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ELECTRO CHEMISTRY

Theories of electrical double layer:

In order to obtain the relation between charge density (q_m) and cell potential (V), various theories have been proposed.

1. HELMHOLTZ-PERRIN THEORY (MODEL)

electrical double layer

*(+) electrode
soln (-) double layer*

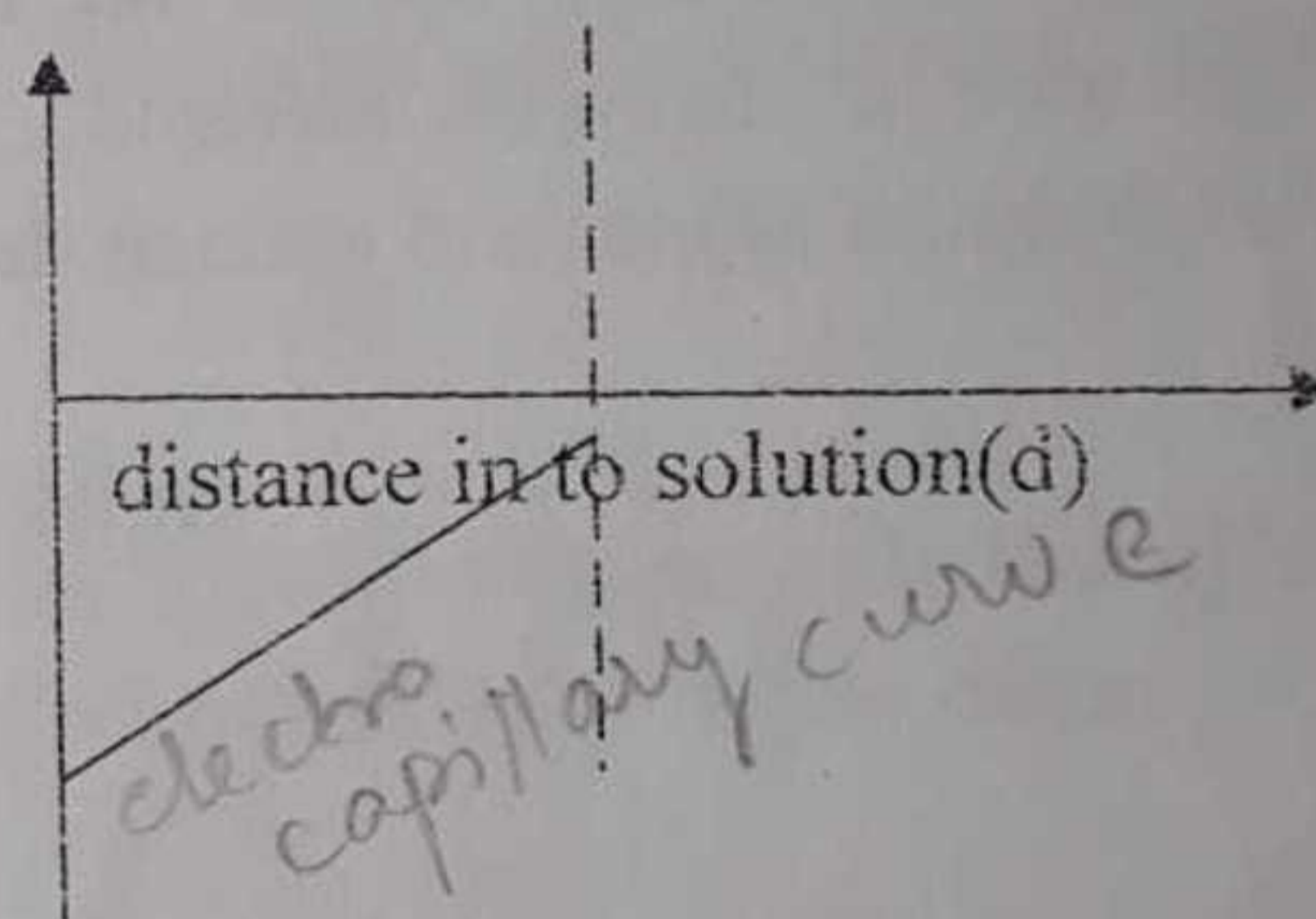
According to this theory, the charge on the metal, draws out in to the solution with counter-layer of charge of opposite sign. Thus the electrified interface consists of two sheets of charge one on the electrode and the other in solution. These are at a certain distance from each other, and together form the "electrical double layer". The charge densities on the two layers is represented by Helmholtz as a parallel plate condenser.

+++++

Therefore the electrostatic theory of capacitors can be applied for double layers. On the basis of parallel plate model of double layer, the potential difference across a condenser of unit area is

$$V = \frac{d}{\epsilon_r \epsilon_0} q$$

Differentiating we get $dV = \frac{d}{\epsilon_r \epsilon_0} dq$ charge (q)



This shows that the potential drop between these two layers of charge is a linear one.

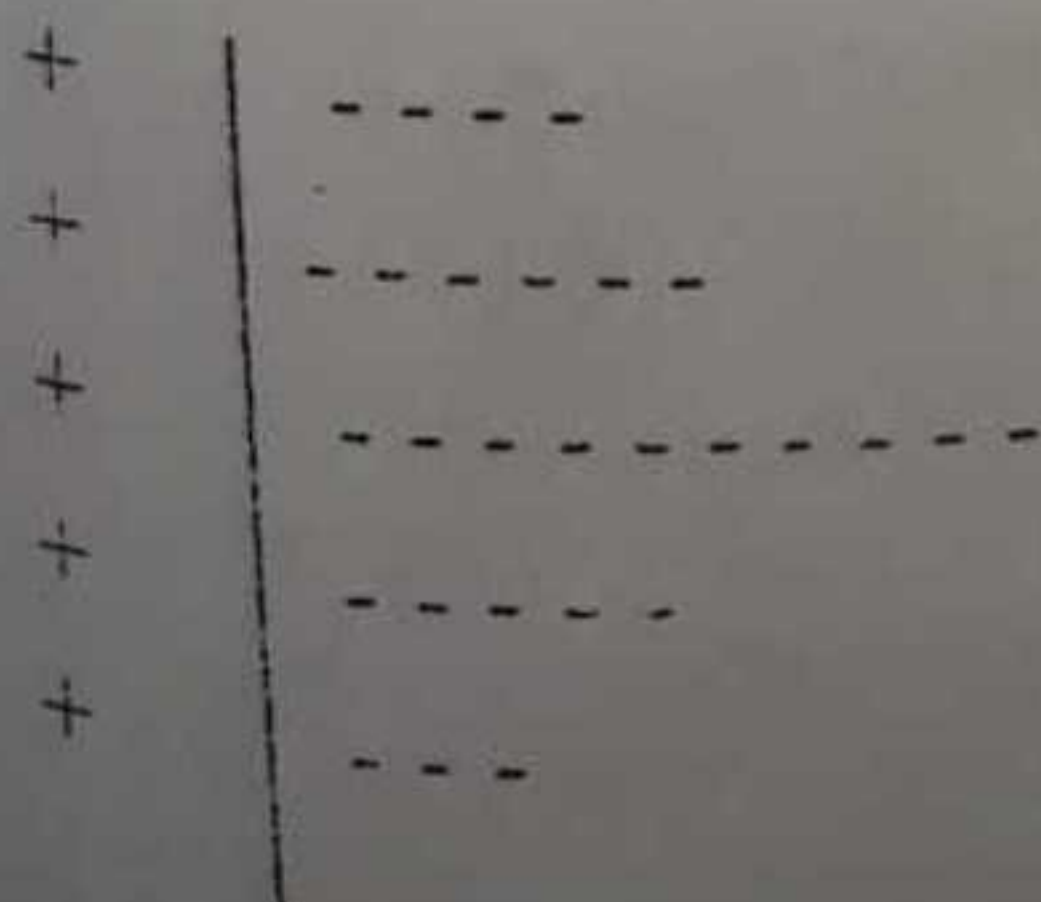
Limitation:

This model predicts that, the electro capillary curves are perfect parabola. But actually, the curves are parabolic but there is a slight asymmetry.

2. Gouy - Chapmann theory

diffused double layer

According to this theory, the ions are spread out in solution forming a diffused double layer. The diffused double layer is controlled by electrostatic forces.



If Ψ is the potential then potential drop in diffused layer, is given by

$$\frac{d\Psi}{dx} = -k\Psi$$

Rearranging, $\frac{d\Psi}{\Psi} = -k dx$

integrating $\int \frac{d\Psi}{\Psi} = -k \int dx$

$$\ln \Psi = -kx + c$$

when $x \rightarrow 0, \Psi \rightarrow \Psi_0$

$$\therefore \ln \Psi_0 = c$$

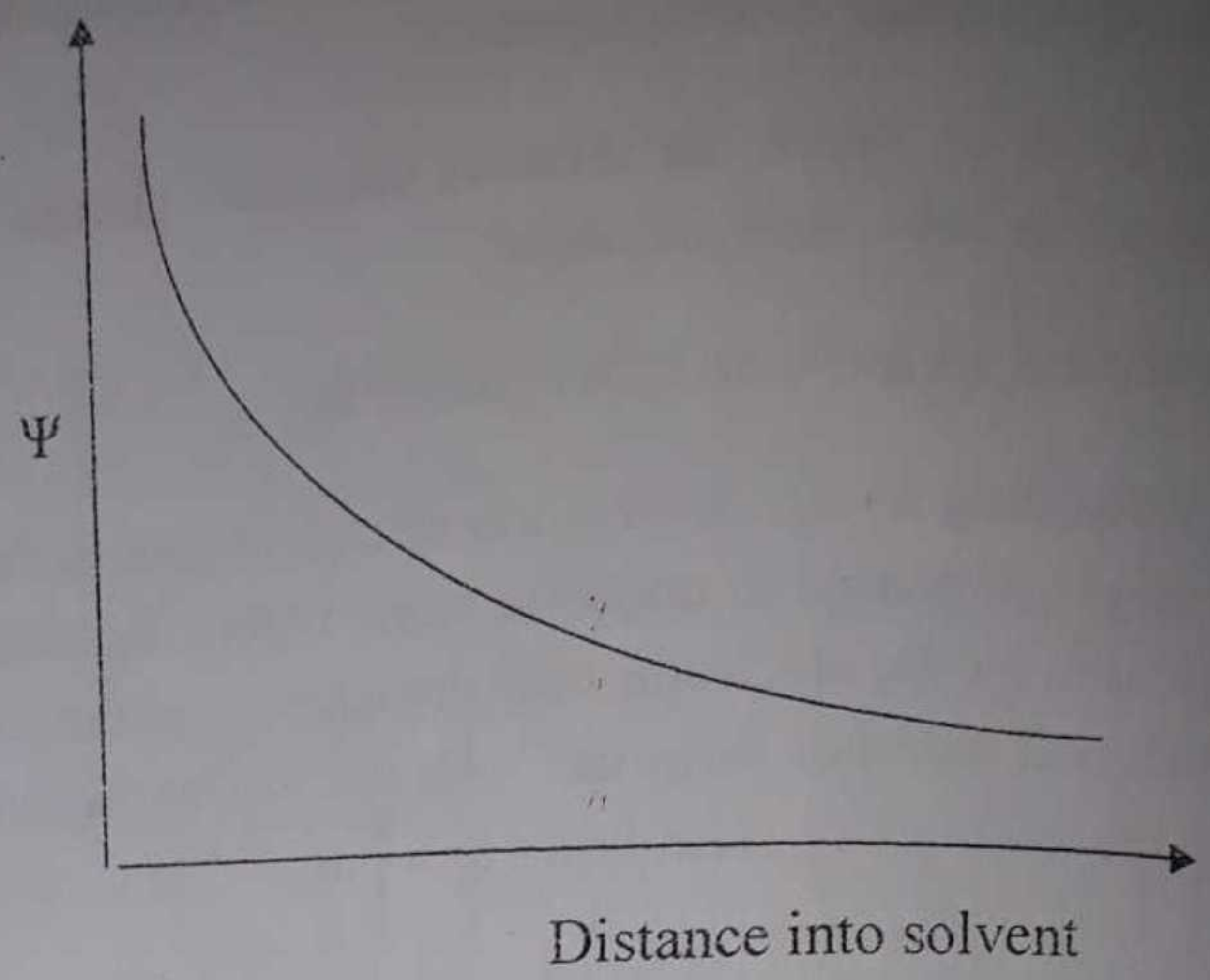
substituting in the above equation

$$\ln \Psi = -kx + \ln \Psi_0$$

$$\ln \Psi - \ln \Psi_0 = -kx$$

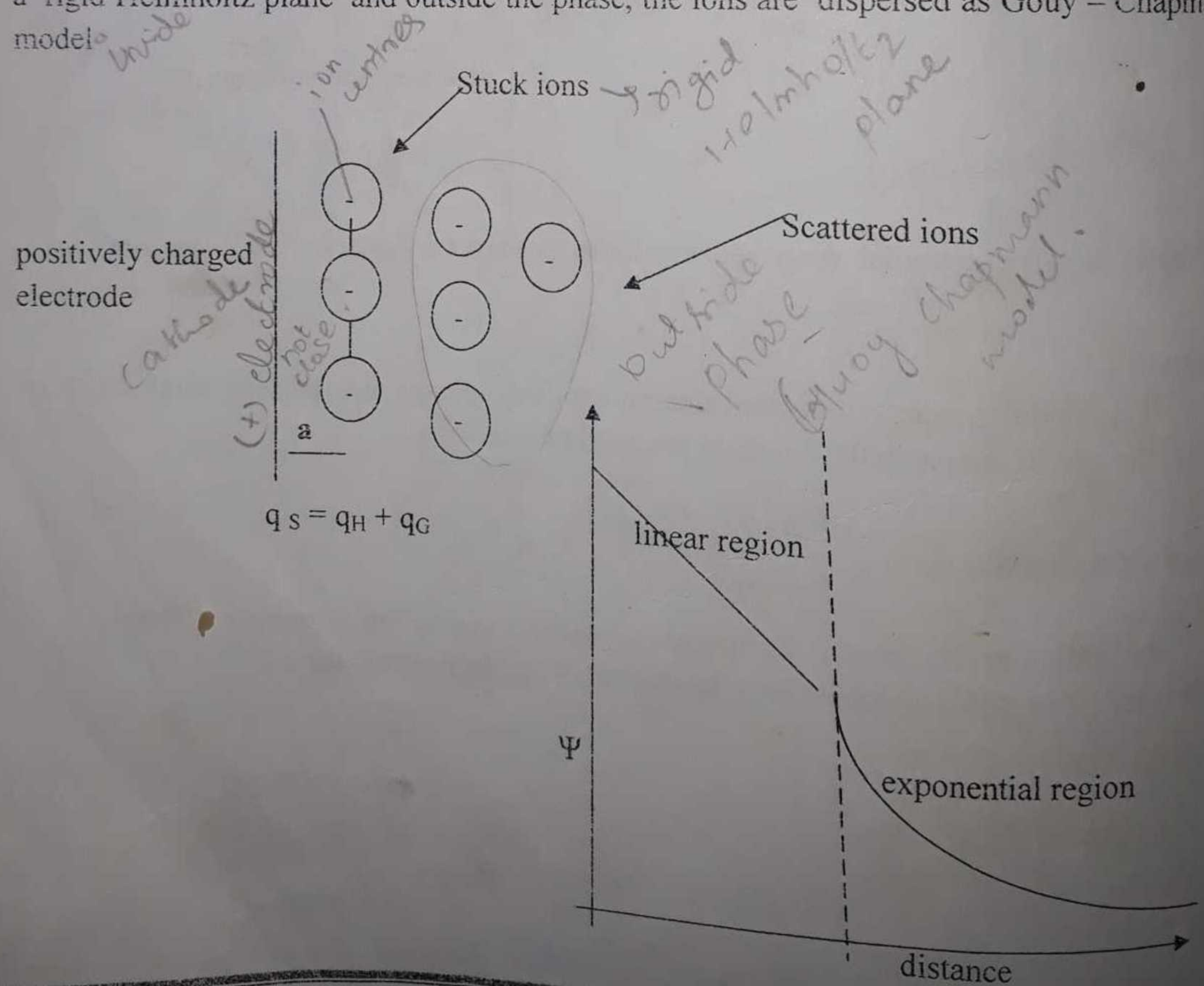
$$\ln \frac{\Psi}{\Psi_0} = -kx$$

taking exponential, $\Psi = \Psi_0 e^{-kx}$



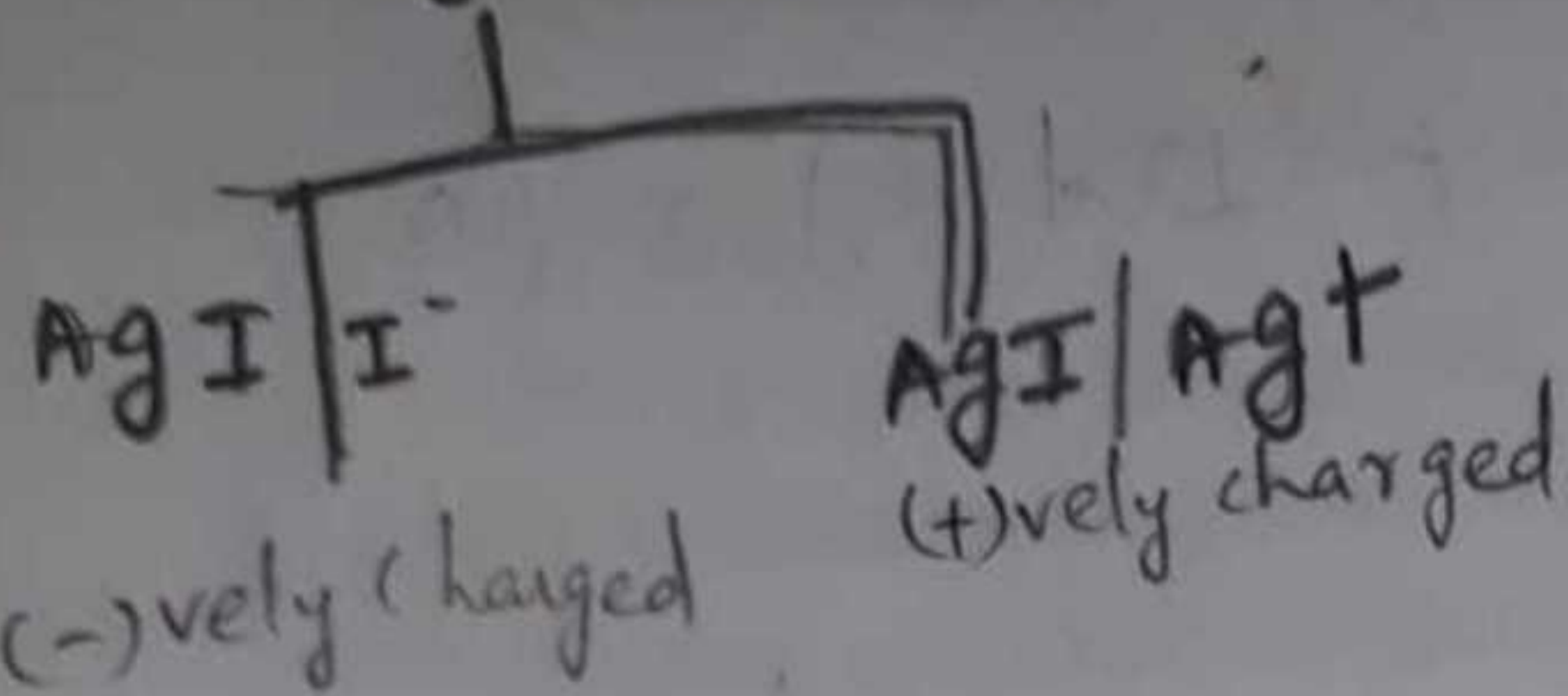
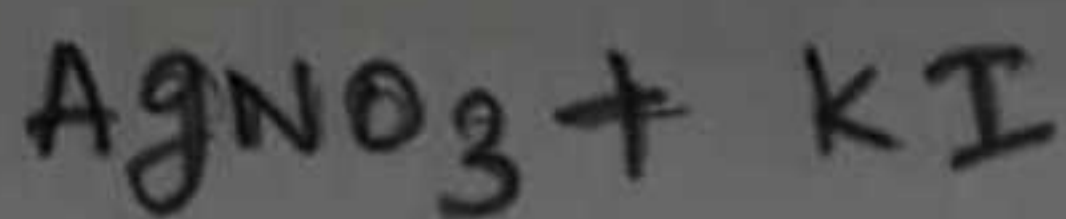
3. The Stern model:

According to this theory, the ion-centres are taken as not coming closer than a certain distance 'a' from the electrode. The ions close to the electrode are constrained into a rigid Helmholtz plane and outside the phase, the ions are dispersed as Gouy - Chapman model.

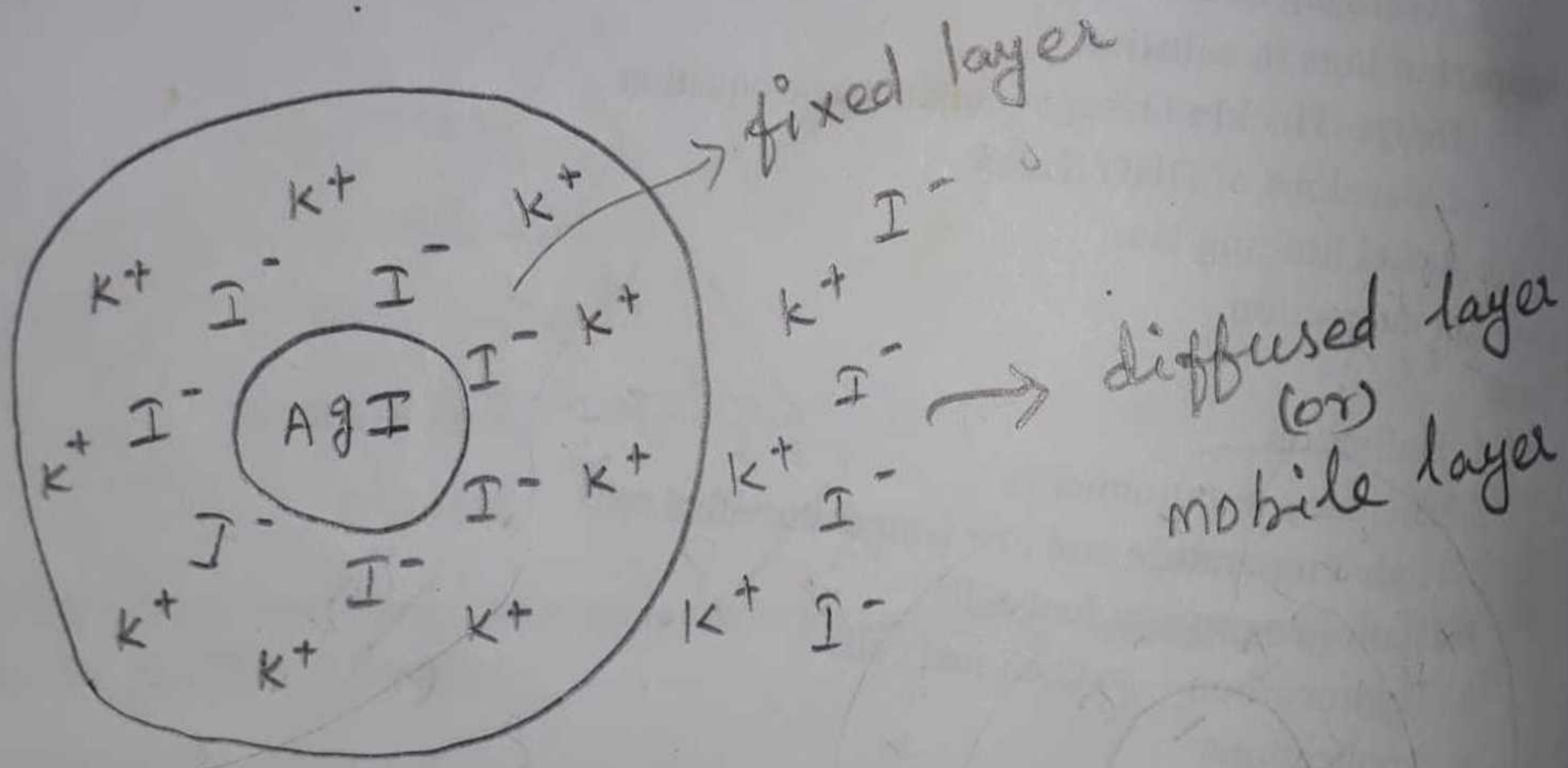
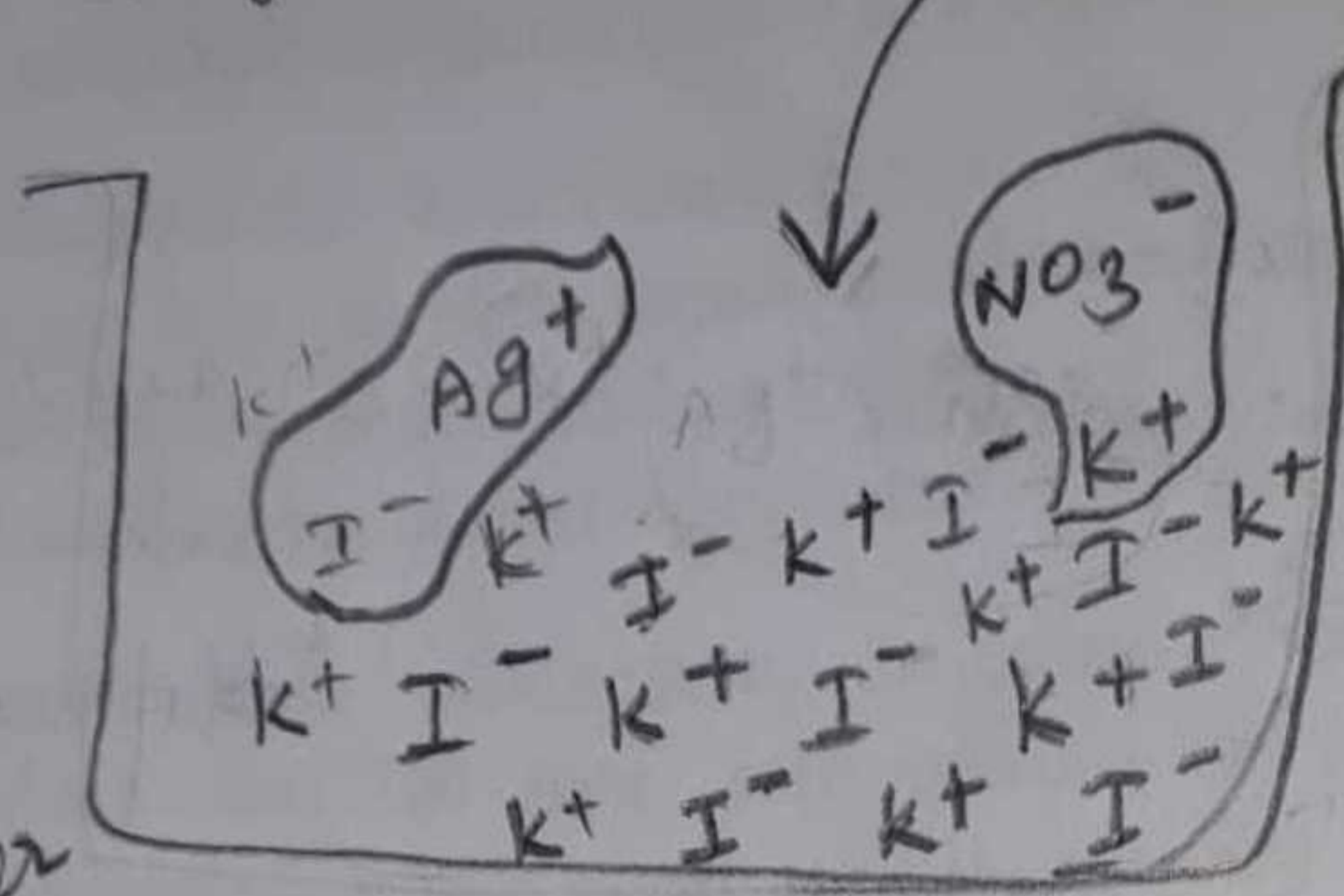
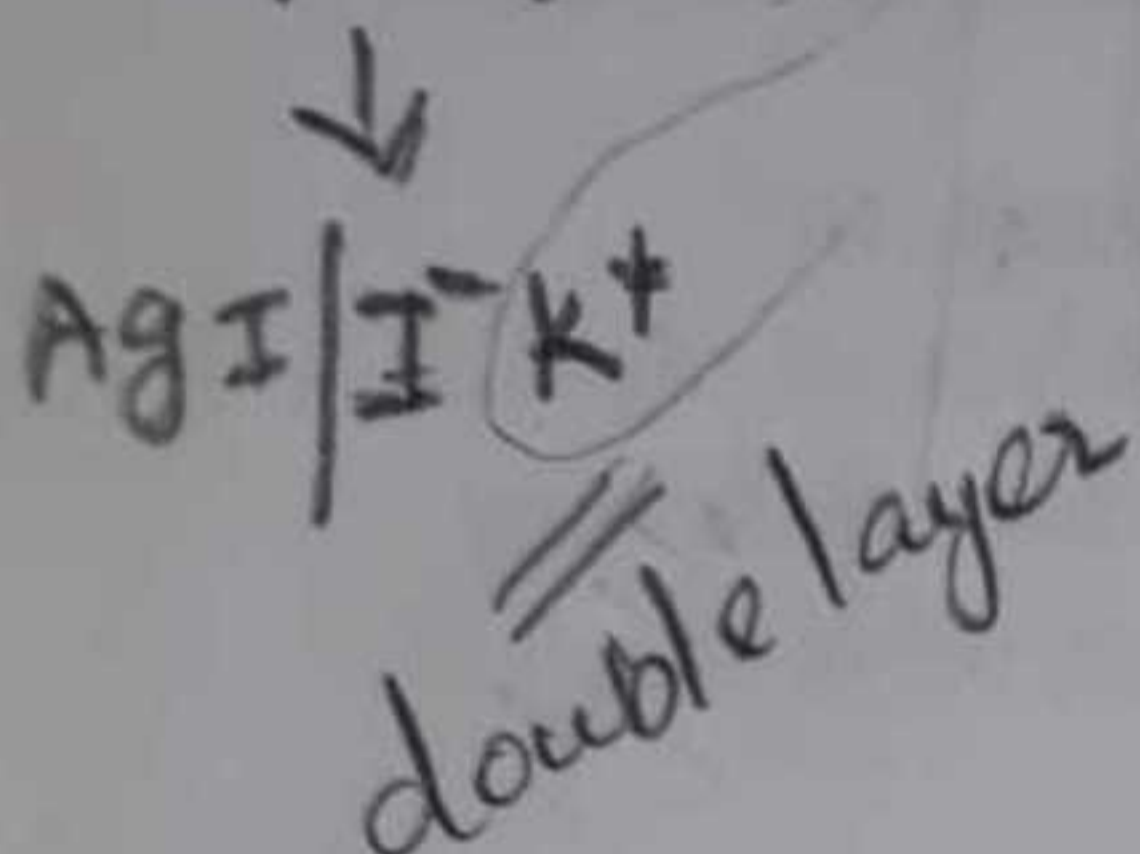
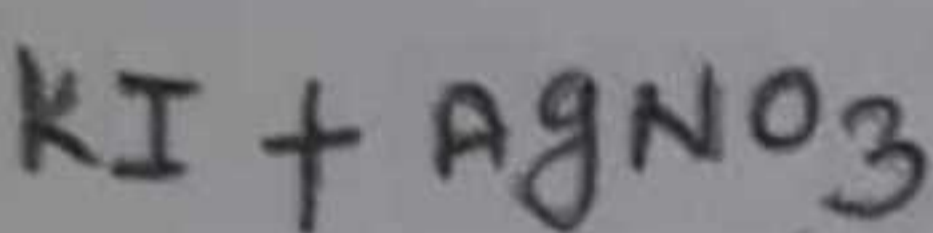


Helmholtz-Perrin theory

chemistry
concept
varinder



single drop
 $AgNO_3$



Zeta potential

$AgI \rightarrow$ colloidal particle
 \downarrow attract common ion on its surface
 will either absorb Ag (or) I on surface on soln.

pot. dif. b/w 2 layers
zeta pot.

ELECTRO KINETIC PHENOMENA

Four types of electro kinetic effects have been categorised.

1. Electro osmosis or Electro-endosmosis.

sol → fixed (diap)

When electric field is applied between a solid and liquid phase, and if the solid phase is fixed (in the form of diaphragm), the liquid will tend to move through the pores of the diaphragm . This movement of liquid, through the pores of the diaphragm, under the influence of electric field is known as **electro osmosis or electro-endosmosis**.

2. Cataphoresis or Electrophoresis

Solid small parti move thro liq.

When electric field is applied between a solid and liquid phase, and if the solid phase consists of small particles suspended in liquid, application of electric field results the movement of solid through the liquid. This is known as **cataphoresis or electrophoresis**.

3. Streaming potential (Quincke's potential)

+ pot. form dif (-) → electric field osmo. pres

When relative motion is brought about mechanically, the displacement of charged layer with respect to each other, will result in the production of difference of potential between any two points in the direction of motion. This potential is known as streaming potential This is reverse of electro osmosis.

4. Sedimentation potential or Dorn effect

The potential arises when small particles are allowed to fall through water under the influence of gravity is known as **sedimentation potential or Dorn effect**

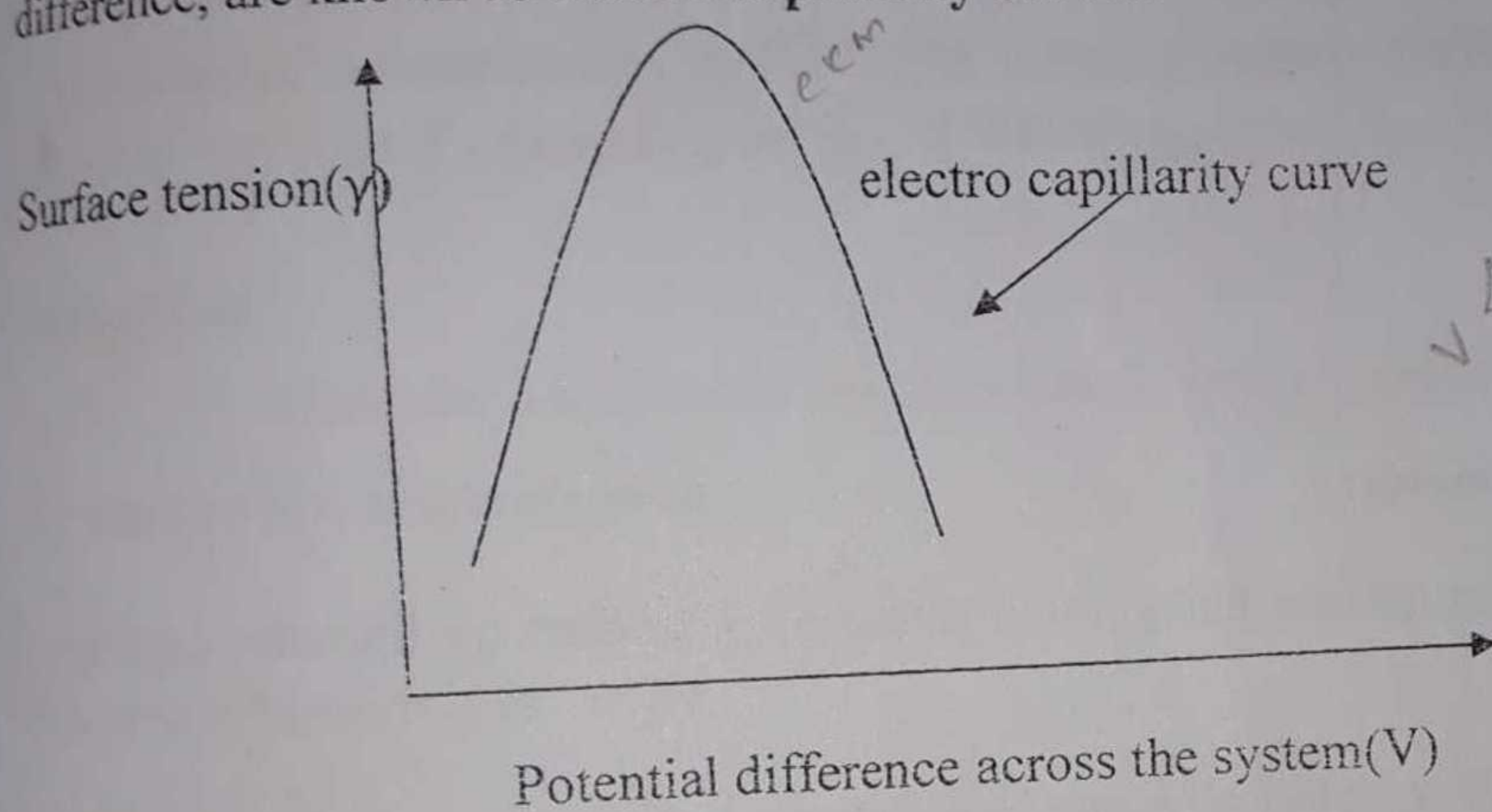
5. Zeta potential

The potential difference , at the interface between any two phases at which movement occurs is known as **zeta potential or electrokinetic potential**.(from Greek alphabet). This is due to the presence of electrically charged layers of opposite signs at the surface of separation between a solid and a liquid.

Electro capillarity:

When an electrode is in contact with a solution, a charge is induced on the metal, which is opposite to that on the electrolyte side. Due to this charge separation, a potential difference is developed across the interface. This potential difference is related to interfacial tension (surface tension). A change in potential difference across the interface, will alter the composition of the interface which in turn changes the interfacial tension. This is known as **electro capillarity**.

The curves obtained by plotting interfacial tension versus changes in potential difference, are known as **electro capillarity curves**.



$v \uparrow \gamma \downarrow$
 $P \uparrow \text{S.T.} \uparrow$
 further
 $P \uparrow \text{S.T.} \downarrow$
 slope gives the value c.d

On changing the potential, the surface tension passes through a maximum, which is called electro capillary maximum (ecm). With further increase in potential, surface tension decreases. The slopes at various values of cell potentials will give the values of charge density (q). If γ is surface tension, q - charge, v - potential, then

$$q = \frac{\partial \gamma}{\partial v} \quad \text{This is known as Lipmann equation.}$$

$$\therefore d\gamma = q \, dv \quad \text{-----1}$$

But parallel plate model

$$dv = \frac{4\pi d}{\epsilon} dq \quad \text{substituting in equation 1, we get}$$

$$d\gamma = q \frac{4\pi d}{\epsilon} dq$$

$$= \frac{4\pi d}{\epsilon} q \, dq$$

$$\int d\gamma = \frac{4\pi d}{\epsilon} \int q \, dq$$

Upon integration,

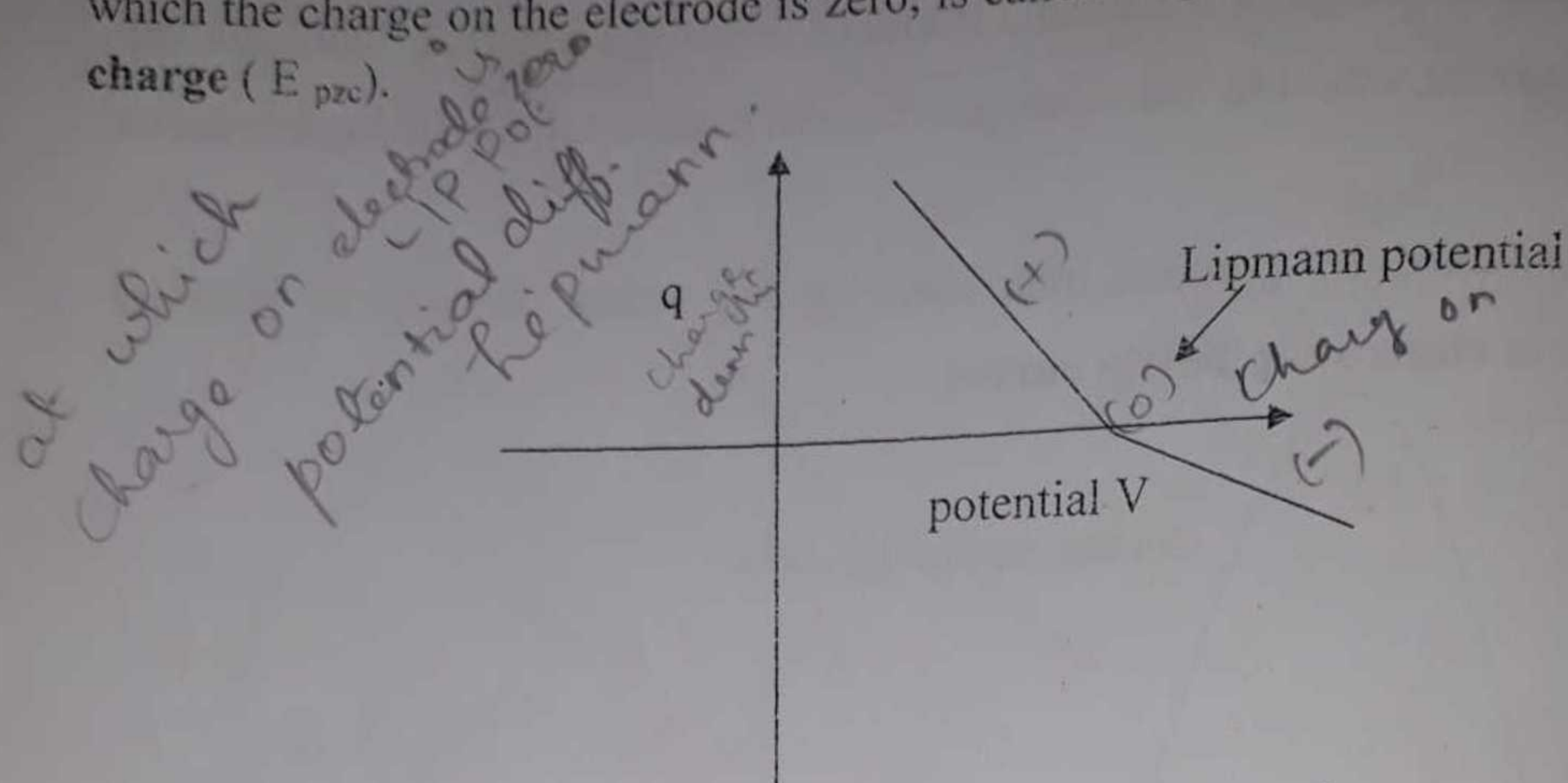
$$\gamma = \frac{4\pi d}{\epsilon} \left[\frac{1}{2} q^2 \right]$$

This is the equation for a parabola.

$$\int q \, dq = \frac{q^2}{2}$$

Lipmann potential

If the charge density is plotted against potential, it is seen that the charge on the electrode passes through a zero-charge value. The potential difference across the cell, at which the charge on the electrode is zero, is called **Lipmann potential or potential of zero charge** (E_{pzc}).

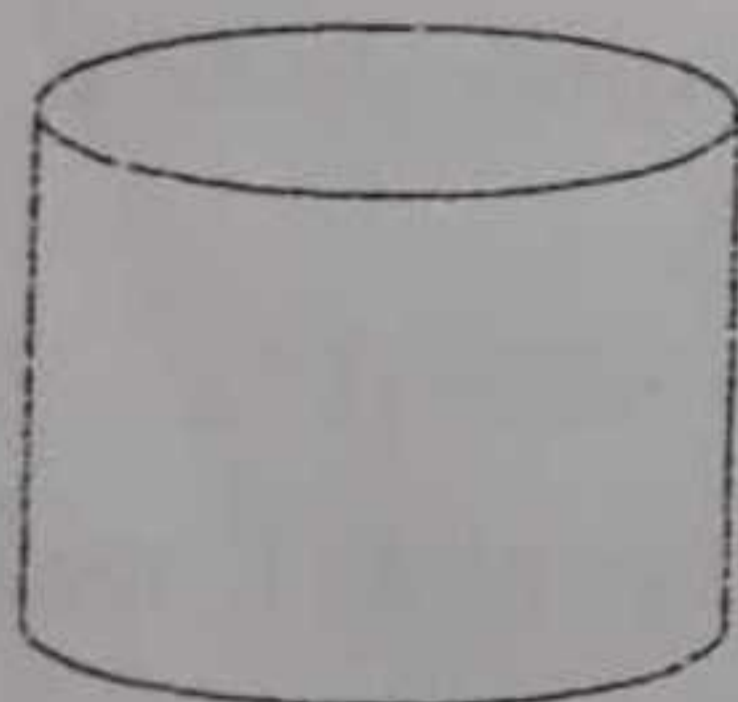


Lipmann capillary electrometer:

The relation between surface tension and potential is studied by lipmann capillary electrometer.

The apparatus consists of 1. A polarisable mercury surface 2. A non polarisable electrode (calomel electrode) 3. An external source for varying potential 4. An arrangement to measure the surface tension of mercury in contact with the solution.

Diagram:



A tube narrowing to a capillary at its end is immersed in the electrolyte. The lower meniscus in the capillary is shifted by raising and lowering the mercury bulb. The height of the mercury column is measured. The surface tension is obtained by the following relation.

$$\gamma = \frac{hr\rho g}{2}$$

where h – height of the mercury column, r – radius of the capillary, ρ – density of mercury.

Inter ionic attraction (Ionic atmosphere):

According to Debye - Huckel theory,

1. Each ion is surrounded by ions of opposite charge giving rise to an **ionic atmosphere**.
2. The thickness of the ion atmosphere is given by $\chi = \left(\frac{4\pi z^2}{DKT} \sum n_i z_i^2 \right)^{1/2}$
Where e - constant = 4.8×10^{-10} es unit, $K = 1.38 \times 10^{-16}$, D - dielectric constant, n_i - number of ions, z_i - valency, $\sum n_i z_i^2$ - ionic strength
3. The net charge of the atmosphere is equal in magnitude but opposite in sign to that of central ion.
4. The charge density will be greater in the vicinity of the ion and will fall off with increasing distance.

Derivation:

The relation between electrical density and potential is given by Poisson's equation

$$\frac{1}{r^2} \frac{\partial}{\partial x} \left(r^2 \frac{\partial \Psi}{\partial x} \right) = - \frac{4\pi\rho}{D} \text{-----1}$$

Where 'r' is the distance between the ion and its atmosphere, ρ - charge density, D - dielectric constant.

$$\rho = - \frac{\epsilon^2 \Psi}{KT} \sum n_i z_i^2$$

substituting in 1 we get

$$\begin{aligned} \frac{1}{r^2} \frac{\partial}{\partial x} \left(r^2 \frac{\partial \Psi}{\partial x} \right) &= \frac{-4\pi}{D} \left(\frac{\epsilon^2 \Psi}{KT} \sum n_i z_i^2 \right) \\ &= \frac{-4\pi\epsilon^2 \Psi}{DKT} \sum n_i z_i^2 \end{aligned}$$

$$\text{Let } k^2 = \frac{-4\pi\epsilon^2}{DKT} \sum n_i z_i^2 \text{-----2}$$

Therefore the above equation becomes

$$\frac{1}{r^2} \frac{\partial}{\partial x} \left(r^2 \frac{\partial \Psi}{\partial x} \right) = k^2 \Psi \text{-----3}$$

Solution of this equation is

$$\Psi = \frac{A e^{-kr}}{r} + \frac{A' e^{kr}}{r} \text{-----4}$$

Where A and A' are constants

To find the constants:

When $r \rightarrow \infty$, $\Psi = 0$

Therefore $0 = 0 + A'$

$$A' = 0$$

Thus the above equation becomes

$$\Psi = \frac{A e^{-kr}}{r} \quad \text{-----5}$$

For dilute solution, $k = 0$

$$\therefore \Psi = \frac{A}{r} \quad \text{-----6}$$

If the ion is regarded as point charge, the potential is

$$\Psi = \frac{z\epsilon}{Dr} \quad \text{-----7}$$

Comparing 6 and 7

$$\frac{A}{r} = \frac{z\epsilon}{Dr}$$

$$A = \frac{z\epsilon}{D}$$

Substituting in 5

$$\Psi = \frac{z\epsilon}{D} \frac{e^{-kr}}{r} \quad \text{-----8}$$

Subtracting and adding $\frac{z\epsilon}{Dr}$

$$\begin{aligned} \Psi &= \frac{z\epsilon}{D} \frac{e^{-kr}}{r} - \frac{z\epsilon}{Dr} + \frac{z\epsilon}{Dr} \\ &= \frac{-z\epsilon}{Dr} (1 - e^{-kr}) + \frac{z\epsilon}{Dr} \\ &= \frac{-z\epsilon}{Dr} (1 - (1 - kr - \dots)) + \frac{z\epsilon}{Dr} \\ &= \frac{-z\epsilon}{Dr} (\cancel{1} - \cancel{1} + kr) + \frac{z\epsilon}{Dr} \\ &= \frac{-z\epsilon k}{D} + \frac{z\epsilon}{Dr} \\ &= \frac{z\epsilon}{Dr} - \frac{z\epsilon k}{D} \end{aligned}$$

The first term represents the potential when there are no surrounding ions and the second term represents potential due to ionic atmosphere..

$$\text{Thus potential due to ionic atmosphere } \Psi = - \frac{z\epsilon k}{D} \quad \text{-----9}$$

To find the thickness of ionic atmosphere

The quantity $\frac{1}{k}$ is called thickness of ionic atmosphere. From equation 2

$$k^2 = \frac{4\pi\epsilon^2}{DKT} \sum n_i z_i^2$$

$$k = \left(\frac{4\pi\epsilon^2}{DKT} \sum n_i z_i^2 \right)^{1/2}$$

$$\frac{1}{k} = \left(\frac{DKT}{4\pi\epsilon^2 \sum n_i z_i^2} \right)^{1/2}$$

This is the expression for thickness of ionic atmosphere

Irreversible electrode process

There are some process in which measurement of EMF is made which involves appreciable current flow. The electrode process studied under these conditions are called Irreversible electrode process Example 1. Over voltage 2. Polarography

1. Over voltage (bubble over voltage)

The difference between the potential of the electrode when gas evolution is actually observed and the theoretical value for the same evolution is called over voltage.

Over voltage = actual potential – theoretical potential.

If the deviation is due to evolution of O_2 it is called oxygen over voltage and if it is due to the evolution of H_2 it is called hydrogen over voltage.

For example the reversible standard electrode potential of Zn is -0.76 V. But when H_2 evolution takes place, the value is -1.4 V

$$\begin{aligned}\text{Therefore over voltage} &= -1.46 - (-0.76) \\ &= -0.7 \text{ V}\end{aligned}$$

Applications of over voltage:

1. Electro deposition of metals in aqueous solution:

Consider the electrolysis $ZnSO_4$ and H_2SO_4 . The reversible standard electrode potential of Zn and H_2 are -0.76 V. and 0.00 V respectively. Therefore the deposition of Zn on the cathode should commence only after all the H^+ ions have been reduced to H_2 gas. But in actual practice, it has been found that zinc starts depositing along with liberation of H_2 gas. The reason lies in the high over voltage of Zn.

2. Corrosion of metals:

Consider the dissolution of Pb in HCl. The reversible standard electrode potential of Pb and H_2 are -0.13 V and 0.00 V respectively. It should readily dissolve in HCl evolving H_2 gas. But in actual practice, Pb does not dissolve in HCl and no evolution of H_2 occurs.

This is because of hydrogen over voltage of Pb which is 0.64 V.

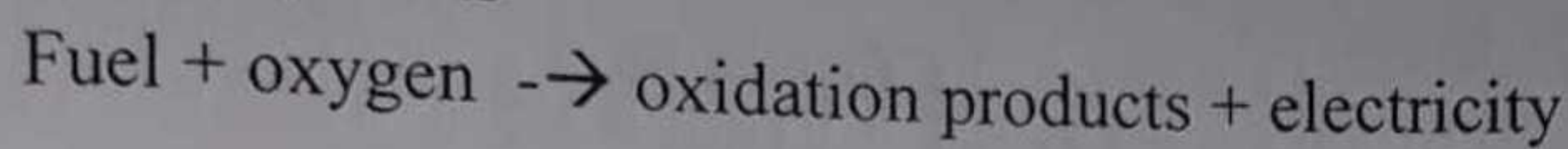
Similar effect is observed if any metal contains any other metal having low hydrogen over voltage as an impurity. This results in corrosion or dissolution of the metal.

FUEL CELLS

1. DEFINITION:

Fuel cells are those voltaic cells in which electrical energy is obtained without combustion from oxygen and a gas that can be oxidised. Hence a fuel cell converts the chemical energy of the fuels directly to electricity.

The essential process in a fuel cell is



Example

1. Hydrogen - oxygen fuel cell
2. Propane - oxygen fuel cell
3. Methanol - oxygen fuel cell

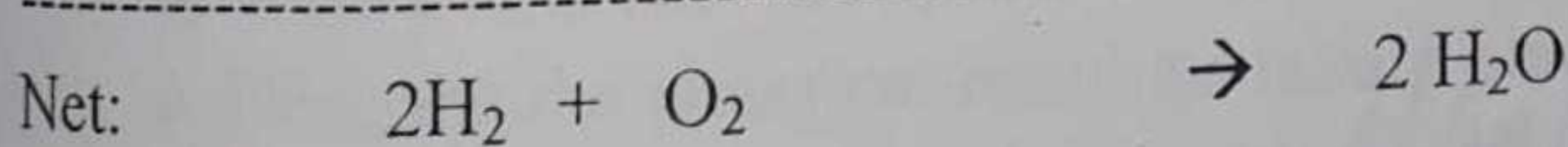
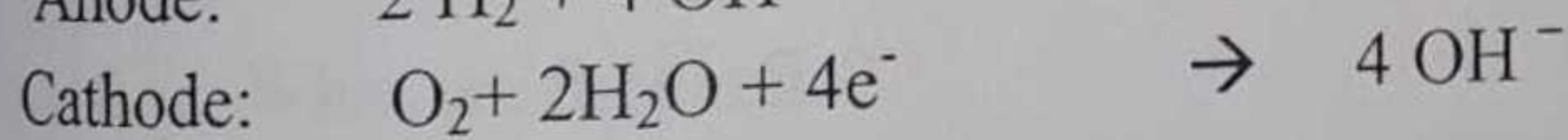
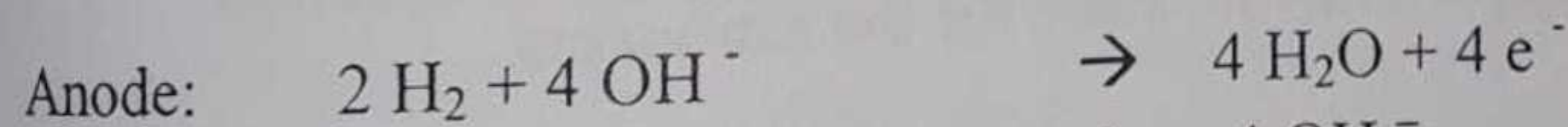
2. EFFICIENCY REQUIREMENTS:

The electrodes must be

1. Good conductors
2. Good electron sources
3. Excellent catalysts for the reactions that take place on their surfaces.
4. Not be deteriorated by the electrode reactions.

3. HYDROGEN - OXYGEN FUEL CELL:

It consists of an electrolytic solution such as 25 % KOH solution and two inert porous electrodes. Hydrogen and oxygen gases are bubbled through the anode and cathode compartment respectively where the following reactions take place.



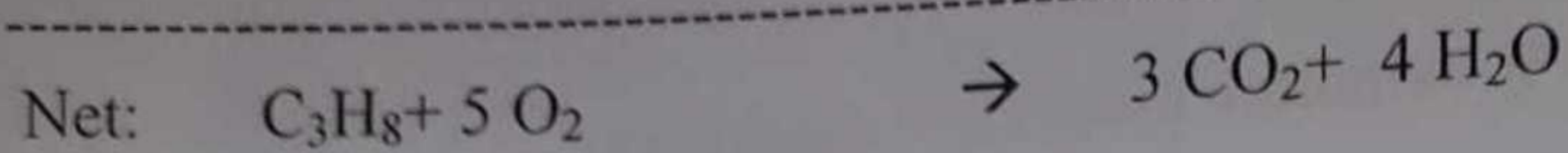
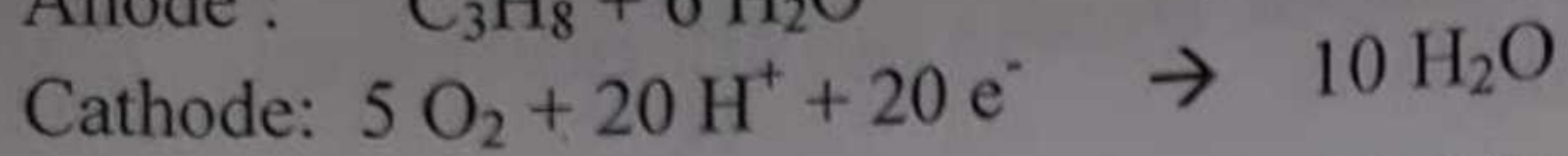
Diagram

The standard emf of the cell is

$$\begin{aligned} E^0 &= E^0_{\text{OX}} + E^0_{\text{RED}} \\ &= 0.83 + 0.4 \\ &= 1.23 \text{ V} \end{aligned}$$

A large number of these cells are stacked together in series to make a battery called fuel battery.

4. PROPANE - OXYGEN FUEL CELL



5. HIGH TEMPERATURE FUEL CELL:

Here hydrogen is used as fuel and the electrodes are made of either graphite impregnated with finely divided platinum or nickel. The electrolyte is aqueous KOH or H₂SO₄ or ion exchange resins saturated with water.

6. LOW TEMPERATURE FUEL CELL:

These cells operate at a temperature range of -54 °C to 72 °C. In this type potassium thio cyanate dissolved in liquid ammonia is used as electrolyte.

7. APPLICATIONS:

1. Hydrogen - oxygen fuel cells are used as auxiliary energy source in space vehicles like Apollo space craft
2. They are used in submarines and military vehicles.
3. H₂/O₂ fuel cell is a valuable source of fresh water for the astronauts.

Thermal power plants
↓
C. e of fossil fuel → coal, gas
produced energy
↓
reacts with water → steam run to
turbines
↓
electricity
air pollute. efficiency is less

CORROSION

Definition:

Corrosion is defined as, the destruction of materials (metal or alloy), either by chemical or by electrochemical reaction, takes place at the surface, which leads to loss of solid.

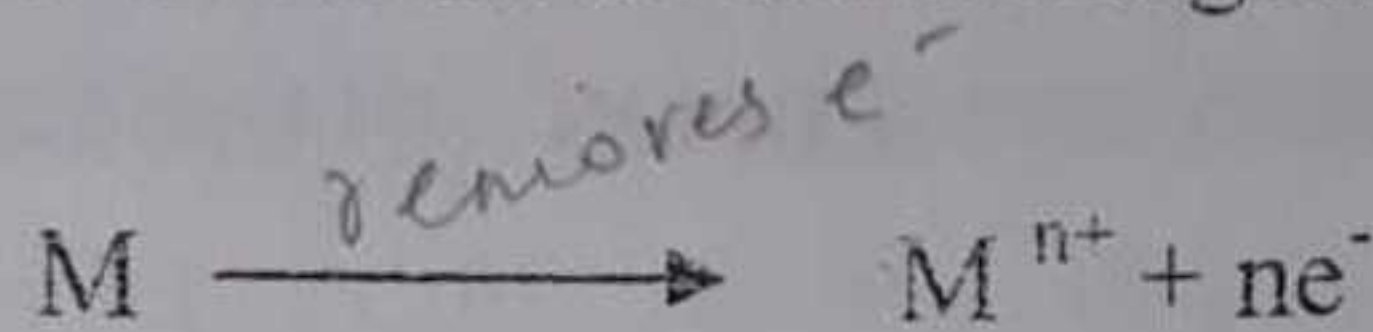
1. Chemical corrosion (dry corrosion)

If corrosion takes place by direct attack of materials by gases like oxygen, hydrogen, hydrogen sulphide, etc., in the absence of moisture, it is known as dry corrosion.

1.1 OXIDATION CORROSION:

When corrosion occurs due to oxygen then the corrosion is termed as oxidation corrosion. The mechanism involves the following stages.

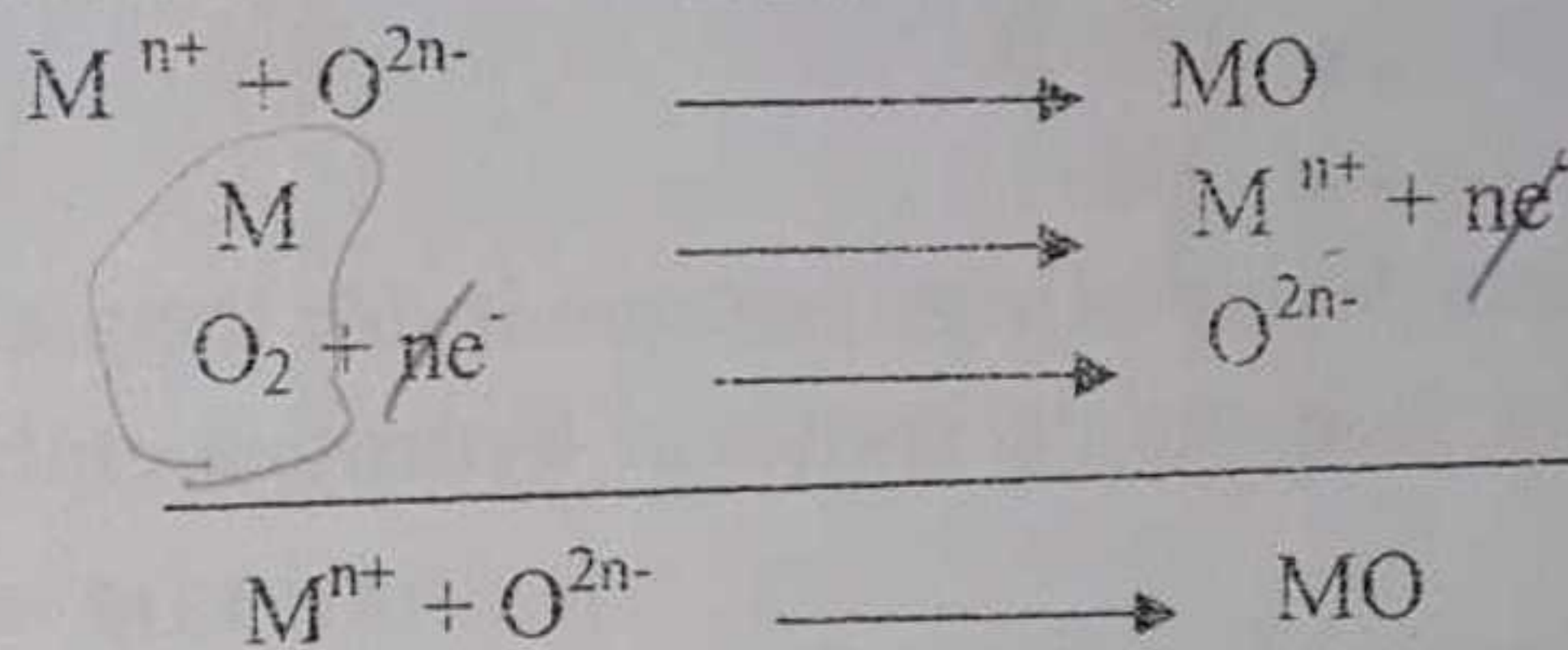
In the first stage the outer most electrons of the metal gets rejected or removed forming metal cation.



In the second stage, the electrons removed from the metal, are absorbed by oxygen forming oxide anion.



The cation and the anion formed combine to form the final product.



*M → out
O → in.*

ROLE OF OXIDE FILM:

The metal oxide formed, acts as barrier for further corrosion. To continue the corrosion, either metal ions should diffuse out or the oxide ion to diffuse in. Thus the continuation of corrosion depends on the nature of the oxide film formed.

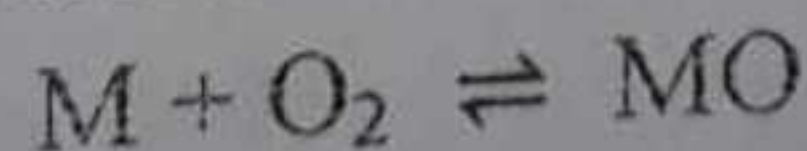
a. STABLE OXIDE:

If the oxide layer is stable, it will not permit atmospheric oxygen to pass through and also it will not permit metal ion to pass out. Thus corrosion will not continue further.

Example : Lead, aluminium, copper

b. UNSTABLE OXIDE:

Some metals form oxide reversibly. i. e The oxide layer is converted back into metal and oxygen, thus leaving fresh surface for oxidation corrosion.



Example : gold, silver, platinum.

c. VOLATILE OXIDE:

If The oxide formed is volatile, as soon as it is formed it gets vaporized leading to the continuation of corrosion.

d. **POROUS AND NON-POROUS OXIDE: (PILLING BEDWORTH RULE):**

Pilling Bedworth rule states that if the volume of the oxide formed is greater than or equal to the volume of the metal, the oxide layer is non-porous and protective. For example metals like aluminium, copper, lead.

$$V_{\text{Aluminium oxide}} \geq V_{\text{Aluminium}}$$

Therefore it is non-porous and protective.

On the other hand if the volume of oxide formed is less than the volume of metal then the oxide layer is porous and non protective.

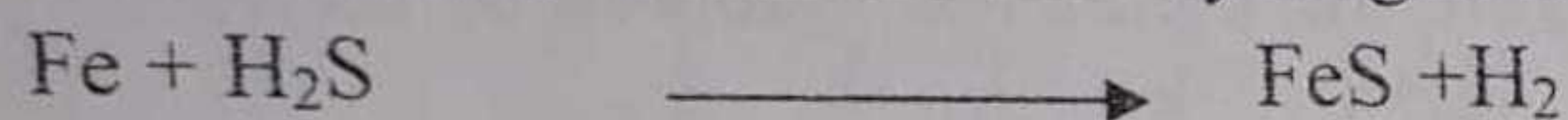
example : Alkali metals (Li, Na)

$$V_{\text{Lithium oxide}} < V_{\text{Lithium}}$$

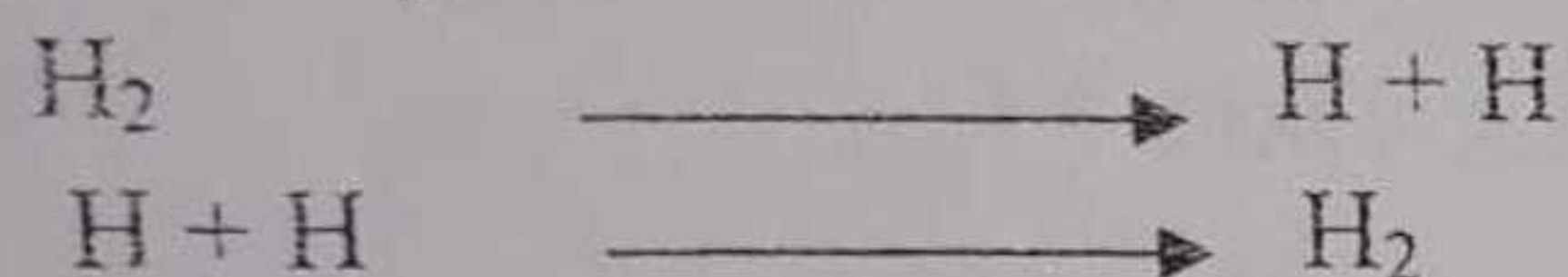
Therefore it is porous and non protective.

1.2 CORROSION DUE TO HYDROGEN:**1.2.1 HYDROGEN EMBRITTLEMENT: (CORROSION AT LOW TEMPERATURE):**

When a metal is in contact with hydrogen sulphide, it produces molecular hydrogen.



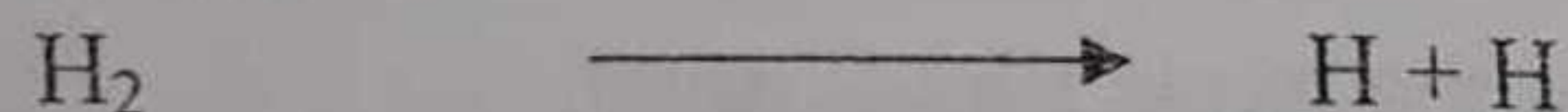
This hydrogen undergoes atomisation to form reactive hydrogen atoms. This reactive hydrogen atoms penetrate inside the metal where it recombines to form hydrogen molecule



This recombination-process develops high pressure inside the metal which leads to formation of cracks. This type of crack formation is known as **hydrogen embrittlement**.

1.2.2 DECARBURIZATION (CORROSION AT HIGH TEMPERATURE):

At high temperature, the hydrogen formed undergoes atomisation to form reactive hydrogen atoms.



These reactive hydrogen atoms combine with the carbon of the material forming methane gas.



This methane gas escapes to the atmosphere. Thus the carbon in the material is being reduced. This type of reduction of carbon in a material by hydrogen at high temperature is called **Decarburization**.

2. ELECTRO CHEMICAL CORROSION(WET CORROSION)

conditions:

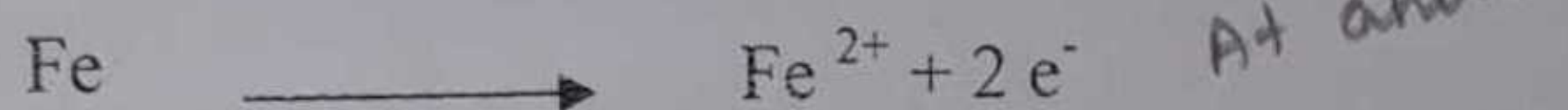
This type of corrosion occurs in two conditions.

- (i) Whenever there is a contact between two dissimilar metals in the presence of moisture or corroding medium.
- (ii) When there is difference in concentration of oxygen, electro chemical corrosion occurs.

Mechanism:

It occurs due to the formation of galvanic cells, one part acts as anode and other part acts as cathode. At anode, the metal undergoes ionisation to form cation with the release of electrons.

For example, in the case of iron



These electrons are not absorbed by cathode instead, they are absorbed by the constituents present in the medium. Depending on the constituents of environment two types of mechanisms were proposed.

a. HYDROGEN EVALUATION MECHANISM:

At cathode

This takes place when the surrounding medium contains H^{+} . The following reaction takes place :

b. OXYGEN ABSORPTION MECHANISM :

This reaction takes place when the medium is basic, neutral or alkaline. In this case electrons are absorbed by oxygen in the presence of water forming hydroxide ions. Here metal oxide is formed first which spreads over the entire surface of the metal. When a crack develops, that portion acts as anode forming cation

The cation and anion move towards each other. Since the speed of metal ions, is greater than that of hydroxide ion, the product is formed more or less near the cathodic region. Thus the overall reaction is

In the presence of excess of oxygen the following reaction takes place.

This is known as rusting of iron.

DIFFERENCES BETWEEN DRY AND WET CORROSION

DRY CORROSION	WET CORROSION
It is due to the direct attack of metals or alloys by gases like O_2 , H_2 , H_2S , etc.	It is due to the formation of galvanic cells.
Corrosion product is formed where the reaction occurs.	Corrosion occurs at anode and product is deposited near the cathode.
A homogeneous material undergoes dry corrosion.	Heterogeneity is the essential condition for the occurrence of wet corrosion.
Example : Formation of scale on metal.	Formation of rust.
It takes place in dry corrosion.	It takes place in wet condition.
It is a self controlled process.	It is a continuous process.

2.2 GALVANIC CORROSION (TWO METAL CORROSION):

When two dissimilar metals are in contact with each other in the presence of a corroding medium, the metal which has lesser electrode potential than hydrogen undergoes oxidation. This type of corrosion is called galvanic corrosion.

*anode (oxidation) lower elec. pot.
cathode*

*1. e. l. pot.
M < H*

In the above diagram Zn and Cu are coupled where Zn acts as anode and undergoes oxidation due to lower electrode potential than copper.

Example: In marine structures, steel screws are fixed in Brass material. Due to this galvanic corrosion nuts and bolts made up of same metals is preferred

By introducing an insulating material between two surfaces, electrons cannot pass from anode to cathode.

2.3 DIFFERENTIAL AERATION CORROSION :

When a metal is partially immersed in water or corroding medium, the portion which is exposed to atmosphere has more amount of oxygen and hence acts as cathode. Whereas the portion which is immersed inside has lesser concentration of oxygen and hence it acts as anode. Thus a galvanic cell is formed and the portion immersed in liquid, undergoes corrosion. This type of corrosion due to difference in concentration of oxygen is known as differential aeration corrosion.

Example: A zinc rod partially immersed in corroding medium. The region inside the liquid has in contact with lesser amount of oxygen when compared to that of exposed region and hence it undergoes corrosion.

a. PITTING CORROSION :

When a water drop rests on a metal surface, the region inside the water drop has lesser concentration of oxygen than the region outside. Thus the inside region acts as anode and undergoes corrosion and outside region acts as cathode. Due to smaller size of anode the corrosion is severe which may lead to the formation of pit (hole). Such corrosion is called pitting corrosion.

b. CORROSION IN PIPELINE :

In a pipe line emerges through variety of soil like clay, sand etc. the region inside the clay has lesser concentration of oxygen, due to closed packing structure of clay, than the region inside the sand where the molecules are loosely packed. Therefore the region inside the clay undergoes corrosion.

c. CREVICE CORROSION :

A narrow gap is called crevice. Here the region under the metal has lesser amount of oxygen and it acts as anode.

d. CORROSION IN FENCES :

In fences the stressed region has lesser oxygen and acts as anode than the other region which acts as cathode. So the stressed region undergoes corrosion.

Prevent

Zn

electroplating

Painting

Galvanisation (metal coated by Zn.)

3. FACTORS INFLUENCING CORROSION :

3.1 METALLIC FACTORS :

a. POSITION OF GALVANIC SERIES :

When elements and alloys are arranged on the basis of corrosion tendency in unpolluted sea water the series obtained is called **Galvanic Series**.

Galvanic Series :Mg, Mg Alloys, Zn, Al, Al Alloys, Cu, Ni, Cr-steel, Ag, Au, Pt

- ⚡ In this series, the elements in the top of the series undergoes more corrosion. For example : Magnesium undergoes more corrosion than silver or gold in the same environment.
- ⚡ The more the distance between the elements in the series, the lesser will be the corrosion that is why Mg - Ag alloy has lesser corrosion than Mg - zinc alloy.

b. RELATIVE AREAS OF ANODE AND CATHODE :

Corrosion tendency depends on the ratio of area between anode and cathode. When the anode is larger in size than cathode, all the electrons released by the anode cannot be absorbed by the small cathode. Therefore the corrosion decreases whereas if the anode area is smaller than cathode area, the want of electrons of larger cathode should be met by smaller anode and hence corrosion is rapid

This is the reason why copper screws in iron plate is preferred than iron screws in copper plate.

c. PURITY OF THE METAL :

Pure metal does not undergo corrosion easily. When impurities are introduced they form heterogeneity which leads to the formation of galvanic cells which in turn leads to corrosion. That is why spelter, an alloy of zinc, undergoes more corrosion than pure zinc.

d. NATURE OF OXIDE FILM :

When volume of oxide formed is greater than or equal to the volume of metal, then the oxide layer is non porous and protective. For example, the volume of Aluminium oxide is greater than that of Aluminium whereas volume of Lithium Oxide is lesser than that of Lithium.

That is why Lithium undergoes rapid corrosion than aluminium.

e. SOLUBILITY OF CORROSION PRODUCT :

If the corrosion product is soluble in the medium it allows fresh surface for further corrosion. On the other hand if the corrosion product is insoluble in the medium, it will be deposited on the surface which acts as a barrier for corrosion. Therefore corrosion will be stopped.

For example : lead undergoes lesser corrosion than copper in acidic involvement because lead sulphate is insoluble and copper sulphate is soluble in the solution.

3.2 ENVIRONMENTAL FACTORS :

a. TEMPERATURE:

An increase in temperature, increased the rate of diffusion of ions which in turn increases the rate of corrosion.

b. pH :

pH is the negative logarithm of hydrogen ion concentrations. Normally most of the metals undergoes corrosion in acidic medium. The effect of pH can be explained by the Pourbaix diagram.

In the above diagram electrode potential values are plotted against the PH values. If the element lies in the corrosive region it undergoes corrosion.

c. HUMIDITY :

The atmospheric humidity introduces moisture in the metal which helps to form galvanic cells which in turn increases the rate of corrosion.

d. IMPURITIES IN THE ATMOSPHERE :

In industrial areas, particles of CO_2 , SO_2 and H^+ ions will be present in the atmosphere which dissolves in the moisture forming corresponding acids. This reduces the pH of the medium and hence corrosion rate is enhanced.

e. NATURE OF THE STATE OF MATERIAL :

The stressed areas will have lesser contact with oxygen than the unstressed areas. So the stressed areas form anode and the unstressed area forms cathode thereby forming a galvanic cell which introduce corrosion.

4. CORROSION CONTROL :

a. CATHODIC PROTECTION :

Principle :

In this method, the structure to be protected is forced to act as cathode and the corrosion is prevented. The two methods under this technique are

4.1 SACRIFICIAL ANODIC PROTECTION :

The structure to be protected is made as cathode by connecting it to a more reactive metal. Thus the corrosion occurs at the more reactive metal and hence the structure is protected. Since the more reactive metal coupled undergoes corrosion. This metal is called sacrificial anode.

Example : for sacrificial anode are Mg, Zn, Al, etc.

applications : Protection of buried pipe lines.

4.2 IMPRESSED CURRENT CATHODIC METHOD :

In this method the structure to be protected is forced to act as cathode by applying direct current in the opposite direction so that the corrosion current is nullified. This is achieved by connecting the negative terminal of the battery to the structure to be protected and the positive terminal of the battery is connected to inert electrode like graphite. In order to increase the conductivity, the inert electrode is surrounded by "Back Fill" which contains Gypsum, Sodium Chloride, Sodium Sulphate and Coke.

Applications :

It is mainly applicable to

- ⊕ To protect buried pipe lines.
- ⊕ To protect corrosion in water tanks.

Differences between sacrificial anode and impressed current cathodic method

SACRIFICIAL ANODIC METHOD	IMPRESSED CURRENT CATHODIC METHOD
Here the structure is protected by using more reactive metal which acts as anode.	Here structure is protected by passing current in opposite direction
More active metals are required.	Current is required.
It is necessary to replace the anode.	No such problem.
It is applicable only for short duration.	It is applicable for long period.
Cost is low.	Cost is high.

4.3 CORROSION INHIBITORS :

Those chemicals which control the rate of corrosion are called corrosion inhibitors. There are three types of corrosion inhibitors. There are

a. ANODIC INHIBITORS :

These are chemicals which prevents the anodic reactions. During corrosion the metals undergo oxidation to form metal cations. Inorganic salts like phosphates, chromates, molybdates of transition metal are added to the corroding medium, the cations generated will form insoluble precipitates which makes a barrier for corrosion and hence corrosion is controlled.

b. CATHODIC INHIBITORS :

These are chemicals which are added to inhibit the cathodic reactions during corrosion. In acidic medium the following cathodic reaction is responsible for corrosion

To control corrosion, the above reaction should be stopped. This can be achieved by adding organic compounds containing Nitrogen, Sulphur, etc. For example : Amines, Pyridine, Pyrone, thio alcohol, etc. When these compounds are added they combine with H^+ in preference to the electron. Thus it prevents corrosion.

In the natural medium, the following reaction is responsible for corrosion

This reaction can be stopped by

Deaeration :

Here reactive chemicals like sodium sulphide (Na_2SO_3), Hydrazine undergo reaction with oxygen in preference to electron and thus they arrest the cathodic reaction.

Deactivation :

In this method metals like magnesium or zinc are added to the corroding environment which combines with hydroxide ions forming insoluble precipitate which will be deposited on the cathodic region thereby it prevents corrosion.

c. VAPOUR PHASE INHIBITORS :

These are organic volatile compounds like dicyclohexyl ammonium nitrate. When these are added to corroding environment they evaporates and form protective layer on either anode or cathode and hence prevents corrosion.

Proper designing:

The design of the material should be such that corrosion even if occurs, should be uniform and does not result intense and localised corrosion.

1. Avoid the contact of dissimilar metals in the presence of corroding solution.

poor design good design

2. Whenever the direct joining of dissimilar metals is unavoidable ,

a. insulation may be applied in- between, to avoid direct metal-metal contact

poor design good design

- b. They should be as close as possible to each other in the electro chemical series.

poor design good design

- c. The anodic material should have as larger area as possible and the cathodic material should have as much smaller area as possible.

poor design good design

- d. The anodic metal should not be painted or coated, because any break in the coating leads to rapid localised corrosion.

poor design good design

3. Avoid presence of crevices between adjacent parts of the structure, Bolt and rivets are should be replaced by weld joint

poor design good design

4. Sharp corners and bent should be avoided.

poor design good design

5. Allow complete cleaning and flushing.

poor design good design

Using pure metal:

Impurities in the metal causes heterogeneity which may lead to electro chemical corrosion.

Modifying the environment.:

The corrosive nature of the environment ca be reduced by

1. **Deaeration:** Exclusion of oxygen from aqueous environment reduces metal corrosion. Expulsion of dissolved oxygen is done by adjustment of temperature together with mechanical deaeration.

2. **Deactivation:** it involves the addition of chemicals capable of combining rapidly with the oxygen in the aqueous solution. For example sodium sulphite and hydrazine.



5. PROTECTIVE COATING :

5.1 PAINTS :

Paints are colloidal dispersion of pigments in a medium called thinners and vehicles. When applied on surface thinner undergoes oxidation and oxidant undergoes oxidation forming a thin film on the surface.

Constituents and their functions :

a. PIGMENTS:

Pigments are solid substance which are dissolved in the medium. They give colour to the paint. They reflect UV rays and protect the thin film formed by the paint.

Example : White - Titanium oxide, Green - Chromium oxide

↓ Red - Red lead, Blue – Ultra marine blue

↓ Yellow – Chrome yellow

b. VEHICLES (DRYING OILS)

These are the liquid medium in which the pigments are involved. They undergo oxidation by absorbing oxygen from atmosphere to form the film. They dissolve the pigments. Example : Linseed oil, Soyabean oil, Tung oil, Dehydrated Caster oil.

c. THINNERS :

These are the liquid component in the paint which are used to reduce the viscosity of the paint, To dissolve the pigments. It helps in drying of oil by evaporation.

Examples : Turbentine, kerosene, benzene, toluene, xylene.

d. EXTENDERS (FILLERS)

These are used to increase the strength of paint. Its other function is to reduce the cost.

Example : Barium sulphate, calcium sulphate Talc, Asbestos, Mica

e. PLASTISIZERS :

These are added to the paint to increase the flexibility of the paint and to avoid cracking in paint. Example : Tricresyl phosphate, tributyl phthalate, triphenyl butates

f. ANTI SKINNING AGENTS :

These are used to reduce gelling of paint and to avoid breaking of paint film.

Example : Polyhydroxy phenols.

2 METALLIC COATING :

5.2.1. ELECTRO PAINTING :

It is the process of deposition of coating metals on base metal by passing direct current through the electrolyte containing the soluble salts of coating.

EXPERIMENTAL SET UP :

In this metal, the article to be coated is connected to the negative terminal of the battery, hence it acts as cathode. The positive terminal of the battery is coupled with either the electrode made up of coating metal or inert elements. The electrolyte is a soluble salt of containing metal dissolved in suitable salt.

Consider gold coating on copper plate. The article copper is taken as cathode and gold plate is taken as anode. The electrolyte is gold chloride dissolved in minimum quantity of HCl. When the direct current is passed through the electrolyte, AuCl_3 undergoes ionisation to form gold cations and chloride anions.

These cations move towards the cathode and there they gets reduced and deposited on the article. The decrease in concentration of gold in the electrolyte is compensated by dissolving the anode.

FACTORS AFFECTING ELECTRO PLATING :

⚡ NATURE OF SURFACE AREA :

If the surface area is clean, the deposit will be uniform. Therefore before electro plating the surface of the article should be cleaned. Cleaning can be done by pickling, solvent cleaning, mechanical cleaning, etc.

⚡ CONCENTRATION OF ELECTROCYTE :

redox reaction Nickel particles are formed and deposited on the article. The reactions are explained below :

During the above reactions H^+ ions are formed which reduces the PH of the medium. In order to compensate the reduction in PH sodium acetate buffer is added so that the PH value is maintained at 4.5. For uniform deposition low concentration of solution is required. In order to achieve lower concentration complexing agent is added along with reducing agent.

ADVANTAGES OF ELECTRO LESS PLATING OVER ELECTO PLATING :

- ↓ No current is required.
- ↓ No anode is required.

DIFFERENCE BETWEEN ELECTRO PLATING AND ELECTRO LESS PLATING

ELECTRO PLATING	ELECTROLESS PLATING
It is a process of deposition of coating metal on the base metal by passing direct current through the electrolyte containing soluble salts of coating.	It is the process of deposition of coating metal on the base metal using redox reaction.
Electricity is required.	Electricity is not required.
It is applicable for the object made up of conducting or semi conducting material.	It can be done even for anon-conducting material.
Complicated shape cannot be plated, uniform plate can be plated.	Complicated material can also be subjected for plating.

DIFFERENCE BETWEEN ELECTROCHEMICAL AND GALVANIC SERIES

ELECTROCHEMICAL SERIES	GALVANIC SERIES
In electro chemical series elements (metals & non-metals) are arranged in increasing or decreasing order on the basis of standard reduction potential.	Here elements or alloys are arranged on the basis of corrosion tendency in unpolluted sea water.
Only metals and non-metals are involved.	Only metals and alloys are involved.
Position of the elements is fixed.	Position of the elements is not fixed.
There is standard (Hydrogen) to compare electrode potential.	No such standard.

The lower is the concentration of electrolyte, the better is the quality of deposition. In order to minimise the concentration the electrolyte is mixed with mineral acids like HCl or we can mix it with complexing agent.

⚡ CURRENT DENSITY :

Current density is defined as the quantity of current per unit. The nature of deposit depends on the current density.

⚡ pH

The PH of the electrolyte also determines the nature of deposition. Usually the pH of 5 to 7 is preferred in gold plate.

5.2.2 ELECTROLESS PLATING :

It is the process of deposition of coating metals on base metal using redox reaction is called as electro less plating.

The solution used to deposit soluble salts of coating. The reducing agent is generally sodium hypo phosphate.

Consider electroless coating by Nickel.

It involves two stages

STEP-1 : PRE- TREATMENT OF THE SURFACE :

The article to be deposited is subjected to pre-treatment process which includes acid pickling, solvent cleaning, degreasing, mechanical cleaning, etc.

STEP-2 : ELECTRO LESS DEPOSITION :

Now the article is immersed in a solution of Nickel chloride. A required amount of sodium hypo phosphate (NaH_2PO_2) as reducing agent. When sodium hypo phosphate is added the Nickel ions (Ni^{2+}) ions undergoes reduction. The PH is maintained at 4.5 in 90 - 100 and at the same time, the sodium hypo phosphate undergoes oxidation. Because of the