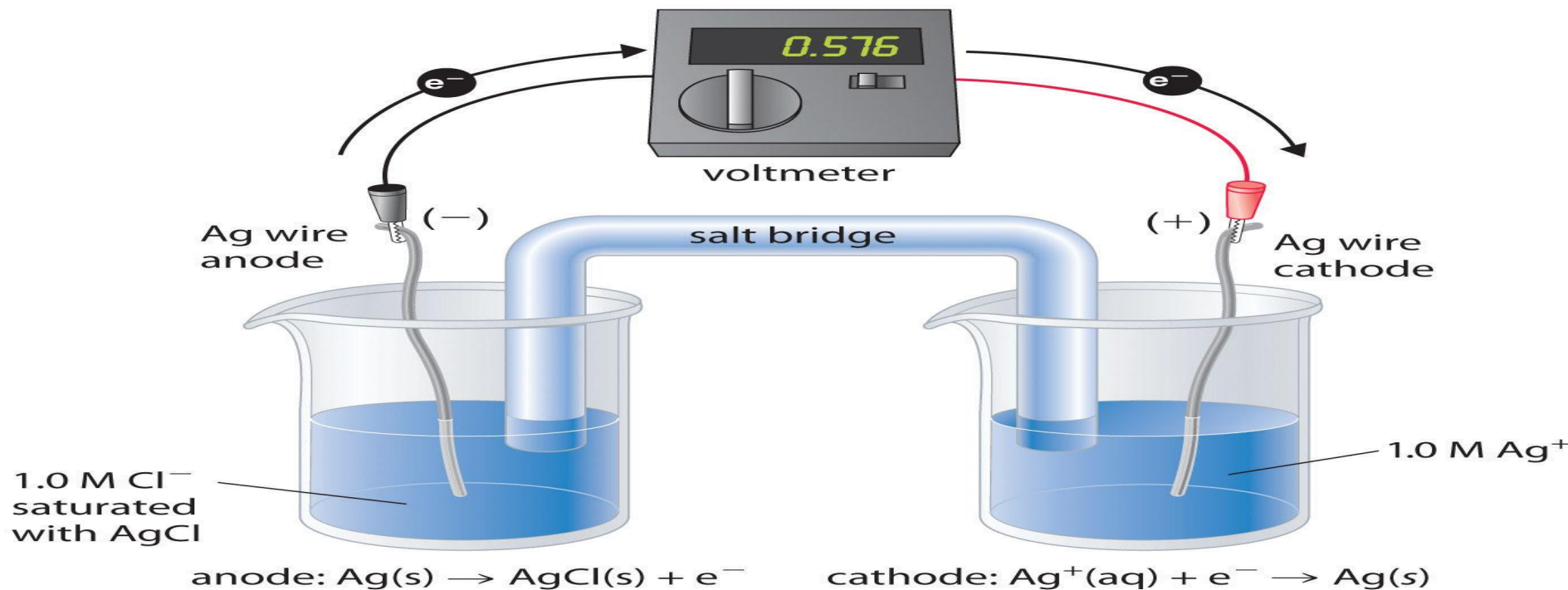


MODULE II

ELECTROCHEMISTRY AND CORROSION



- **Electrochemistry is the study of interconversion of electrical energy and chemical energy.**
- **In galvanic cell or voltaic cell, the chemical energy is converted to electrical energy.**
- **In electrolytic cell the electrical energy is converted to chemical energy.**

Classification of materials on the basis of conduction

1. conductors-

substance which allow to pass electricity through them is called conductors.

Eg-metals, alloys, graphites, NaCl in fused or dissolved state

2.insulators-

substance which does not allow to pass electricity through them is called insulators.

Eg- wood , plastic , glass

3.semiconductors-

substance whose conductivity lies between conductors and insulators.

Eg-silicon , germanium

4.superconductors-

Which offer no resistance to the flow of electricity.

Most metals become superconductors at 2 to 5K

Eg- mercury at 4 K

Materials

Conductors

Insulators

Eg. Glass, Wood, Paper,
Organic compounds like
benzene, sugar etc.

*Electronic or
metallic conductors*
Eg: Copper, Silver,
Aluminium, Brass,
Bronze etc.

*Electrolytic
Conductors*
Eg.: Acids, Bases,
Salt solutions

Semi conductors
Germanium doped
with Arsenic or
Gallium

*Super
Conductors*
Mercury at 4K

Types of conductors

1. Metallic conductors/ electronic conductors-

They conduct electricity by the movements of electrons.

Cu,Al

2.Electrolytic conductors/ electrolytes/ionic conductors-

They conduct electricity by the movements of ions.

They decomposes by the passage of electricity.

Eg-NaCl in fused or in solution , sulphuric acid

etc

Distinction between metallic conductors and electrolytic conductors-

Metallic Conductors (Electronic Conductors)	Electrolytic Conductors (Ionic Conductors)
1. Conductance is due to the movement of free electrons	1. Conductance is due to movement of ions.
2. No chemical change takes place	2. Electrolysis takes place involving chemical change
3. There is no transfer of matter	3. Results in the transfer of matter in the form of ions.
Conductance of metals decreases with increase of temperature.	4. Conductance of electrolytes increases with increase of temperature.
Example : Metallic elements and their alloys.	Example: ionic compounds in molten or dissolved state

Electrolyte-

Substance which conduct electricity through them either in molten state or in dissolved state.

Eg- HCl , HNO_3 , H_2SO_4
 NaOH , KOH , NaCl , CuSO_4 , acetic acid, oxalic acid, NH_4OH

Nonelectrolytes-

A substance which do not conduct electricity through them in molten state or in dissolved state.

Eg-sugar , urea, alcohol

Strong and weak electrolytes-

Strong electrolytes:-

Substance which undergo complete ionisation when dissolved in water.

Eg- HCl , HNO_3 , H_2SO_4
 NaOH , KOH , NaCl , CuSO_4

Weak electrolytes-

Substance which undergo partial decomposition when dissolved in water.

Eg- acetic acid, oxalic acid, NH_4OH

Electrolysis-

The decomposition of electrolyte by the passage of electricity is called electrolysis.

- The apparatus used for electrolysis is called electrolytic cell or electrolytic tank.**

Mechanism of electrolysis-

- ❖ The metal rods dipped electrolytes are called electrodes, and connected to a battery.
- ❖ The electrode connected to negative pole of battery is called **cathode**.
- ❖ The electrode connected to the positive pole of the battery is called **anode**.
- ❖ When the current is passed through the electrolyte the positive ions move towards cathode

- ❖ **The negative ions move towards anode .**
- ❖ **These ions are discharged at the electrodes.**
- ❖

Electrolysis of molten NaCl:-

- Sodium chloride undergo decomposition



- On passing current Na^+ ions move towards cathode and discharged there.



- The Cl^- ions move towards anode and discharged there.



- Thus sodium is deposited at cathode and Chlorine gas is evolved at anode.

Electrolysis of aqueous NaCl

- In aqu.NaCl contain NaCl and H₂O which ionize to give-



- When current is passed , Na⁺ and H⁺ ions moves towards cathode and Cl⁻ and OH⁻ ions moves towards anode
- At cathode-
The discharge potential of H⁺ ions are lower than Na⁺ ions, so H⁺ ions discharged at cathode .



- At anode,

The discharge potential of Cl^- ions are lower than OH^- ions, so Cl^- ions discharged at anode.



Faraday's laws of electrolysis-

Faraday's first law

The amount of substance liberated or deposited at an electrode is directly proportional to the quantity of electricity passed through it.

If w gm of the substance liberated or deposited at the electrode by the passage of electricity Q then

$$W \propto Q$$

$W = ZQ$, where Z is the proportionality constant called electrochemical equivalent.

Q = current strength in I ampers X times in t seconds

Then

$$Q = I \times t$$

Therefore

$$W = ZIt$$

One faraday, $1F = 96500C$

One faraday is the amount of charge carried by one mole of electrons.

Electrochemical equivalent ,Z

It is the mass of substance deposited or liberated at the electrode by the passage of one coulomb of electricity through the electrolyte.

Faraday's second law

When the same quantity of electricity passed through solutions of different electrolytes connected in series, the mass of the substance deposited or liberated at the electrode is directly proportional to their equivalent masses.

Mass of A deposited is proportional to equivalent mass of A and Mass of B deposited is proportional to equivalent mass of B.

ie $W_A \propto E_A$ and $W_B \propto E_B$

Or

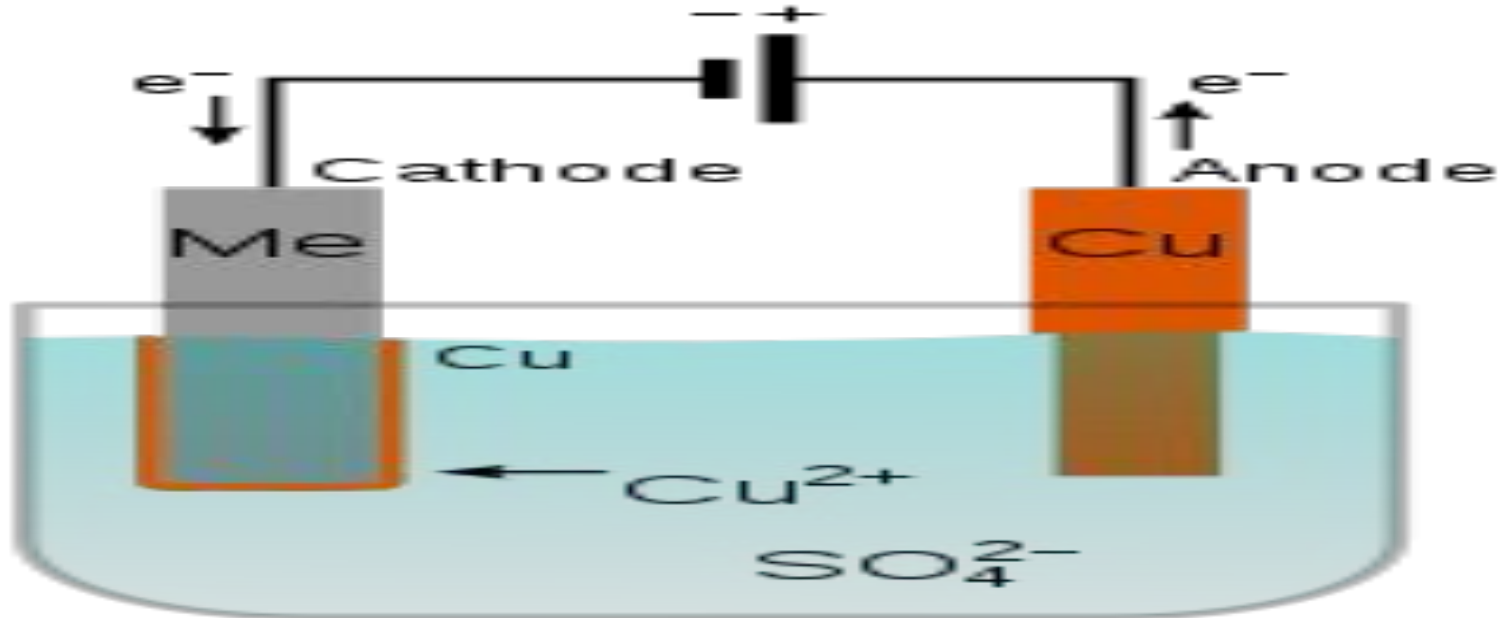
$$\frac{W_A}{W_B} = \frac{E_A}{E_B}$$

Application of Electrolysis

1. Electroplating.
2. Refining of metals like Cu, Ag, Sn etc...
3. Determination of equivalent mass of metals.
4. Manufacture of chemicals like NaOH, Chlorine, Hydrogen, Oxygen etc...
5. Electrometallurgy- for extraction of metals like sodium , potassium, calcium etc'...
6. Anodising.

Electroplating

The process of depositing one metal on the surface of another metal by passing electric current is called electroplating.



<https://www.youtube.com/watch?v=iLxCLVA6TgM>

→ Watch this video carefully to understanding the concept of electroplating.

Steps involving in electroplating-

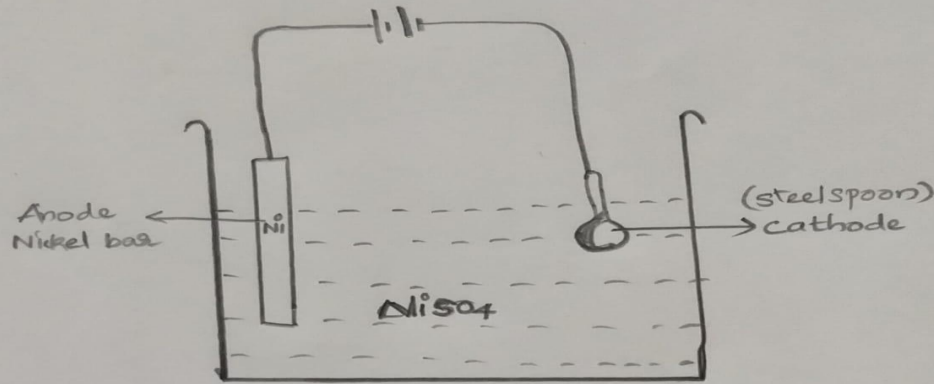
- The base metal on which coating is formed act as **cathode**.
- The metal which is form coating act as **anode**
- Electrolyte is the **soluble salt of coating metal**.
- When current is passed , metal ions from the electrolyte moves towards cathode and deposited there.

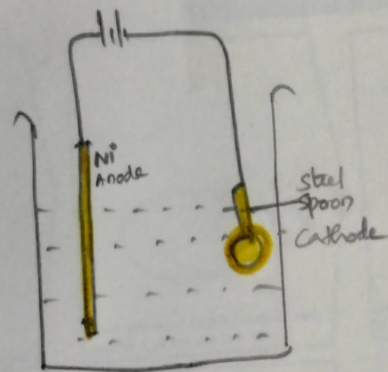
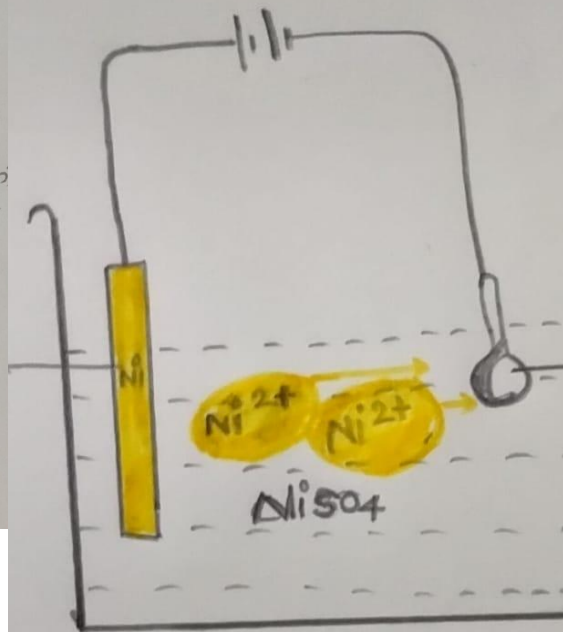
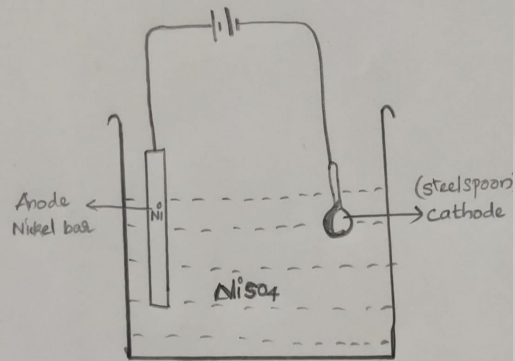
- simultaneously an equal amount of metal from anode dissolved into the electrolyte.
- The process continued until required thickness of metal coated on the base metal.

★ For example copper is coated on any metal bar then **Cu** act as anode and **metal bar** act as cathode , **CuSO_4** act as electrolyte

Electroplating of nickel on mild steel spoon

https://www.youtube.com/watch?v=abMcjHau_Fc





Steps:-

1. Wash the spoon with organic solvent to remove any grease or oil, then wash with dilute hydrochloric acid to remove any oxide film and finally with chromic acid or detergent to clean the surface.
2. The metal surface should be rough so that the deposit sticks on it firmly and permanently.
3. pH of the electrolyte should be between 4 and 5.
4. The cleaned spoon is set as cathode and pure nickel bar is taken as anode.
5. On passing electric current nickel from anode dissolves and is deposited on spoon.



Application/ uses of electroplating-

1. To protect from corrosion.
2. To increase the resistance to chemical attack.
3. To improve the physical appearance.
4. To modify hardness.
5. To repair the damaged parts of machinery by electrodeposition.
6. To strengthen the non metallics like wood, glass etc....

The electrolyte used in electroplating should be -

- A. Highly soluble .**
- B. Stable towards oxidation, reduction or hydrolysis.**
- C. Good conductor.**

Electrolytic refining of metals

- **Purification of impure metals by electrolytic methods.**
- **Impure metal plate as anode and pure metal as cathode.**
- **Salt solution of metal is electrolyte.**
- **On passing current , oxidation take place at anode and anodic metal ions dissolved in electrolyte and discharged at cathode.**

Electrolytic refining of copper

- 1. Crude copper bar as anode , and pure copper as cathode .**
- 2. CuSO_4 with little sulphuric acid is electrolyte.**
- 3. Anode and cathode hanged into the electrolyte using a conducting rods.**
- 4. On electrolysis cu dissolved in electrolyte and get reduced at cathode.**

Redox reaction

Reduction-Gain of electron

Oxidation-loss of electron

If oxidation and reduction reaction are taking place simultaneously called redox reaction.

Reaction in which loss of electron take place is called oxidation half cell.

Reaction in which gain of electron take place is called reduction half cell.

Electrochemical cell/ Galvanic cell

A device used to convert chemical energy to electrical energy called electrochemical cell.

Daniel cell is the modified form of electrochemical cell in which Zn-CuSO_4 reaction take place.

In an electrochemical cell

- 1. The spontaneous redox reaction which consist of oxidation and reduction carried out separately.**
- 2. The electrode where the electrons are released or oxidation take place called anode.**
- 3. The electrode where the electrons are accepted or reduction take place called cathode.**
- 4. Electrons from anode to cathode flow through a external circuit.**
- 5. A salt bridge complete the circuit.**
- 6. Ions are current carriers in solution inside the cell.**

General representation of an electrochemical cell

- Anode is written on the LHS and cathode on RHS
- A salt bridge is indicated by two vertical lines in between the two half cells
- $\text{Zn}_{(\text{s})}/\text{Zn}^{2+}(\text{1M})//\text{Cu}^{2+}(\text{1M})/\text{Cu}_{(\text{s})}$

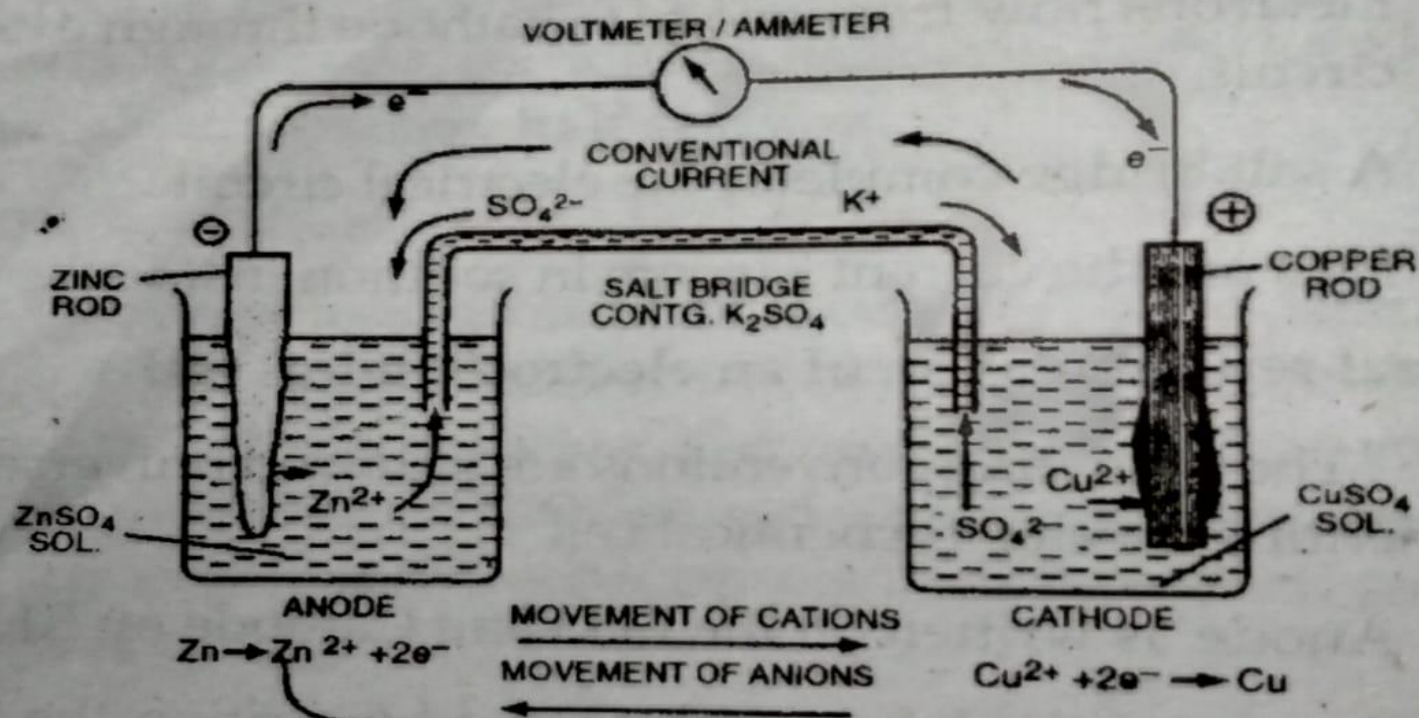


FIGURE 5.11(a). Electrochemical cell based on the redox reaction.
 $\text{Zn} + \text{CuSO}_4 \longrightarrow \text{ZnSO}_4 + \text{Cu}$

Salt bridge

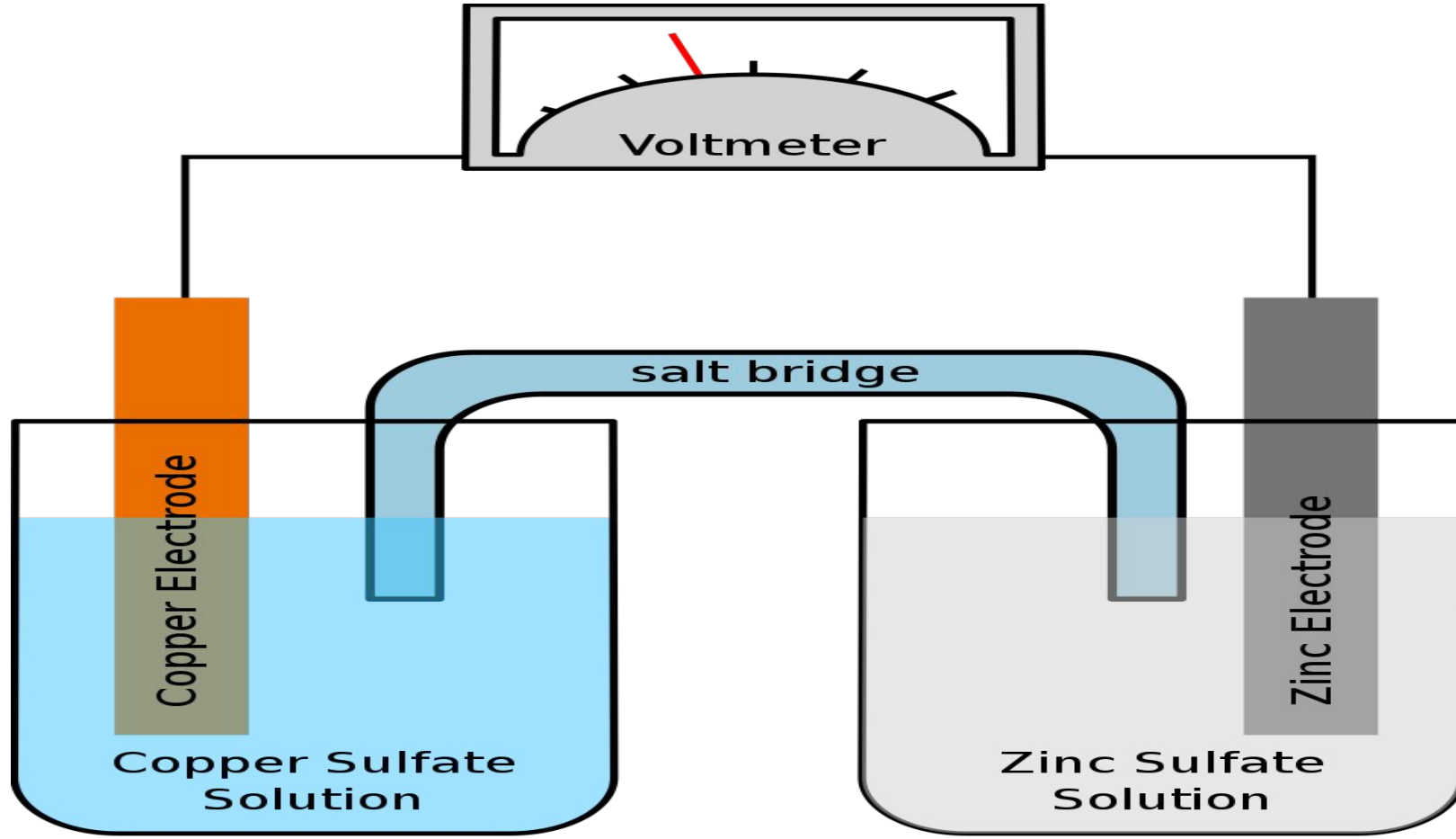
It is a U shaped tube containing concentrated solution of an inert electrolyte like KCl . KNO_3 etc to which some agar-agar or gelatin has been added to convert it to a gel. The end of the U tube are plugged with glass wool.

Functions of a salt bridge:-

1. A salt bridge maintain the electrical neutrality of the electrolyte in the two half cells.
2. It complete the circuit.

- 3.It prevent the intermixing of two electrolyte in the two half cells,**
- 4.It avoid the liquid junction potential between the solutions.**

Daniel cell



- It consist of two half cells ,The half cell on the right consist of zinc metal electrode dipped in zinc sulphate solution.The half cell on the left side consist of copper metal electrode dipped in copper sulphate solution.
- The two half cells are internally connected by a salt bridge and externally connected by a metal wire.
- There is a flow of electron through the external circuit.
- Zinc rode loses its mass and copper rode gain mass.
- Concentration of zinc in ZnSO_4 solution increased and concentration of Copper in CuSO_4 solution decreases.

Reaction take place-

At anode-Oxidation of zinc



At Cathode-



Net reaction -



There are Three category of energy producing galvanic cells-

- 1. Primary cells**
- 2. secondary cells**
- 3. Fuel cells**

Primary cells -

The redox reaction take place in once and after it dead , the chemical reaction in which is not reversible.

Ex- daniel cell, Mercury cell.

secondary cell-

The chemical reaction take place is reversible.

The cells can be charged. Used again and again.

Ex-lead storage battery,Nickel- cadmium cell

Fuel cell-

Chemical energy of the combustion of fuel like H_2 , O_2 , CH_4 etc can be converted into electrical energy. About 75% of chemical energy converted to electrical energy.

Fuel+ Oxygen \rightarrow Oxidation products + electrical energy

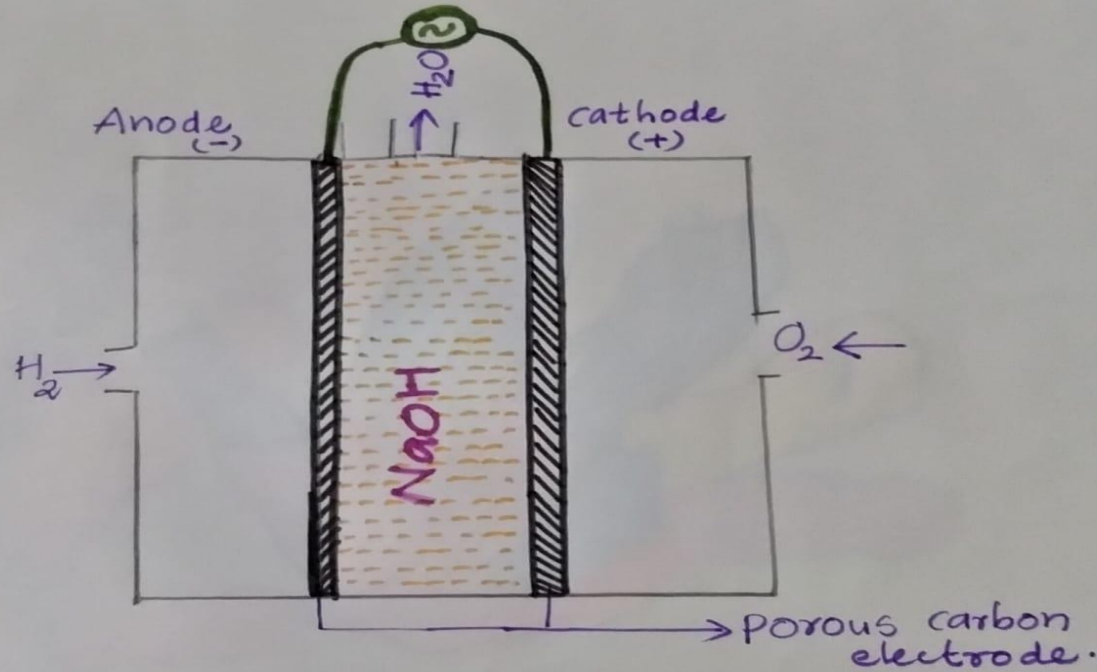
Advantages of fuel cell

- 1. Convert energy of the fuel directly into electrical energy.**
- 2. Do not cause pollution .**
- 3. Light and compact.**
- 4. High efficiency (75%)**
- 5. Energy supply is continuous.**
- 6. Cells can be converted to series to get higher voltage.**

Uses

1. **Used as energy source in space vehicles.**
2. **Used as energy source in submarines.**
3. **Used as energy source in military vehicles.**
4. **Used as energy source in automobiles.**

Hydrogen - oxygen fuel cell.



- The cell consist of three compartments,anodic cathodic and electrolytic compartment.
- They are separated by a porous graphite electrode impregnated with Pt or Ag.
- Anode and cathode are externally connected by a metal wire .
- H₂ gas is bubbled through anodic compartment and O₂ gas is bubbled through cathodic compartment.
- The electrolyte is aqueous concentrated (35%) solution of NaOH,KOH.

The reaction in the electrodes are



Overall reaction is



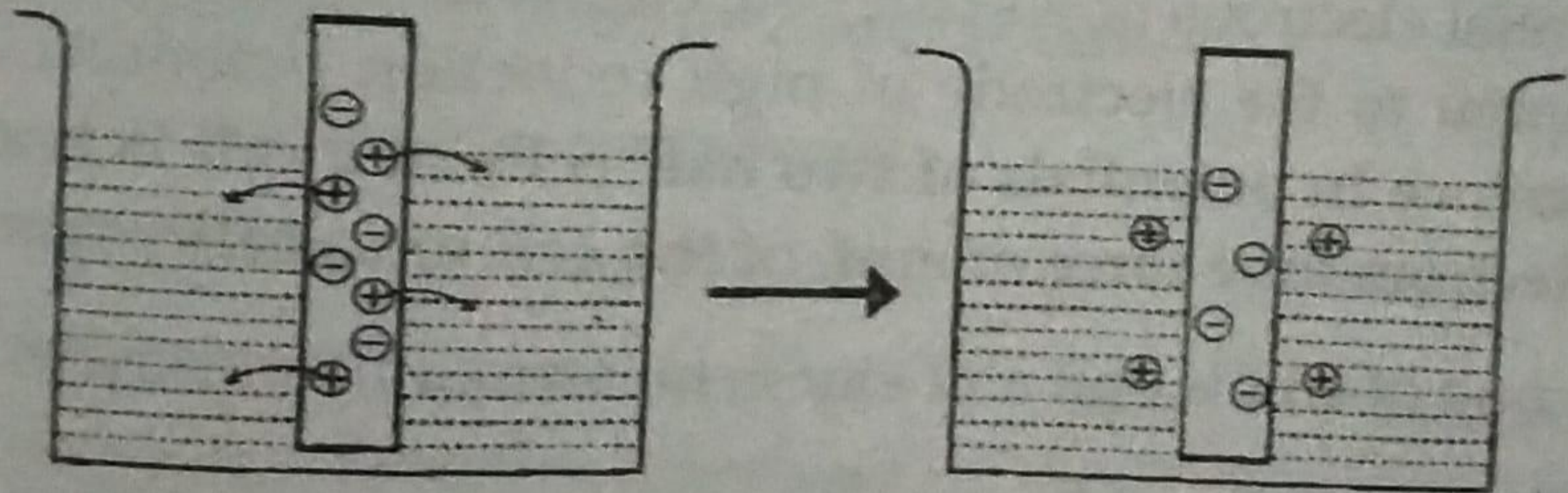
- The cell work continuously and has a emf of 1 Volt

Electrode potential

When metal ions are dipped in its own solution



The metal ions go into the solution and electrons are left into the metal making it negatively charged. An electrical double layer is set up, which generate a potential difference.



\oplus Metal ions

\ominus Electrons

The potential difference set up between metal and its ions in the solution is called **electrode potential**.

The tendency of electrode to lose electrons is called **oxidation potential**.

The tendency of electrode to gain electrons called **reduction potential**.

- The electrode potential at 298 K, one atm pressure and 1M of concentration of electrolyte is called **standard electrode potential E^0** .

EMF

The difference in potentials of two half cells of a cell is known as electromotive force or emf of a cell.

$$EMF = E_{\text{cathode}} - E_{\text{anode}}$$

Daniel cell , cathode is copper and anode is Zinc.
Potential of zinc is -0.76v and potential of copper is +0.34V

$$\begin{aligned}\text{EMF of cell} &= E_{\text{cu}} - E_{\text{Zn}} \\ &= +0.34 - (-0.76) \\ &= +0.34 + 0.76 \\ &= 1.1\text{V}\end{aligned}$$

Electrochemical series

It is an arrangement of electrodes(elements) in the order of increasing values of standard reduction potentials.

- Negative values of reduction potential indicate the tendency of oxidation.**
- Positive values of reduction potentials indicates the tendency of reduction.**

Electrode	Electrode reaction (reduction)	E° (V)
Li, Li^+	$\text{Li}^+ + e^- \rightarrow \text{Li}$	-3.05
K, K^+	$\text{K}^+ + e^- \rightarrow \text{K}$	-2.93
Ba, Ba^{2+}	$\text{Ba}^{2+} + 2e^- \rightarrow \text{Ba}$	-2.90
Ca, Ca^{2+}	$\text{Ca}^{2+} + 2e^- \rightarrow \text{Ca}$	-2.87
Na, Na^+	$\text{Na}^+ + e^- \rightarrow \text{Na}$	-2.71
Mg, Mg^{2+}	$\text{Mg}^{2+} + 2e^- \rightarrow \text{Mg}$	-2.37
Al, Al^{3+}	$\text{Al}^{3+} + 3e^- \rightarrow \text{Al}$	-1.66
Zn, Zn^{2+}	$\text{Zn}^{2+} + 2e^- \rightarrow \text{Zn}$	-0.76
Fe, Fe^{2+}	$\text{Fe}^{2+} + 2e^- \rightarrow \text{Fe}$	-0.44
Pb, $\text{PbSO}_4, \text{SO}_4^{2-}$	$\text{PbSO}_4 + 2e^- \rightarrow \text{Pb} + \text{SO}_4^{2-}$	-0.31
Co, Co^{2+}	$\text{Co}^{2+} + 2e^- \rightarrow \text{Co}$	-0.28
Ni, Ni^{2+}	$\text{Ni}^{2+} + 2e^- \rightarrow \text{Ni}$	-0.25
Sn, Sn^{2+}	$\text{Sn}^{2+} + 2e^- \rightarrow \text{Sn}$	-0.14
Pb, Pb^{2+}	$\text{Pb}^{2+} + 2e^- \rightarrow \text{Pb}$	-0.13
Pt, H_2, H^+	$2\text{H}^+ + 2e^- \rightarrow \text{H}_2$	+0.00
Cu, Cu^{2+}	$\text{Cu}^{2+} + 2e^- \rightarrow \text{Cu}$	+0.34
Ag, Ag^+	$\text{Ag}^+ + e^- \rightarrow \text{Ag}$	+0.80
$\text{Cl}^-; \text{Cl}_2, \text{Pt}$	$\text{Cl}_2 + 2e^- \rightarrow 2\text{Cl}^-$	+1.36

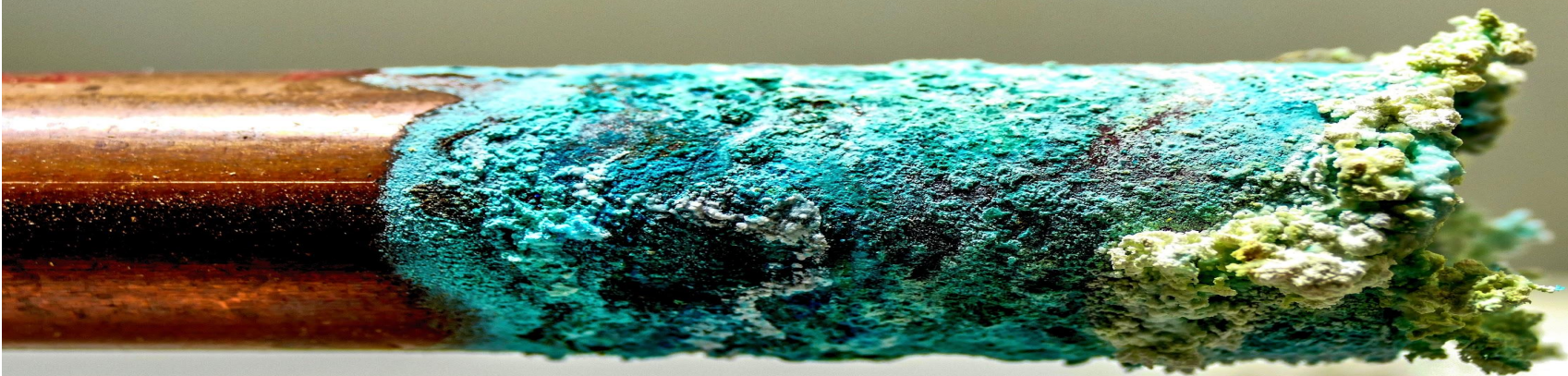
(Reducing agent)
Oxidation



(Oxidizing agent)
Reduction

Application of electrochemical series

- 1. It help to compare the reducing and oxidising power of various elements used as electrodes.**
- 2. It help to predict which elements would act as anode and which element would act as cathode.**
- 3. It help to compare the various properties such as i)reactivity ii)electropositive character iii)reducing power. iv)ability of evolving H_2 gas from dilute acids.**
- 4. The metal which are above the hydrogen in electrochemical series like Zinc , Mg, Al etc evolve hydrogen gas from dilute acids.**



CORROSION

Process of slow conversion of metals into their undesirable compounds by the action of air and moisture.

Condition for rusting

- 1. Impurity of metal**
- 2. Presence of oxygen**
- 3. Presence of moisture**
- 4. Presence of electrolyte**
- 5. Presence of Cl_2 and SO_2 in the atmosphere**
- 6. Strains of metals**

Types of corrosion

1. Dry or chemical corrosion

- ❖ Direct action of chemical gases like O_2 , H_2S , SO_2 , halogens.
- ❖ No water content.

2. Wet or electrochemical corrosion

- Occurs due to anodic and cathodic areas in the system.
- Current flow through conducting liquid and anode get oxidised and wasted.
- Eg- rusting of iron.

Rusting of iron

- A piece of iron get exposed to the atmosphere, it is covered with a reddish brown deposit called rust.
- $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$
- Hydrated ferric oxide .
- In rusting a galvanic cell setup between two dissimilar part of the same metal.

Mechanism of rusting

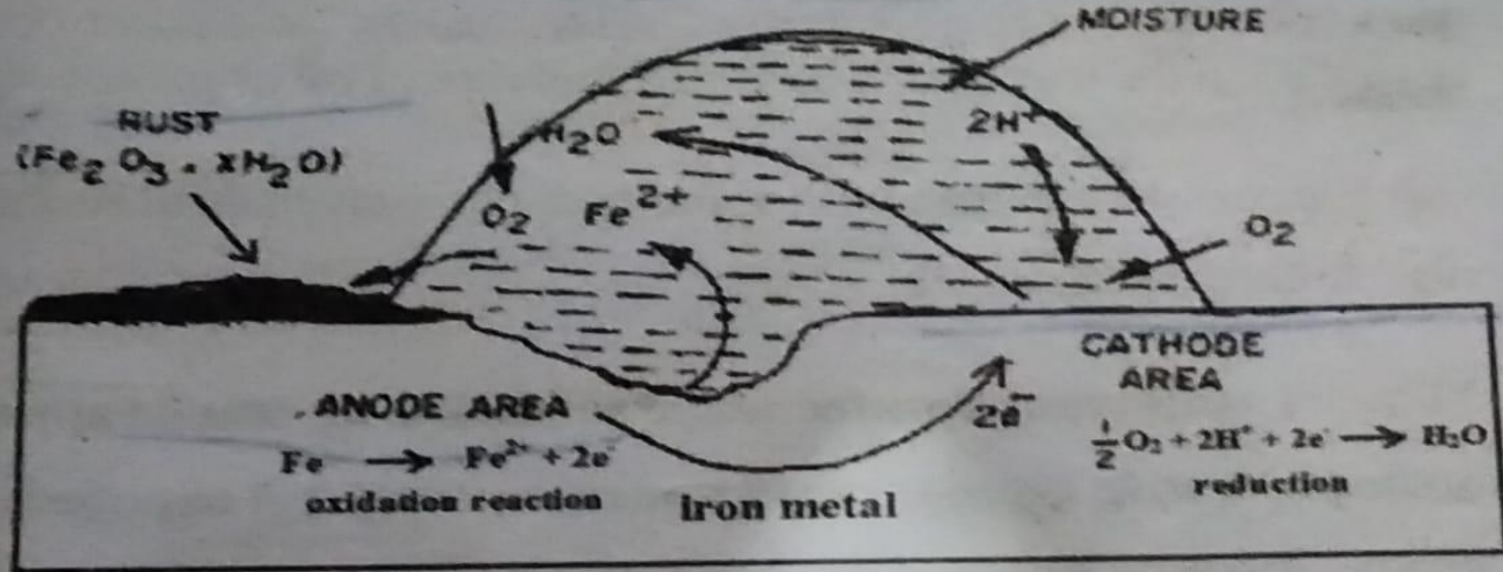
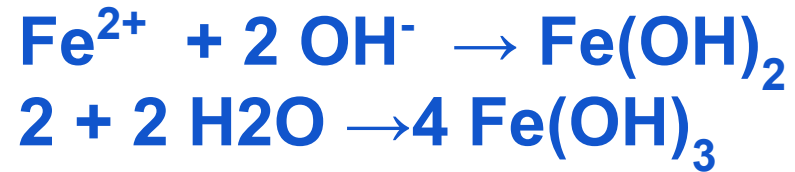


Fig. Rusting of iron.

1. The portion of iron which is in contact with water act as **anode** , and other portion which is in contact with air act as **cathode**.
2. Anodic iron get oxidised to Fe^{2+} ion.
The electron released from the anode move through the metal to cathodic site.
3. The oxygen at the cathode changes to OH^- ion by reduction.



4. Fe^{2+} and OH^- combine to form Fe(OH)_2 which get oxidised to Fe(OH)_3



The product 4Fe(OH)_3 corresponding to $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$

The overall reaction is



Prevention of corrosion / corrosion control

- 1.maintain the purity of the metal
- 2.alloying with other metal
- 3.modification of environment.

4. Barrier protection or protective coating

- Chemically inert physical barrier is created between the metal and environment.**
- It may be metallic , non metallic or organic**
- Eg-plastic coating, rubber coating, oil or grease or electroplating with some other metal.**
- Thus prevent the direct contact with air .**

Drawback

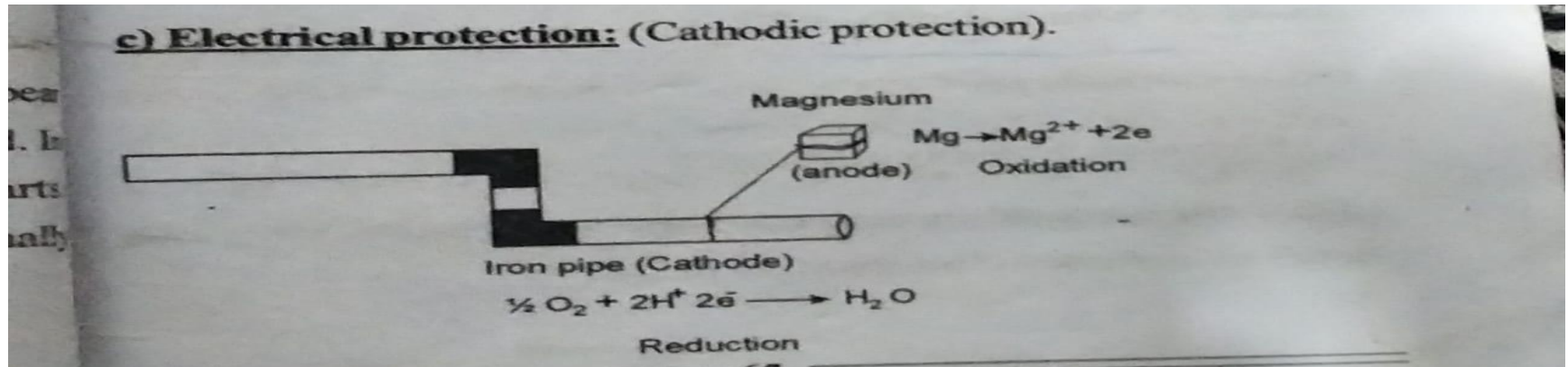
- 1. If a scratches or cracks appear on the layer , iron get exposed and rusting get started. It extended and eventually peels off the protective layer.**

5.Sacrificial protection

- ❖ Surface iron covered with more active metal like zinc.
- ❖ The active metal get oxidise(act as anode) and protect iron from rusting.
- ❖ Method of protecting one metal by more active metal suffering the damages it self.
- ❖ Even if covered metal almost exposed but still the iron get protected by act as cathode.
- ❖ Galvanisation is an eg for this

6. Cathodic protection /Electrical protection

- ❑ Surface of iron connected to more active metal like magnesium through a metal wire .
- ❑ Iron metal act as cathode and active metal act as anode (suffer damage)



7. Using anti rust solution

Iron articles are dipped into boiling anti rust solution like **sodium phosphate** . a protective layer is formed.