Observations

→ Cathode increases in size/mass

→ Deposition of a grey solid at the cathode

→ Evolution of a reddish brown ~~gas~~ fumes at the anode

→ Solution around the anode will turn ~~reddish brown~~ orange red

Lish
⇒ Aqueous Bromine is orange red.
⇒ Aqueous Iodine is reddish brown.

Nature of left over solution

The left over solution will be neutral due to same number of hydrogen and hydroxide ions.

Excellent

13/09/2021

③ Electrolysis of aq. $CuSO_4$

Cathode (−)

$Cu^{+2}_{(aq)} + 2e^- \longrightarrow Cu_{(s)}$

Anode (+)

$4OH^-_{(aq)} \longrightarrow O_{2(g)} + 2H_2O_{(l)} + 4e^-$

Overall Equation

$2Cu^{+2}_{(aq)} + 4OH^-_{(aq)} \longrightarrow 2Cu_{(s)} + O_{2(g)} + 2H_2O_{(l)}$

Observations

→ Bubbles are seen at the anode
→ Deposition of a pink solid at the cathode
→ Cathode increases in size and mass
→ Blue solution will fade away (or turn colourless)

Nature of left-over solution

The left over solution will be acidic due to the discharge of hydroxide ions at the anode which leaves behind a greater concentration of hydrogen ions which are acidic.

④ Electrolysis of aq $AgNO_3$

Cathode (−)

$Ag^+_{(aq)} + 1e^- \longrightarrow Ag_{(s)}$ (Reduction)

Anode (+)

$4OH^-_{(aq)} \longrightarrow O_{2(g)} + 2H_2O_{(l)} + 4e^-$

Overall Equation

$4Ag^+_{(aq)} + 4OH^-_{(aq)} \longrightarrow 4Ag_{(s)} + O_{2(g)} + 2H_2O_{(l)}$

Observations:

→ Cathode increases in size and mass.
→ Deposition of a grey solid at the cathode.
→ Bubbles are seen at the anode.

Nature of left over solution

The left over solution will be acidic due to the discharge of hydroxide ions at the anode which leaves behind an excess of hydrogen ions (which are acidic) in the remaining solution.

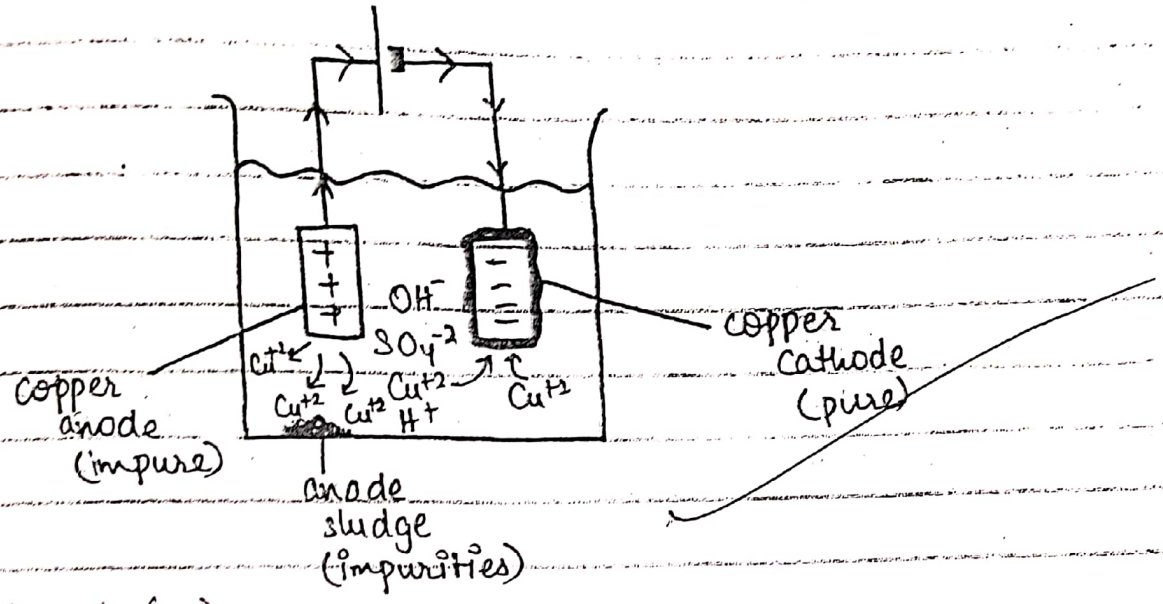
Effect of nature of Electrode on the discharge of ion

Types of Electrodes

Inert electrode
e.g graphite, platinum

Reactive electrode
e.g copper, silver, gold, iron etc.

① Electrolysis of aq $CuSO_4$ using copper electrodes



Cathode (−)

$$Cu^{+2}_{(aq)} + 2e^- \longrightarrow Cu_{(s)}$$

Anode (+)

$$Cu_{(s)} \longrightarrow Cu^{+2}_{(aq)} + 2e^-$$

No overall equation!

Observations

⇒ Cathode increases in size and mass

⇒ Anode decreases in size

⇒ Anode sludge (impurities) are seen below the anode

Note:-

⇒ The blue colour of the solution will remain blue because the concentration of Cu^{+2} ions in the solution will remain the same

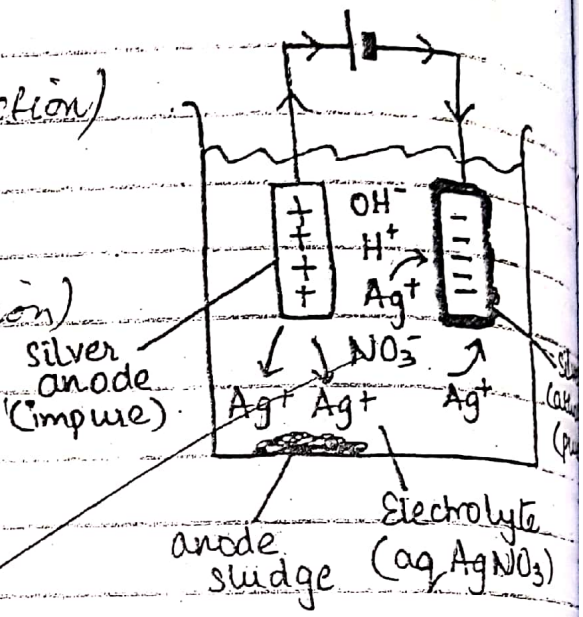
(2) Electrolysis of aq $AgNO_3$ using silver electrodes

Cathode (−)

$Ag^+_{(aq)} + 1\bar{e} \longrightarrow Ag_{(s)}$ (Reduction)

Anode (+) (Oxidation)

$Ag_{(s)} \longrightarrow Ag^+_{(aq)} + 1\bar{e}$



Observations

→ Cathode increases in size and mass.

→ Anode decreases in size.

→ Anode sludge (impurities) are seen below the anode.

Applications of Electrochemistry or Electrolysis

1. Purification or extraction of metals
2. Electroplating
3. Production of electricity by a chemical reaction (redox reaction)

(2) Electroplating

It is a process in which an expensive metal (for example copper, silver, gold, nickel) is deposited over a cheap metal by the process of electrolysis.

Purpose of Electroplating

→ To protect iron from rusting. (or to make metals resistant to corrosion)

→ To enhance the beauty of metals.

Types of Electroplating

→ Silver plating

→ Copper plating

→ Nickel plating

→ Gold plating

Excellent
29/09/2021

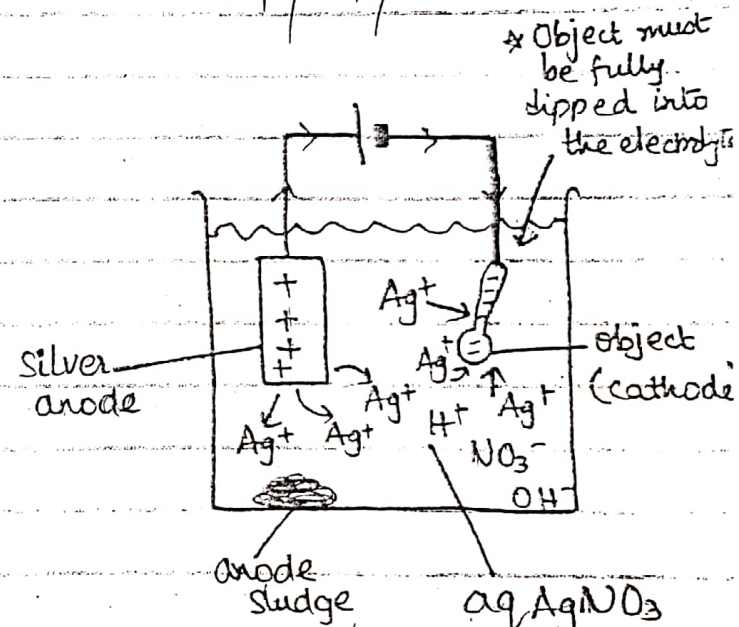
① Silver Plating

Cathode (−)

$Ag^{+}_{(aq)} + 1e^{-} \longrightarrow Ag_{(s)}$

Anode (+)

$Ag_{(s)} \longrightarrow Ag^{+}_{(aq)} + 1e^{-}$



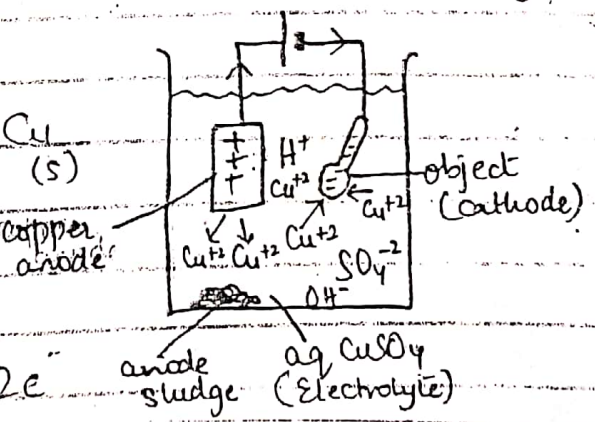
② Copper Plating

Cathode (−)

$Cu^{+2}_{(aq)} + 2e^{-} \longrightarrow Cu_{(s)}$

Anode (+)

$Cu_{(s)} \longrightarrow Cu^{+2}_{(aq.)} + 2e^{-}$



It must be a soluble compound of the metal to be electro-plated over the object. NO_3^- is the best option because all nitrates are soluble.

NOTE :⇒ The plate of the more reactive metal will be anode because anode is the electrode where oxidation takes place. Oxidation is the loss of electrons and more reactive metals have a greater tendency to loose electrons.

→ **Cathode**
Electrode where reduction takes place (reduction is the gain of electrons)

→ Electric current flows from the more reactive metal to the less reactive metal.

→ **Anode**
Electrode where oxidation takes place. (Oxidation is the loss of electrons)

⇒ $Cu + H_2SO_4 \longrightarrow$ No reaction

Eq. → $Zn_{(s)} + H_2SO_{4(aq)} \longrightarrow ZnSO_{4(aq)} + H_{2(g)}$

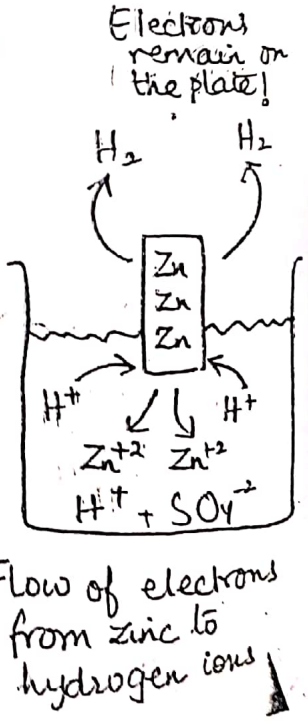
Ionic Eq → $Zn^0_{(s)} + 2H^+_{(aq)} \longrightarrow Zn^{+2}_{(aq)} + H_2^0{}_{(g)}$

reduced

Oxidised.

$Zn_{(s)} \longrightarrow Zn^{+2}_{(aq)} + 2e^-$ (Oxidation)

$2H^+ + 2e^- \longrightarrow H_{2(g)}$ (Reduction)



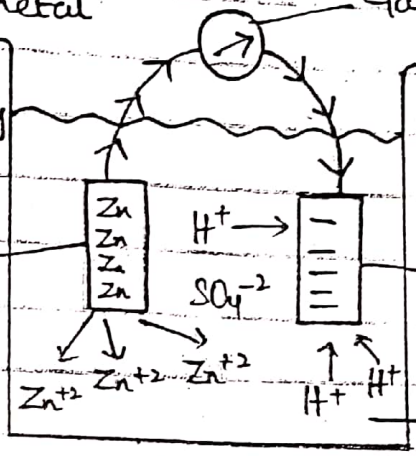
Flow of electrons from zinc to hydrogen ions

③ Production of Electricity by a Redox Reaction

Voltaic, Galvanic or Simple Chemical Cell.

Note :-

- Electrons will flow from the more reactive metal to the less reactive metal. The more the difference in reactivity of the metals, the greater will be the voltage produced.



(Tells the amount of voltage produced & the direction of flow of current)

Zinc plate (anode) → copper plate (cathode)

dillute H_2SO_4

↓

Plate will become negatively charged when zinc will form Zn^{+2} ions by the loss of electrons → The excess of electrons will produce a current as they will move to the copper plate.

(Electrons move from higher potential to lower potential)

Anode

$$Zn_{(s)} \longrightarrow Zn^{+2}_{(aq)} + 2e^- \quad \text{(Oxidation)}$$

Cathode

$$2H^+_{(aq)} + 2e^- \longrightarrow H_{2(g)} \quad \text{(Reduction)}$$

(3) Production of Electricity by a Redox Reaction

Voltaic, Galvanic or Simple chemical cell.

Note :-

* Electrons will flow from the more reactive metal to the less reactive metal. The more the difference in reactivity of the metals, the greater will be the voltage produced.

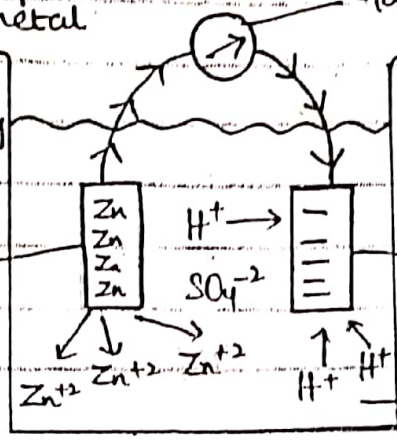


Plate will become negatively charged when zinc will form Zn^{+2} ions by the loss of electrons → The excess of electrons will produce a current as they will move to the copper plate. (Electrons move from higher potential to lower potential)

Anode

$Zn_{(s)} \longrightarrow Zn^{+2}_{(aq)} + 2e^-$ (Oxidation)

Cathode

$2H^+_{(aq)} + 2e^- \longrightarrow H_{2(g)}$ (Reduction)

⇒ Voltaic cells does not have a battery

Best voltaic cell is Mg, Ag cell because the first three metals are very reactive & the last two are very expensive!

Oxidation Half Cell

Excess of positive ions build up in the "oxidation half cell", due to the formation of Zn^{+2} ions from the zinc plate. This is due to the displacement reaction taking place:

$$Zn_{(s)} + CuSO_{4(aq)} \rightarrow ZnSO_{4(aq)} + Cu_{(s)}$$

Reduction Half Cell

Excess of negative ions build up in the "reduction half cell" due to the discharge of Cu^{+2} ions at the cathode.

This builds up a concentration difference that allows a fast flow of positive ions from the oxidation half cell to the reduction half cell. (Function of porous partition)

not in syllabus!

⇒ Reactivity does not depend upon the number of electrons gained or lost, but it depends on "how EASILY" electrons are lost or gained by an atom

The voltaic cell will stop working either when the zinc plate finishes or when there are no more positive ions in the reduction half cell.

Redox Reaction is producing an electric current!

⇒ Reactivity of metals depends on their tendency to loose electrons. Metals form cations (+ive ions)

Construction of a voltaic cell by using a porous partition or a salt bridge.

$$Zn^{0}_{(s)} + Cu^{+2}SO_4{}_{(aq)} \longrightarrow Zn^{+2}SO_4{}_{(aq)} + Cu^{0}$$

(Blue ⟶ Colourless)

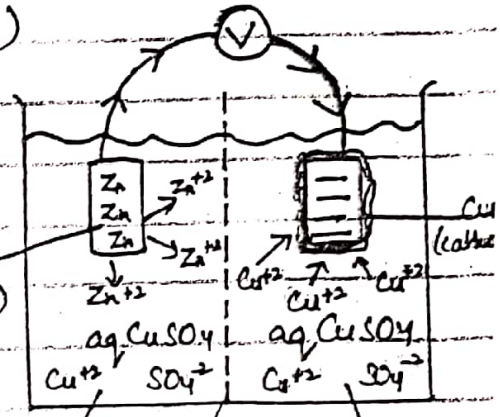
☆ ⇒ To increase the voltage produced, metals with a greate difference in their reactivity should be used! (as in the simple voltaic cell)

Anode

$$Zn_{(s)} \longrightarrow Zn^{+2}_{(aq)} + 2e^{-} \quad \text{(Oxidation)}$$

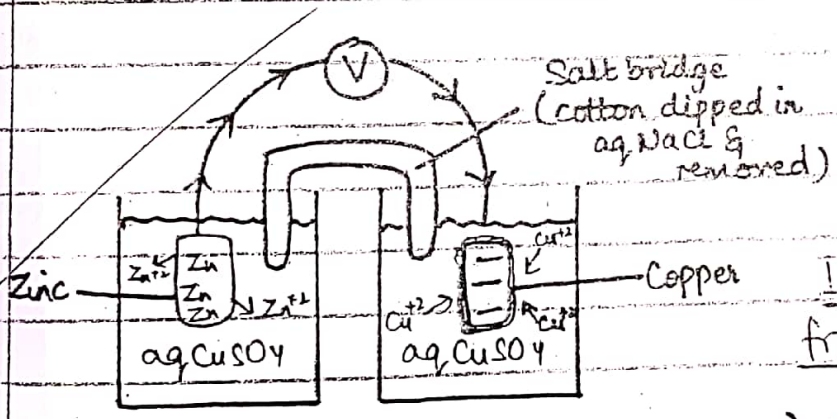
Cathode

$$Cu^{+2}_{(aq)} + 2e^{-} \longrightarrow Cu_{(s)} \quad \text{(Reduction)}$$



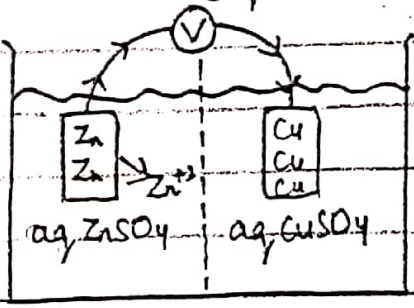
Oxidation Half Cell

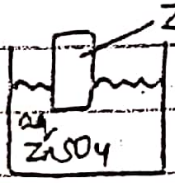
Reduction Half Cell



Porous Partition (purpose not in syllabus!)

If the voltaic cell is made from $ZnSO_4{}_{(aq)}$ & $CuSO_4{}_{(aq)}$





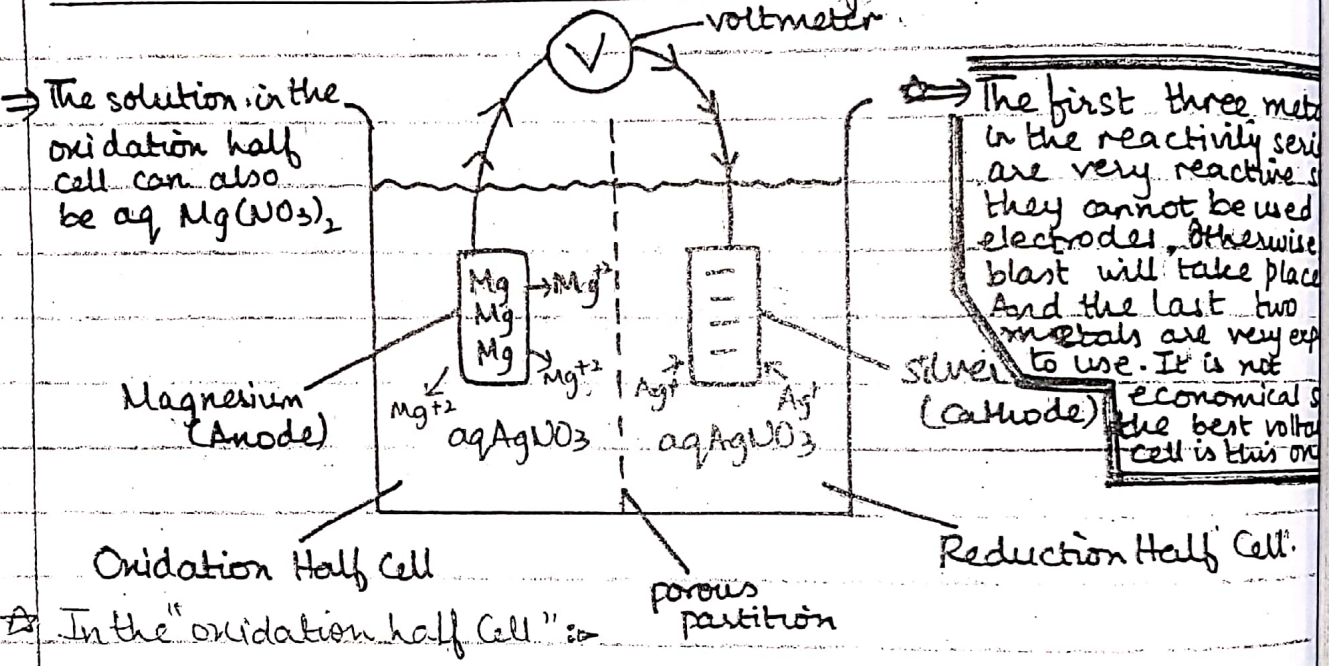
Even if one electron is excess on the plate, a p.d will be created & electrons will flow towards the copper plate

Apparently no reaction is taking place, but actually it is! There is no overall equation for such a reaction

Voltage of a cell

Voltage of a cell can be increased by increasing the differe of reactivity between the metals that are used as electr For example, the highest voltage can be produced by using Magnesium and Silver as electrodes.

A voltaic cell with maximum voltage



☆ In the "oxidation half Cell" :-

$$Mg^{\circ}_{(s)} + 2AgNO_{3(aq)} \longrightarrow Mg(NO_3)_{2(aq)} + 2Ag^{\circ}_{(s)}$$

Anode

$$Mg_{(s)} \longrightarrow Mg^{+2}_{(aq)} + 2\bar{e}$$

Cathode

$$Ag^{+}_{(aq)} + 1e \longrightarrow Ag_{(s)}$$

⊙⇒ PAST PAPER QUESTION

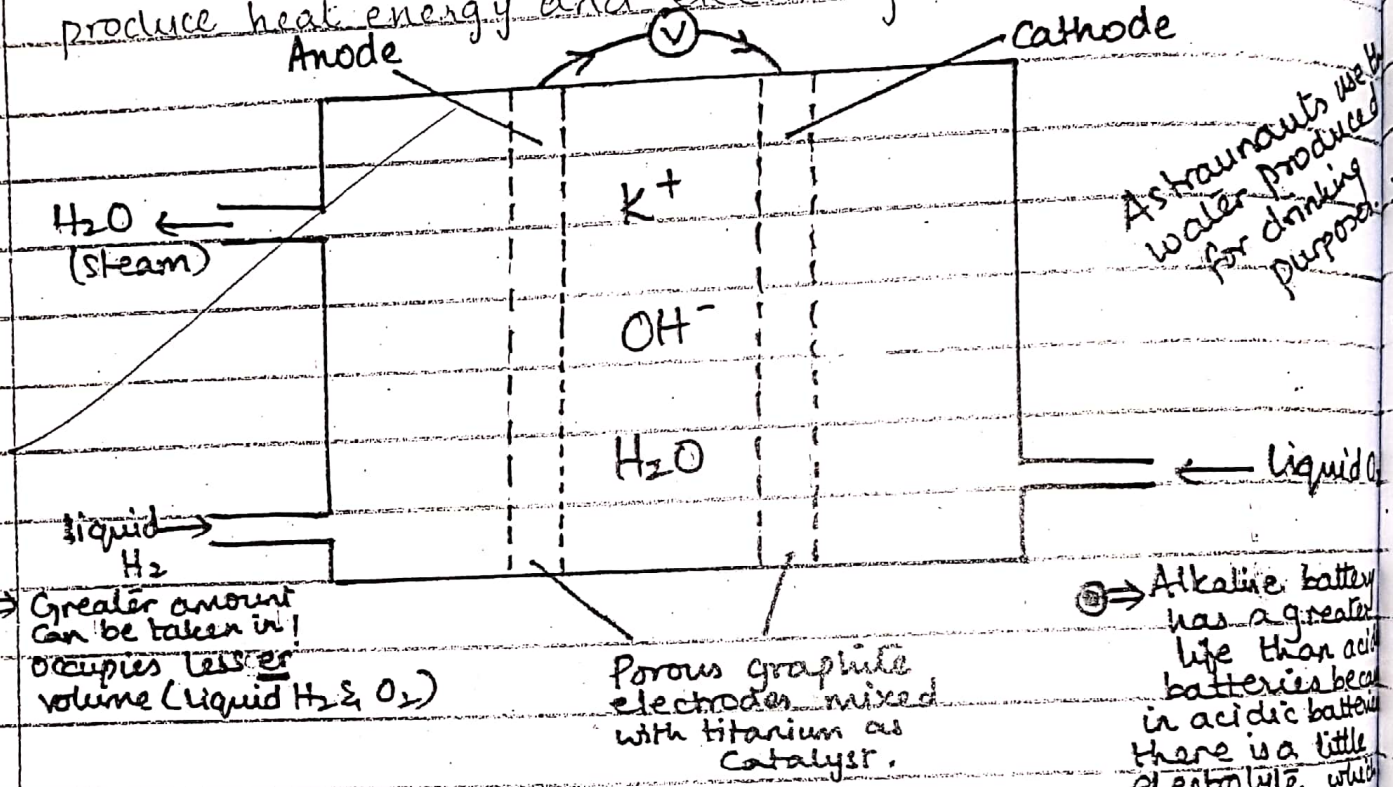
Source of gases entering the fuel cell:-

① Oxygen: fractional distillation of liquid air

② Hydrogen: Cracking of alkanes

Fuel Cell

A type of a voltaic cell which is used to move space rocke
This cell uses H_2 as a fuel which reacts with O_2 in the presence of
produce heat energy and electricity.



Astraunauts use the water produced for drinking purpose.

⊕ ⇒ Greater amount can be taken in! occupies lesser volume (Liquid H_2 & O_2)

⊖ ⇒ Alkaline battery has a greater life than acid batteries because in acidic batteries there is a little electrolyte which finishes + Every time electrolyte is added, water contain minerals which depait on the electrodes + KOH is not used as OH^- ions are generated in reduction after being used in oxidation.

⊕ ⇒ Plus point of this cell is that it has alkaline electrolyte (Potassium Hydroxide).

Anode

$$2(H_2 + 2OH^- \longrightarrow 2H_2O + 2e^-)$$

Oxidation

Cathode

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

Reduction

Overall Equation

$$2H_2 + O_2 \longrightarrow 2H_2O \quad -\Delta H$$

Advantages & Disadvantages of Fuel Cell

Advantage in space

→ Water produced in the fuel cell is condensed and is used for drinking purposes by the astronauts.

Advantage in daily life

→ It is environment friendly as it does not produce any atmospheric pollutants. (produces only water).

→ Hydrogen is a renewable source of energy while fossil fuels are non-renewable.

Disadvantages

→ It is more expensive than fossil fuels.

→ Carrying and storage of liquid hydrogen is very risky as it is highly combustable.

→ Dust particles from the air can block the pores in the electrodes due to which the fuel cell will stop working.