CHAPTER 9

ELECTROCHEMISTRY

9.1.0 INTRODUCTION

"Electrochemistry is that branch of science which deals with the study of all physical and chemical processes, which can be carried out by electrical energy. It also includes those processes which proceed with the generation of electricity. Simply, we can say that electrochemistry deals with the conversion of electrical energy into chemical energy and chemical energy into electrical energy."

9.1.1 Metallic conductor or electronic conductors:

"In metallic conductors the current is transported by the electrons and the conducting material does not undergo any chemical change." For this reason they are called electronic conductors. Almost all the metals, alloys and graphite are the best examples of electronic conductors.

9.1.2 Electrolytic conductors:

"In electrolytic conductors, the current is transported due to the migration of the ions." These ions move towards the respective electrodes. The solutions of acids, bases, fused salts and the aqueous solution of some of the salts are the best examples of electrolytic conductors.

COMPARISON OF METALLIC AND ELECTROLYTIC CONDUCTORS:

Metallic conductors	Electrolytic conductors
(1) The electricity is conducted by the flow of electrons from negative potential to positive potential.	(1) The electric current is carried by charged ions moving towards the respective electrodes.
(2) No chemical change takes place during the conduction of electrical current.	(2) A chemical change takes place during the process of electrolytic conduction.
(3) The increase of temperature decreases the conductance.	(3) The conductance increases with the rise of temperature.

9.1.3 Electrical resistance:

The idea of the electrical resistance or the electrical conductance can be best understood from the Ohm's law.

According to this law, the resistance of a conductor is the ratio of applied voltage (E) to the current strength (I) flowing through the conductor

$$R = \frac{E}{I} \qquad \ldots\ldots (1)$$

The current 'I' is measured in amperes and voltage (E) is measured in volts.

Units of resistance:

"When one ampere current flows though a conductor and a voltage of one volt is applied, then the resistance of the conductor is taken as 1 ohm." It is represented by 'Ω'.

This law is obeyed by metallic conductors and electrolytic conductors.

9.1.4 Conductance:

Conductance is reciprocal of resistance. Let us denote it by 'C'. So, the resistance 'R' and the conductance 'C' are just opposite to each other.

$$C = \frac{1}{R} \qquad \ldots\ldots (2)$$

Keep it in mind that it is more common practice to talk about the conductance of the solution rather than its resistance.

"The units of conductance are the reciprocal of resistance." It is denoted by ohm^{-1} or mho. It is also expressed in Siemen's (S)

$$1 \text{ Siemen} = 1 \text{ mho}$$
$$1 \text{ S} = 1 \Omega^{-1}$$

9.1.5 Specific conductance:

The idea of the specific conductance can be deduced form the idea of the resistance of a conductor. The resistance of a conductor is directly proportional to its length 'l' and inversely proportional to the area of cross section 'a'.

So, $$R \propto \frac{l}{a}$$

$$R = \rho \frac{l}{a} \qquad \ldots\ldots (3)$$

Here 'ρ' is the constant of proportionality. This is called specific resistance or resistivity of the conductor. The value of the 'ρ' depends upon the nature of the conductor.

According to equation (3), the resistance of a conductor depends upon the length of the conductor, area of cross section of conductor and its resistivity.

When we take the reciprocal of resistivity 'ρ' then it is called specific conductivity or simple conductivity. Let us denote it by 'K'.

So, $$\rho = \frac{1}{K}$$

Since, $$R = \frac{1}{C}$$

Putting these things in equation (3),

$$\frac{1}{C} = \frac{1}{K} \cdot \frac{l}{a}$$

Rearranging this equation,

$$K = C \cdot \frac{l}{a} \qquad \cdots\cdots (4)$$

So, specific conductance 'K' is related with the conductance of substance 'C', length of the conductor 'l' and area of cross section 'a'. In order to define 'K', let us suppose that

$$l = 1 \text{ cm}$$

$$a = 1 \text{ cm}^2$$

$$K = C \cdot \frac{1}{1} = C \qquad \cdots\cdots (5)$$

"So, specific conductivity 'K' of a solution is the conductance of a solution whose length is 1 cm and area of cross section is 1 cm^2."

If the length is 1 cm and area of cross section is 1 cm^2, than the solution is placed in such a box, which is 1 cm cube. It means that the specific conductivity is the conductance of 1 cm cube of a solution of an electrolyte. Following diagram (1) makes the idea clear.
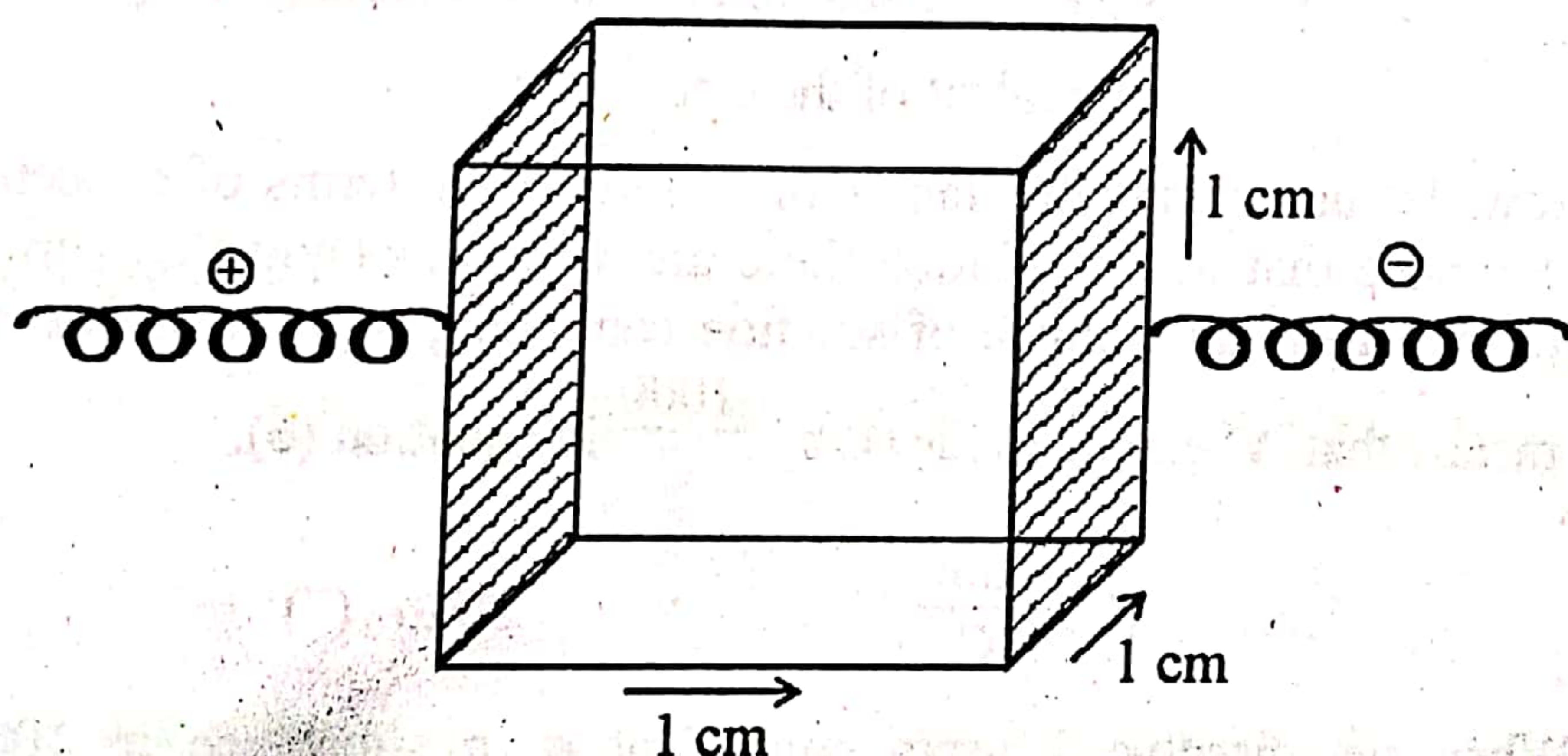

Fig. (1) Specific conductivity, when current passes through a 1 cm^3.

In order to derive the units of specific conductance, we take the following equation:

$$R = \rho \cdot \frac{l}{a}$$

$$\rho = R \cdot \frac{a}{l}$$

$$\rho = \text{ohm} \cdot \text{cm}^2 / \text{cm} = \text{ohm cm}$$

The specific conductance 'K' is the reciprocal of specific resistance 'ρ'.

$$K = \frac{1}{\rho} = \frac{1}{\text{ohm} \cdot \text{cm}} = \text{ohm}^{-1} \text{cm}^{-1} = \text{S cm}^{-1}$$

i.e. Siemen cm^{-1}.

Conc t
temp t nature
of solution.
Conductivity

free electron
availability

1 g
equivalent

Equivalent
Conductance
Λ/d.

9.2.0 EQUIVALENT CONDUCTANCE:

Introduction:

The conductivity of a metallic conductor depends upon the availability of free electrons in the metal structure. The conductivity of an ionic solution depends upon the concentration of the solution along with the temperature and nature of the solution. Concentration of the electrolytes gives us the idea about the number of charged ions present per unit volume. If we want to compare the conductivities of different electrolytes, then we should dissolve definite mass of the electrolyte in same volume of water. For that purpose, we either dissolve one gram equivalent of the electrolyte or one mole of the substance. *"Equivalent conductance of an electrolyte is the conductance of all the ions produced from one gram equivalent of the electrolyte dissolved in V cm³ of the solution, when the distance between the electrodes is 1 cm and the area of the electrode is so large, that whole of the solution is contained between them."* The equivalent conductance is represented by 'Λ'.

Equivalent conductance is related with the specific conductivity by the following relationship,

$$\Lambda = K.V. \qquad \cdots\cdots (6) \qquad [K = kappa]$$

V = Volume of solution in cm³, containing one gram equivalent of the electrolyte

Now, let us convert this factor of volume 'V' in terms of concentration of solution. Suppose that in the solution there are 'C' grams equivalents in 1000 cm³ of the solution, then the volume of solution containing 1 gram equivalent will be $\frac{1000}{C}$. It means that 'V' can be replaced by $\frac{1000}{C}$ in equation (6).

$$\Lambda = K.\frac{1000}{C} \qquad \cdots\cdots (7)$$

When we dissolve 1 gram equivalent of a substance in 1000 cm³ of solution, then 'C' corresponds to normality. So, equation (7) can be written as,

$$\Lambda = K.\frac{1000}{normality} \qquad \cdots\cdots (8)$$

In order to derive the units of equivalent conductance take above equation (8),

$$\Lambda = K\frac{1000}{normality} = ohm^{-1}\ cm^{-1} \times \frac{cm^3}{gram\ equivalent}$$

or $\quad \Lambda = ohm^{-1}\ cm^2\ (g\ eq)^{-1}$

or $\quad \Lambda = S\ cm^2\ (g\ eq)^{-1}$

or $\quad \Lambda = \Omega^{-1}\ cm^2\ (g\ eq)^{-1}$

9.2.1 Molar Conductance:

If the quantity of electrolyte is expressed in terms of moles of the substance, then the term molar conductivity evolves. *"It is the conductivity of a solution produced by the conductance of all the ions from one mole of the electrolyte dissolved in V cm³ of solution."* The electrodes should be 1 cm apart and the area of the electrode should be so large, that whole of the solution is contained between them. Let us denote it by $\wedge_m$.

It is related to the specific conductivity by the following relationship

$$\wedge_m = K.V$$

$$\wedge_m = K . \frac{1000}{C} = K . \frac{1000}{molarity} \qquad \cdots (9)$$

The units of $\wedge_m$ will be ohm^{-1} cm^2 mol^{-1}.

9.2.2 Measurement of electrolytic conductance:

Conductance can be obtained by the measurement of resistance, because the conductance is reciprocal of resistance.

The measurement of resistance can be done by wheadstone bridge method. This arrangement is shown in the following diagram (2).
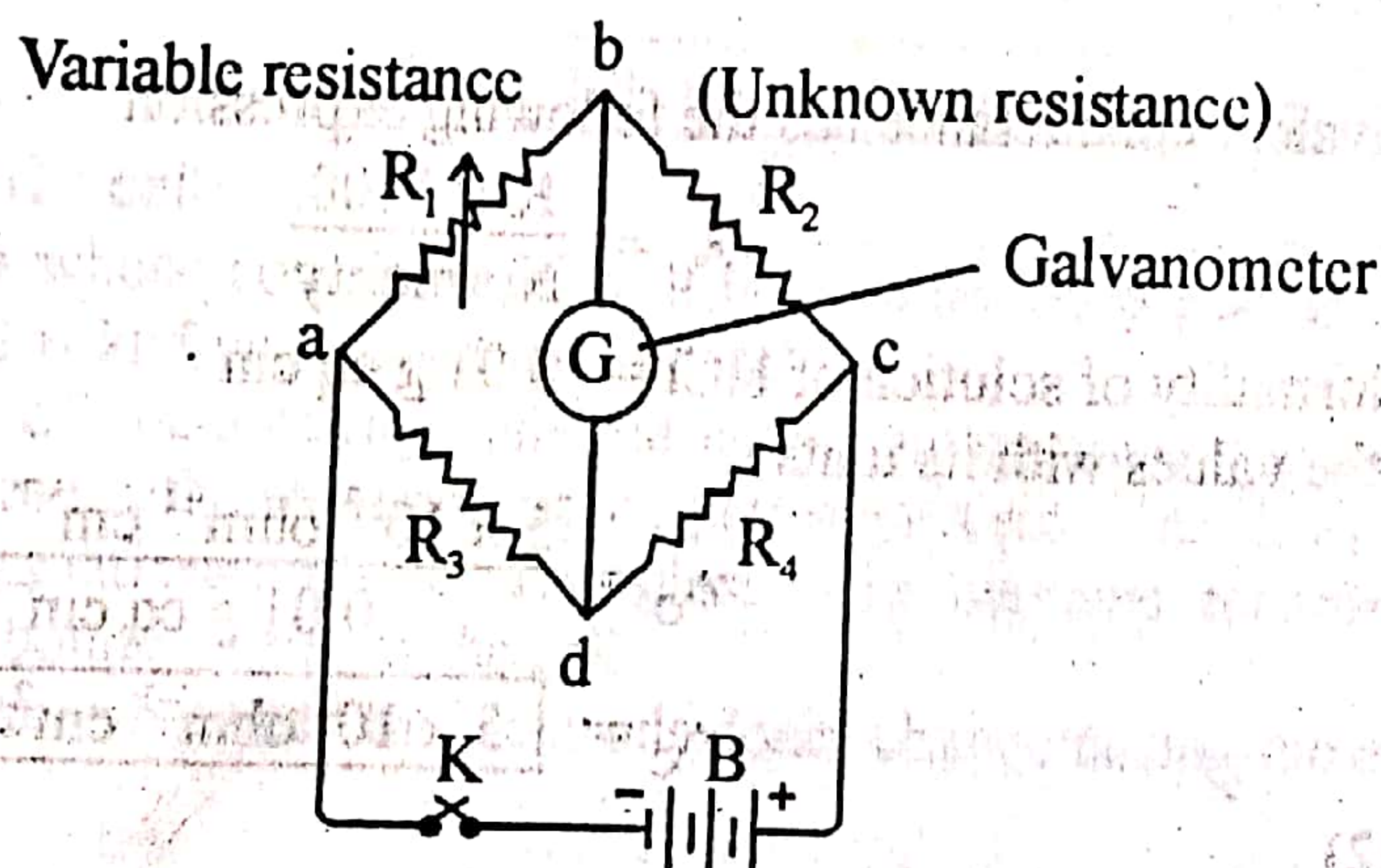

Fig. (2) *Principle of wheadstone bridge method to measure electrolyte conductance.*

The arrangement shows four resistances as 'R_1', 'R_2', 'R_3' and 'R_4'. 'R_1' is the variable resistance. 'R_2' is unknown resistance at which the solution whose resistance is to be determined is connected. A source of A.C. current is connected across, the points 'a' and 'c'. The current detect or 'D' is attached between 'b' and 'd'.

Let the current in the four arms be 'I_1', 'I_2', 'I_3', 'I_4'. According to ohm's law,

$$E_1 = I_1R_1$$

$$E_2 = I_2R_2$$

$$E_3 = I_3R_3$$

$$E_4 = I_4R_4$$

Now, if the resistances are adjusted in such a way, that there is no net flow of the current through the detector 'D', then this bridge is said to be balanced. At that situation, following relationship is applicable

$$\frac{R_1}{R_2} = \frac{R_3}{R_4} \qquad \ldots \ldots (10)$$

Equation (10) is used from the sense that, if we know the resistances of three arms i.e. 'R_1', 'R_3' and 'R_4', then 'R_2' can be calculated.

EXAMPLE (1)

Calculate equivalent conductance of solution of 0.01 N HCl, whose resistance at 25°C is 200 ohms. The cell constant of the conductivity cell is unity.

SOLUTION:

Data: Resistance (R)   = 200 ohms

Cell constant   = 1 cm^{-1}

Formula:

Since the specific conductance, (K) = $\frac{1}{R}$ × cell constant.

Putting the values and units

$$K = \frac{1}{200 \ ohm} \times 1 \ cm^{-1}$$

$$K = 5 \times 10^{-3} \ ohm^{-1} \ cm^{-1}$$

Formula:

The equivalent conductance has the following expression

$$\Lambda_c = \frac{K \times 1000}{Normality}$$

Normality of solution of HCl = 0.01 g eq cm^{-3}

Putting the values with its units

$$\Lambda_c = \frac{5 \times 10^{-3} \ ohm^{-1} \ cm^{-1} \times 1000}{0.01 \ g \ eq \ cm^{-3}}$$

$$\Lambda_c = \boxed{5 \times 10^2 \ ohm^{-1} \ cm^2 \ eq^{-1}} \quad Ans.$$

EXAMPLE (2)

One g of BaCl$_2$ is dissolved in 200 cm^3 of solution. The conductivity of solution comes out to be 0.0058 mho cm^{-1}. Calculate the molar conductivity and equivalent conductivity of this solution.

SOLUTION:

Data:

Conductivity of solution, (K) = 0.0058 mho cm^{-1}

Molar mass of   BaCl$_2$ = 137 + 2 × 35.3 = 208 g mol^{-1}

Volume of solution   = 200 cm^2 = 0.2 dm^3

Formula:

$$Molarity = \frac{Mass}{Molar \ mass} \times \frac{1}{Vol. \ of \ solution \ in \ dm^3}$$

$$Molarity = \frac{1}{20} 8 \times \frac{1}{0.2 \ dm^3}$$

$$= 0.0240 \ mol \ dm^{-3}$$

Putting the values in formula to get $\wedge_m$

Molar conductivity, $\qquad \wedge_m = K \times \dfrac{1000}{C}$

Putting values

$$\wedge_m = 0.0058 \text{ mho cm}^{-1} \times \dfrac{1000}{0.0240 \text{ mol dm}^{-3}}$$

$$= \boxed{241.67 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}} \quad \text{Ans.}$$

Equivalent weight of $BaCl_2 = \dfrac{\text{Molar mass}}{2} = \dfrac{208}{2} = 104$

Formula:

∴ Concentration of the solution in gram equivalent dm^{-3}

$$\text{Normality} = \dfrac{\text{Mass}}{\text{Eq. wt.}} \times \dfrac{1}{\text{Vol. of solution in dm}^3}$$

$$\text{Normality} = \dfrac{1}{104} \times \dfrac{1}{0.2} = 0.0480$$

Equivalent conductivity $\wedge_{eq} = K \times \dfrac{1000}{\text{Normality}}$

Putting the values

$$\wedge_{eq} = 0.0058 \text{ mho cm}^{-1} \times \dfrac{1000}{0.0480 \text{ eq. dm}^{-3}}$$

$$\wedge_{eq} = \boxed{120.83 \text{ ohm}^{-1} \text{ cm}^2 \text{ eq}^{-1}} \quad \text{Ans.}$$

9.2.3. Conductivity cell:

The solution whose conductance is to be determined is placed in a special type of cell. That cell is known as conductivity cell.

A few types of conductivity cells are shown in the following diagram (3). The electrodes of these cells are made up of platinum discs. The discs are coated with finally divided platinum black. The glass tube contains mercury and are finally fixed in an embonite cover of the cell.

In this way the distance between the electrods donot change during the experiment.
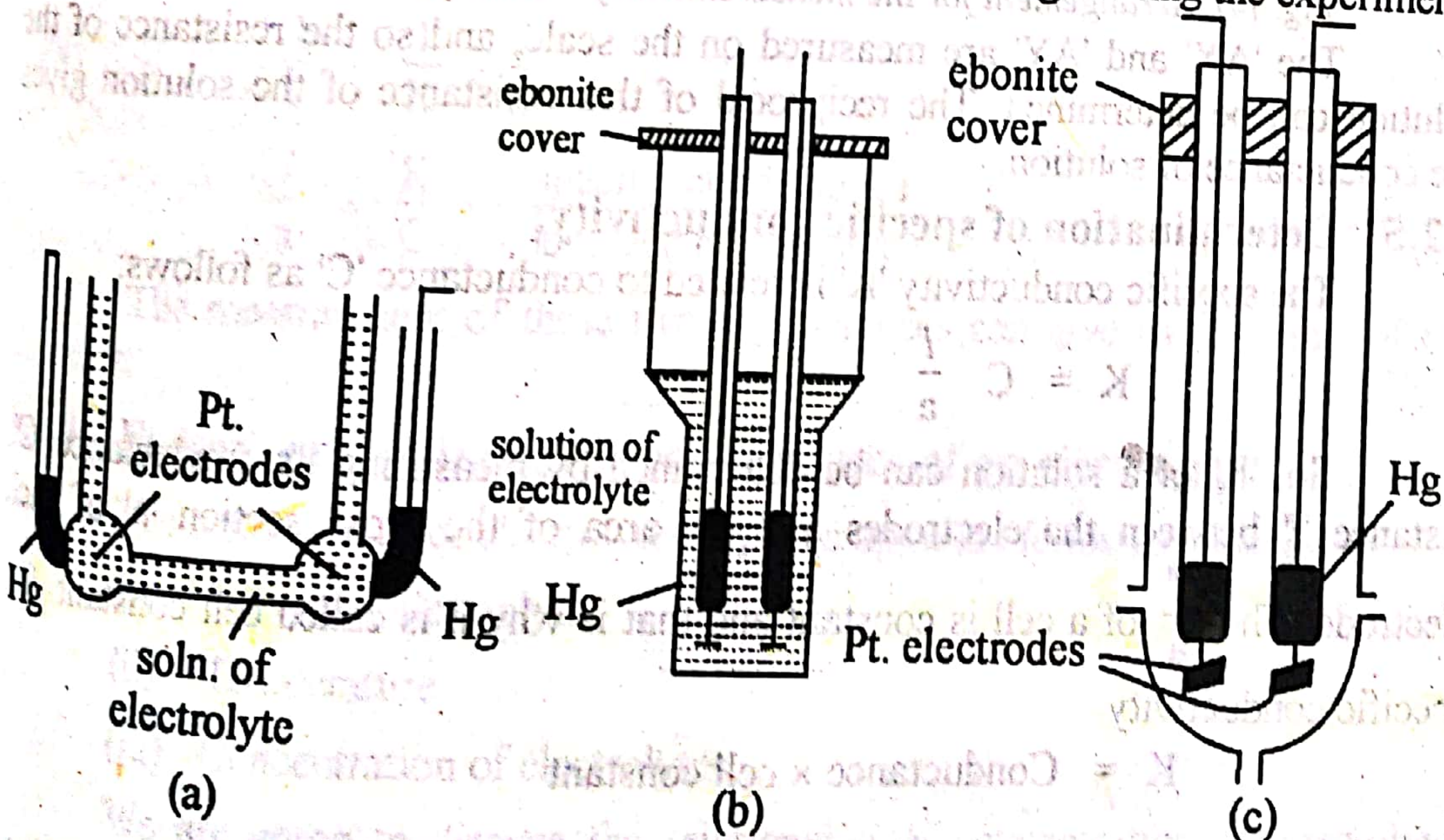

Fig. (3) Types of conductivity cells.

The contact between the platinum electrodes is made by dipping the copper wires of the circuit in the contained mercury of the tubes.

9.2.4 Problems of conductivity cells:

One of the major difficulties arises, when the electrolysis of the solution takes place. Due to this reason, two complications arise.

(i)   Resistance changes due to polarization.

(ii) The concentration of the solution changes.

In order to avoid these complicacies, an alternating current is employed, and the galvanometer of wheadstone bridge in circuit is replaced by the head phone. Following arrangement Fig. (4) shows the apparatus where 'R' is the resistance box 'XY' is, the uniform wire. At the beginning a known resistance which is approximately of the same order as that of solution is introduced from the resistance box. The sliding contact is moved on the uniform wire and the point of minimum sound is detected.

Let this point be 'A'. Following equation can be used.

$$\frac{\text{Resistance of solution}}{\text{Resistance R}} = \frac{\text{Length AY}}{\text{Length AX}}$$

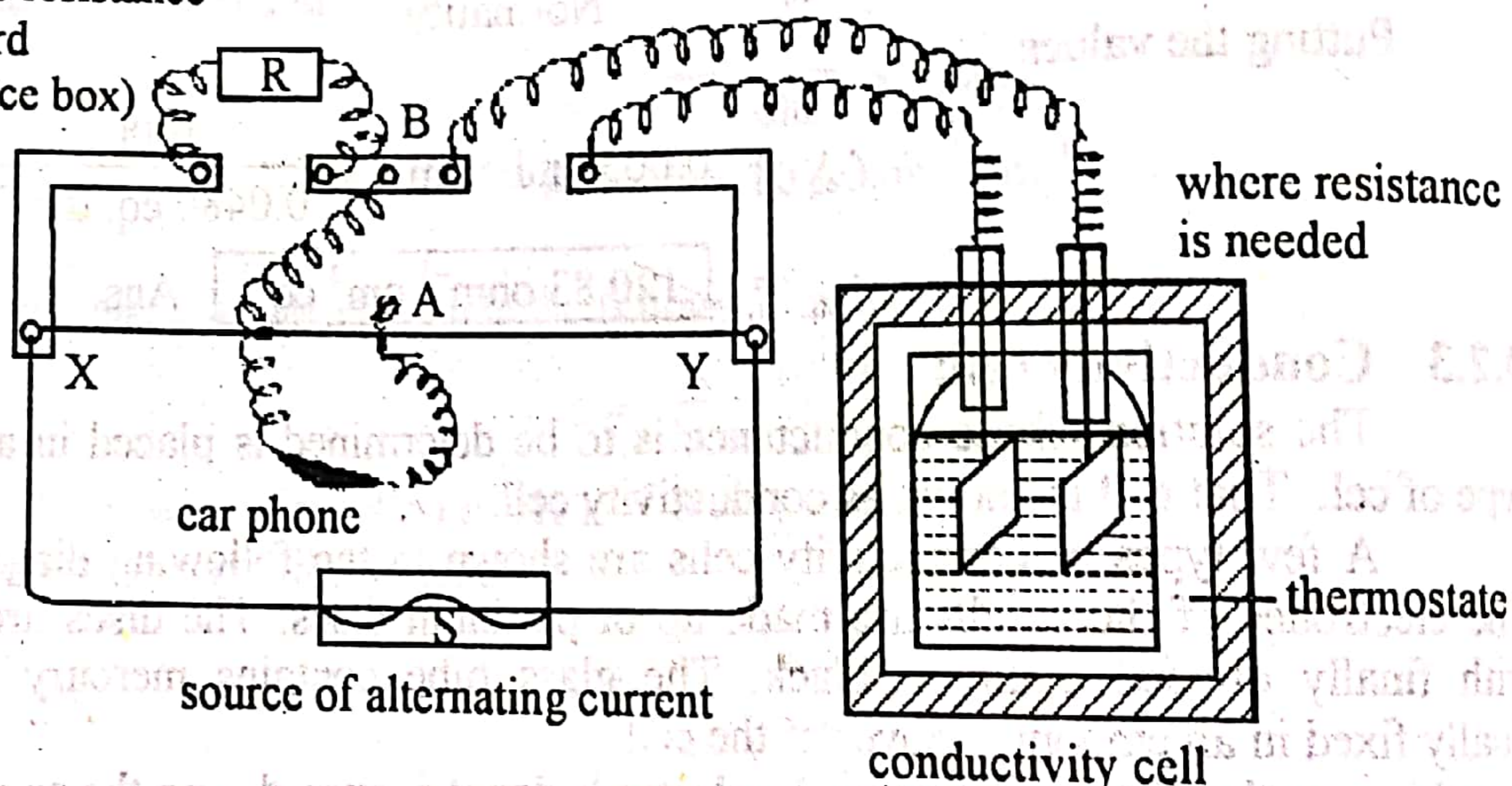Variable resistance
(standard
resistance box)

where resistance
is needed

Fig. (4) Arrangement for the measurement of electrolytic conductance.

The 'AX' and 'AY' are measured on the scale, and so the resistance of the solution can be determined. The reciprocal of this resistance of the solution gives the conductance of solution.

9.2.5 Determination of specific conductivity:

The specific conductivity 'K' is related to conductance 'C' as follows:

$$K = C \cdot \frac{l}{a}$$

So, 'K' of a solution can be determined by measuring its conductance 'C', distance 'l' between the electrodes and the area of the cross section 'a' of each electrode. The $\frac{l}{a}$ of a cell is constant and that is why it is called cell constant. So, specific conductivity

$$K = \text{Conductance} \times \text{cell constant}$$

9.2.6 Determination of equivalent conductivity:

The relationship between equivalent conductivity '$\wedge$' and specific conductivity 'K' is as follows:

$$\wedge = K \cdot \frac{1000}{C}$$

Where

C = concentration of solution in gram equivalent dm^{-3}. It is simply the normality of the solution.

9.2.7 Determination of molar conductivity:

The molar conductivity is related with the specific conductivity by the following relationship:

$$\wedge_m = K \cdot \frac{1000}{C_m}$$

This 'C_m' is related to molar concentration.

9.2.8 Determination of cell constant:

$$\text{Cell constant} = \frac{l}{a}$$

Where,

l = Distance between the electrodes of the cell

a = Surface area of the electrode.

So, if we measure 'l' and 'a', the cell constant can be obtained. Anyhow, following equation may be used to calculate the value of $\frac{l}{a}$

$$R = \rho \times \frac{l}{a}$$

$$\frac{1}{C} = \frac{1}{K} \times \frac{l}{a}$$

$$\frac{l}{a} = \frac{K}{C} = \frac{\text{specific conductance}}{\text{observed conductance}}$$

The measurement of these two conductances can give us the value of cell constant.

9.2.9 Factors determining the conductance of an electrolyte:

The conductance of electrolytes depends upon the following factors:

(i)   Nature of electrolyte

(ii) Temperature

(iii) Concentration of electrolytes.

We are going to discuss the relationship of concentration of electrolytes with the specific conductance and equivalent conductance.

Dilution factor:

Specific conductance decreases with dilution. The reason is that, the number of the current carrying particles i.e. ions cm^{-3} of solution become less at low concentration due to dilution. Now doubt, the degree of dissociation increases with dilution but the number of ions cm^{-3} is decreased to such an extent that even a complete dissociation does not produce as many ions cm^{-3} as are present before dilution.

The equivalent conductance increases with dilution and finally attains a maximum value at infinite dilution. The reason is that, equivalent conductance is the product of specific conductance and the volume 'V' of the solution, containing one gram equivalent of the electrolyte

$$\Lambda = K \cdot \frac{1000}{C} = K.V.$$

The decreasing value of specific conductance due to dilution is more than compensated by increasing value of 'V' and so, the value of Λ increases with dilution.

9.3.0 VARIATION OF CONDUCTANCE WITH CONCENTRATION OF STRONG AND WEAK ELECTROLYTES

As we have discussed above that equivalent conductivity of an electrolyte increases on diluting the solution. Following diagram (5) shows the graphs between equivalent conductances of some of the electrolytes against the square root of concentration.

We can study two types of graphs, i.e. for strong electrolytes and weak electrolytes. Let us discuss them one by one.

(i) In the graphs of strong electrolytes like HCl and KCl, the equivalent conductance, approaches a certain limiting value at which the solution is so dilute that the concentration approaches zero. This is the value of equivalent conductance at infinite dilution. In is denoted by 'Λ_o'. We get this value of 'Λ_o' by the extrapolation of the graph.

(ii) In the case of weak electrolytes like CH_3COOH, there is no limiting value, even when the concentration approaches zero. So, equivalent conductance of a weak electrolyte at zero concentration can not be obtained by extrapolation of the curve. The conductance of a solution depends upon the degree of ionization of the electrolyte. With the increasing degree of ionization with dilution, the value of equivalence conductance increases.
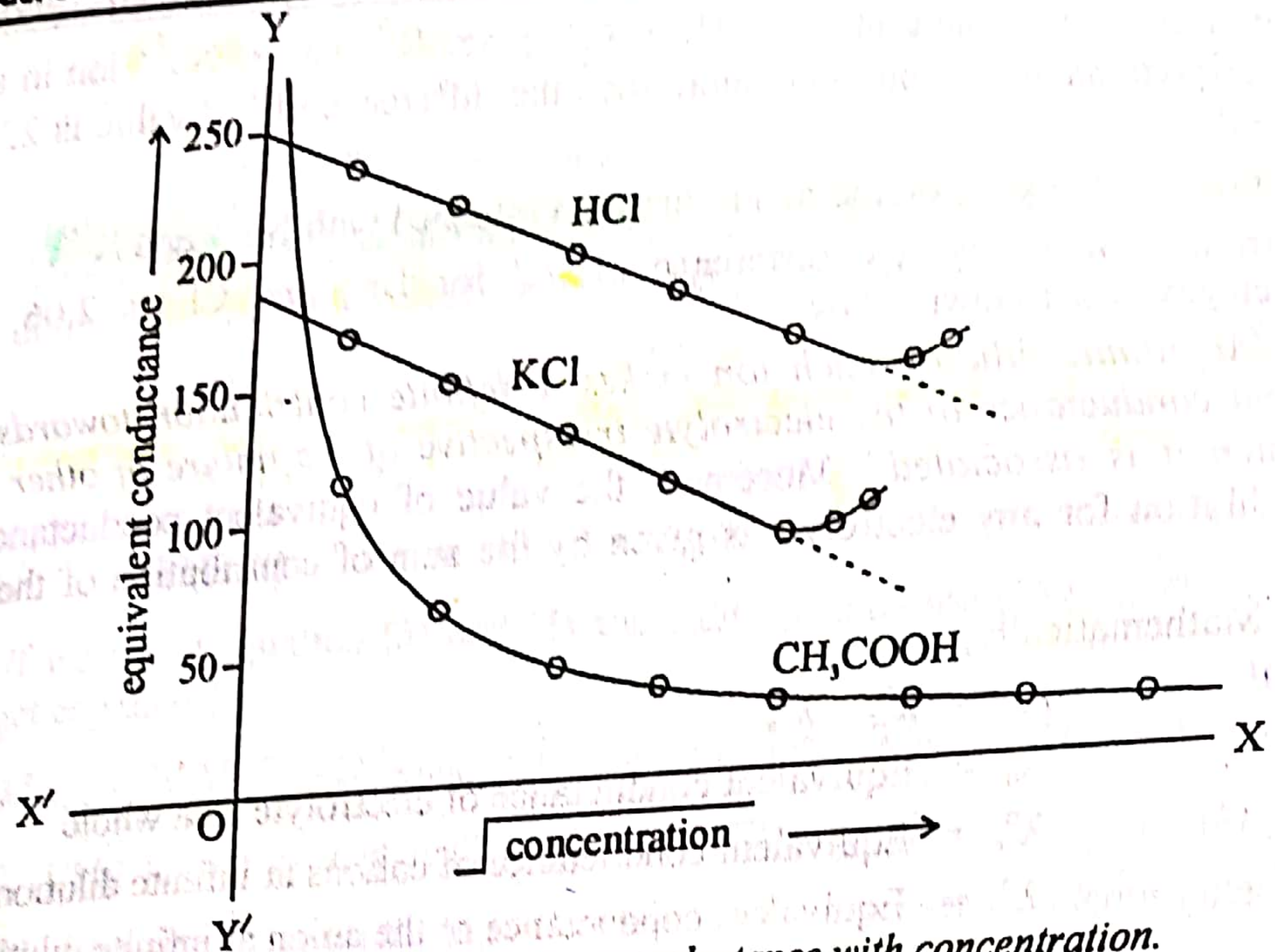
Fig. (5) *Variation of equivalent conductance with concentration.*

When the limiting value of equivalence conductance is reached, then the degree of dissociation is unity. At this stage, there is complete dissociation of electrolyte. This is true for strong electrolytes.

In the case of weak electrolytes, the degree of dissociation 'α' is not completed even at great dilution. The degree of dissociation 'α' bears the following formula:

$$\alpha = \frac{\text{Equivalent conductance at given concentration}}{\text{Equivalent conductance at zero concentration (or infinite dilution)}}$$

$$\alpha = \frac{\Lambda}{\Lambda_0}$$

The value of 'Λ_0' can be found out by Kohlrausch law of independent migration of ions.

Λ_m° = molar conductance @ zero conc.

9.3.1 Kohlrausch law of independent migration of ions:

Kohlrausch law can be understood from the studies which were carried out by measuring the equivalent conductances of some strong electrolytes at infinite dilution. In other words, he measured the values of 'Λ_0'. Following table (1) shows the electrolytes in pairs.

Table (1) Values of Λ_0 for various electrolytes and differences due to ions

Electrolyte	Λ_m^0 at 298 K	Difference	Electrolyte	Λ_m^0 at 298 K	Difference
KCl	149.86	23.41	KBr	151.92	2.06
NaCl	126.45		KCl	149.86	
KBr	151.92	23.41	NaBr	128.51	2.06
NaBr	128.51		NaCl	126.45	
KNO₃	144.96	23.41	LiBr	117.09	2.06
NaNO₃	121.5		LiCl	115.03	

It is clear from the table that when we replace $K^{\oplus}$ ion by $Na^{\oplus}$ ion in any of the electrolyte having a common anion, then the difference of 'Λ_o' value is 23.41 ohm^{-1} . cm^2.

It does not depend on the nature of anion attached with $Na^{\oplus}$ and $K^{\oplus}$.

In the same way, the difference of 'Λ_o' for Br^-, and Cl^- is 2.06. So, Kohlausch gave the following law.

"At infinite dilution each ion makes a definite contribution towards the equivalent conductance of the electrolyte irrespective of the nature of other ions with which it is associated." Moreover, the value of equivalent conductance at infinite dilution for any electrolyte is given by the sum of contribution of the two ions.

Mathematically,

$$\Lambda_o = \lambda^{\circ}_c + \lambda^{\circ}_a$$

Λ_o = Equivalent conductance of electrolyte as a whole

λ°_c = Equivalent conductance of cations at infinite dilution

λ°_a = Equivalent conductance of the anion at infinite dilution

λ°_c and λ°_a are also called ionic conductances. This law is valid at any dilution, but it is mostly applied at infinite dilution. Moreover, the ionic conductance of an ion is fixed at a given temperature, whatever might be the nature of other ion association with it.

Let us take a general compound, '$A_X B_Y$' which dissociates reversibly, according to the following equation:

$$A_X B_Y \longrightarrow xA^{\oplus Y} + yB^{\ominus X}$$
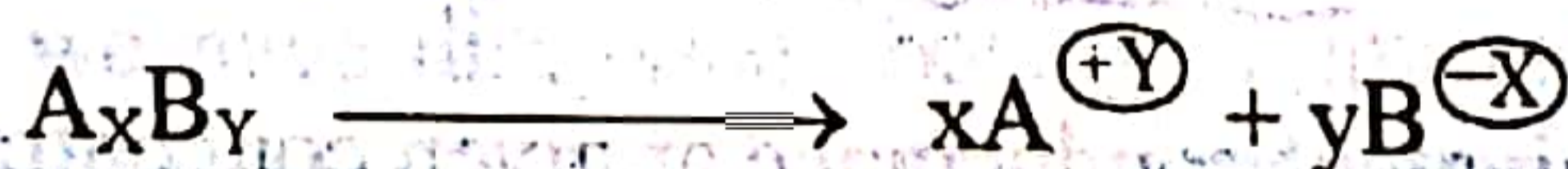
$$\Lambda_o = x\lambda^{\circ}_A + y\lambda^{\circ}_B$$

This equation is valid for the following substances.

$$\Lambda^{\circ}_{NaCl} = \lambda^{\circ}_{Na^{\oplus}} + \lambda^{\circ}_{Cl^{\ominus}}$$

$$\Lambda^{\circ}_{BaCl_2} = \lambda^{\circ}_{Ba^{+2}} + 2\lambda^{\circ}_{Cl^{\ominus}}$$

$$\Lambda^{\circ}_{AlCl_3} = \lambda^{\circ}_{Al^{+3}} + 3\lambda^{\circ}_{Cl^{\ominus}}$$

Similarly, in terms of molar conductivities the Kohlrausch law is defined as follows:

"The molar conductivity of electrolyte at infinite dilution is the sum of two values, one depending upon the cation and other on the anion."

$$\Lambda^{\circ}_m = \lambda^{\circ}_c + \lambda^{\circ}_a$$

9.3.2 Applications of Kohlrausch law:

Kohlraush law has numerous applications in the field of chemistry. Some of them are discussed as follows:

(i) Calculation of equivalent conductance at infinite dilution for weak electrolytes:

As we have mentioned earlier that the equivalent conductance of weak electrolyte at infinite dilution can not be obtained graphically by extrapolation.

Valid for infinite dilution

Independent of nature of ion

Kohlraush law enables us to have indirect measurements. For example, acetic acid has equivalent conductance as follows:

$$\wedge^{\circ}(CH_3COOH) = \lambda^{\circ}_{CH_3COO-} + \lambda^{\circ}_{H^+} \qquad \ldots\ldots (I)$$

This equation can be obtained, if we know the equivalent conductivities at infinite dilution for the strong electrolytes as KCl, CH_3COOK, and HCl.

$$\wedge^{\circ}(KCl) \qquad = \lambda^{\circ}_{K^{\oplus}} + \lambda^{\circ}_{Cl^{\ominus}} \qquad \ldots\ldots (2)$$

$$\wedge^{\circ}(CH_3COOK) = \lambda^{\circ}_{CH_3COO^{\ominus}} + \lambda^{\circ}_{K^{\oplus}} \qquad \ldots\ldots (3)$$

$$\wedge^{\circ}(HCl) \qquad = \lambda^{\circ}_{H^{\oplus}} + \lambda^{\circ}_{Cl^{\ominus}} \qquad \ldots\ldots (4)$$

If we added equation (3) and (4) and subtract equation (2) from them, then we can get equation (5)

So, $\quad \lambda^{\circ}_{CH_3COO^{\ominus}} + \lambda^{\circ}_{H^{\oplus}} = (\lambda^{\circ}_{CH_3COO^{\ominus}} + \lambda^{\circ}_{K^{\oplus}}) + (\lambda^{\circ}_{H^{\oplus}} + \lambda^{\circ}_{Cl^{\ominus}}) - (\lambda^{\circ}_{K^{\oplus}} + \lambda^{\circ}_{Cl^{\ominus}})$

$$\lambda^{\circ}(CH_3COOH) = \lambda^{\circ}(CH_3COOK) + \lambda^{\circ}(HCl) - \lambda^{\circ}(KCl) \qquad \ldots\ldots (5)$$

All the electrolytes on the R.H.S of equation (5) are strong electrolytes and their '$\wedge^{\circ}$' values can be calculated by the extrapolation of the graphs.

(ii) · **Calculation of degree of dissociation of weak electrolyte:**

The degree of dissociation of a weak electrolyte at infinite dilution can be determined by dividing equivalent conductivity of the electrolyte at a given concentration by the equivalent conductivity of the same electrolyte at infinite dilution. The formula is as follows:

$$\text{Degree of dissociation } (\alpha) = \frac{\wedge}{\wedge_0}$$

We can calculate the 'α' value for CH_3COOH, NH_4OH, oxalic acid etc.

Similarly the degree of dissociation 'α' can be calculated from molar conductivities

$$\alpha = \frac{\wedge_m}{\wedge^{\circ}_m}$$

(iii) **Calculation of solubility of sparingly soluble salts:**

Certain salts are very slightly soluble in water. They are called sparingly soluble salts. For example the salts like AgCl, $BaSO_4$ and $PbSO_4$ are sparingly soluble. This solubility of such salts cannot be determined by any of the known chemical methods. Anyhow, conductivity measurement can help to do such calculations.

Since, these salts dissolve to a very small extent, their solutions are considered as infinitely dilute. Similarly, as their solution are saturated, then their concentrations are equal to their solubilities. Hence by determining their specific conductivities and equivalent conductivities, we can calculate their solubilities in terms of gram equivalence or molarity

$$\wedge^{\circ} = K \cdot \frac{1000}{gram \cdot equivalement}$$

$$\wedge^{\circ} = K \cdot \frac{1000}{molarity}$$

or $\quad Solubility = K \cdot \frac{1000}{\wedge^{\circ}}$

$\wedge^{\circ}$ can be obtained by using Kohlaursch law.

(iv) Determination of solubility product:

The solubility product of the sparingly soluble salts is the product of the concentration of soluble ions. When we know the solubility of salt by the above method, then the concentration of the soluble ions can be calculated easily. Hence, the solubility product can be evaluated.

EXAMPLE (3)

The molar conductivity at infinite dilution of NaCl, HCl and CH_3COONa are 126.4, 426.1 and 91.0 ohm^{-1} cm^2 mol^{-1}, respectively. Calculate molar conductivity of CH_3COOH at infinite dilution.

SOLUTION:

This problem is solved by applying Kohlrauch law

$$\wedge^{0}_{m} (CH_3COOH) = \lambda^{0}_{CH_3COOH^{\ominus}} + \lambda^{0}_{H^{\oplus}}$$

Data:

According to the information in the problem

$\wedge^{0}_{m}(NaCl) \qquad = \lambda^{0}_{Na^{\oplus}} + \lambda^{0}_{Cl^{\ominus}} \qquad = 126.4$ ohm^{-1} cm^2 mol^{-1} (i)

$\wedge^{0}_{m}(HCl) \qquad = \lambda^{0}_{H^{\oplus}} + \lambda^{0}_{Cl^{\ominus}} \qquad = 426.1$ ohm^{-1} cm^2 mol^{-1} (ii)

$\wedge^{0}_{m}(CH_3COONa) = \lambda^{0}_{CH_3COO^{\ominus}} + \lambda^{0}_{Na^{\oplus}} = 91.0$ ohm^{-1} cm^2 mol^{-1} (iii)

We have to calculate $\wedge^{0}(CH_3COOH)$ i.e. $= \lambda^{0}_{CH_3COO^{\ominus}} + \lambda^{0}_{H^{\oplus}}$

The equations (i), (ii) and (iii) are handled in such a way, that we get the required equation

Formula:

We add equation (ii) and (iii) and subtract (i) from them

$$\lambda^{0}_{H^{\oplus}} + \lambda^{0}_{Cl^{\ominus}} + \lambda^{0}_{CH_3COO^{\ominus}} + \lambda^{0}_{Na^{\oplus}} - \lambda^{0}_{Na^{\oplus}} - \lambda^{0}_{Cl^{\ominus}}$$

Putting values

$\qquad = 426.1 + 91.0 - 126.4$ ohm^{-1} cm^2 mol^{-1}

$\lambda^{0}_{CH_3COO^{\ominus}} + \lambda^{0}_{H^{\oplus}} = 390.7$ ohm^{-1} cm^2 mol^{-1}

So, $\boxed{\wedge^{0}_{m} (CH_3COOH) = 390.7 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}}$ **Ans.**

EXAMPLE (4)

Calculate the degree of dissociation of CH_3COONa at 25°C, when the specific conductance of a 0.01 N solution of acetic acid at 25°C is 1.63×10^{-4} mhos cm^{-1}. The ionic conductances at infinite dilution at the same temperature for $H^{\oplus}$ and $CH_3COO^{\ominus}$ ions are 349.8 and 40.9 mho cm^2 eq^{-1} respectively. Calculate the $H^{\oplus}$ concentration in the solution.

SOLUTION:

Data:

Specific conduction (K) = 1.63×10^{-4} mhos cm^{-1}

$\lambda^0_{H^\oplus}$ = 349.8 mhos cm^2 eq^{-1}

$\lambda^0_{CH_3COO^\ominus}$ = 40.9 mhos cm^2 eq^{-1}

The value of λ_0 for CH$_3$COOH = 349.8 + 40.9 = 390.7 mhos cm^2 eq^{-1}

In order to calculate the equivalent conductance at any concentration ($\wedge_c$) proceed as follows.

As the solution is 0.01 N, volume of solution in cm^3 containing one 1 gram equivalent of acetic acid = $\dfrac{1000}{0.01}$ = 10^5 cm^3.

Formula:

$\wedge_c$ = Specific conductance × Vol. in cm^3 containing one equivalent of electrolyte

$\wedge_c$ = $1.63 \times 10^{-4} \times 10^5$ = 16.3 mhos cm^2 eq^{-1}

Putting values

The degree of dissociation α, = $\dfrac{\wedge_c}{\wedge_D}$ = $\dfrac{16.3}{390.7}$ = 0.0417

Calculation of H$^\oplus$:

$[H^\oplus]$ = 0.01 α = 0.01 × 0.0417 = $\boxed{4.17 \times 10^{-4} \text{ g ions dm}^{-3}}$ Ans.

EXAMPLE (5)

A 18°C, the equivalent conductance at infinite dilutions of NH$_4$Cl, NaOH and NaCl are 129.8, 217.4 and 108.9 ohm^{-1} cm^2 respectively. The equivalent conductivity of 0.01 N solution of NH$_4$OH is 9.33 ohm^{-1} cm^2. What is the percentage dissolution of NH$_4$OH at this dilution?

SOLUTION:

Data:

$\wedge_0$ for NH$_4$Cl = 129.8 ohm^{-1} cm^2

$\wedge_0$ for NaOH = 217.9 ohm^{-1} cm^2

$\wedge_0$ for NaCl = 108.9 ohm^{-1} cm^2

Formula:

By Kohlrausch's Law

$\wedge_0$ for NH$_4$OH = $\lambda_{NH_4^\oplus} + \lambda_{OH^\ominus}$

= $\wedge_0$ (NH$_4$Cl) + $\wedge_0$ (NaOH) − $\wedge_0$ (NaCl)

= 129.8 + 217.4 − 108.9

= 2300.3 ohm^{-1} cm^2

Eq. conductance of 0.01 N NH$_4$OH ($\wedge$) = 9.33 ohm^{-1} cm^2

Degree of dissociation (α) = $\dfrac{\wedge}{\wedge_0}$ = $\dfrac{9.33}{238.3}$ = 0.0392

% Dissociation = 100 α = 100 × 0.0392 = $\boxed{39.2}$ Ans.

9.4.0 FARADAY'S LAWS OF ELECTROLYSIS

Faraday discussed the quantitative relationship between the quantities of substances deposited at the electrodes and the quantity of electricity passed. He has given two laws which are discussed as follows:

(i)   Faraday's first law of electrolysis:

"*According to this law, the mass of any substance deposited or liberated at any electrode is directly proportional to the quantity of the electricity passed.*"

Let 'w' grams of the substance is deposited on passing 'q' coulombs of electricity, then

$$w \propto q$$

$$w = Zq \qquad \qquad \cdots \cdots \ (1)$$

This 'Z' is the constant of proportionality and it is called electrochemical equivalent of the substance deposited. It depends upon the nature of the substance.

The quantity of electricity in coulombs is the product of the current in amperes and time in seconds.

$$q = C \times t \qquad \qquad \cdots \cdots \ (2)$$

Putting equation (2) in (1),

$$w = Z \times C \times t \qquad \qquad \cdots \cdots \ (3)$$

In equation (3), 'C', is current in amperes.

$$Z = \frac{w}{C \times t} \qquad \qquad \cdots \cdots \ (4)$$

When $C = 1$ amperes, and $t = 1$ sec

$$Z = w$$

"*So, the electrochemical equivalent 'Z' of a substance is the mass of that substance deposited when a current of one ampere is passed for one second.*" This quantity of electricity is one coulomb. So, we can say that electrochemical equivalent is the mass of the substance deposited, when one coulomb of electricity is passed through the substance.

Faraday as quantity of electricity:

Coulomb is a unit of electricity and

1 coulomb   =   1 ampere × 1 second

A Faraday is a bigger unit of electricity

1 Faraday   =   96,500 coulombs

It has been found that, when one Faraday of electricity is passed through an electrolyte then one gram equivalent of the substance is deposited

Mass deposited by 1 Faraday   =   1 gram equivalent

Mass deposited by 1 coulomb   = $\dfrac{1 \text{ gram equivalent}}{96,500}$

= Electrochemical equivalent

When one Faraday of electricity is passed through $AgNO_3$ solution, then 108 grams of Ag is deposited. 108 grams of Ag is the equivalent weight of the silver.

So, electrochemical equivalent of silver (Ag)

$$= \frac{108}{96,500} = 0.0011181$$

(ii) **Faraday's second law of electrolysis:**

This law is defined as follows:

"When the same quantity of electricity is passed through the solutions of different electrolytes connected in series, then the weights of the substances produced at the electrodes are directly proportional to their equivalent weights."

In order to understand it, pass the same quantity of electricity through $CuSO_4$ and $AgNO_3$ solutions, which are connected in series, then

$$\frac{\text{Weight of Cu deposited}}{\text{Weight of Ag deposited}} = \frac{\text{Equivalent weight of Cu}}{\text{Equivalent weight of Ag}}$$

9.4.1 Applications of Faraday's laws of electrolysis:

(1) We can calculate the amount of the substance deposited, when certain amount of electricity for certain time is passed through the solutions. Similarly, if the amount of the substance deposited is calculated, then it is possible to calculate the electrochemical equivalent of the substance.

(2) By using Faraday's second law, we can determine the quantity of electricity passed through a circuit. The circuit is connected in series with silver voltmeter or coulometer having platinum anode.

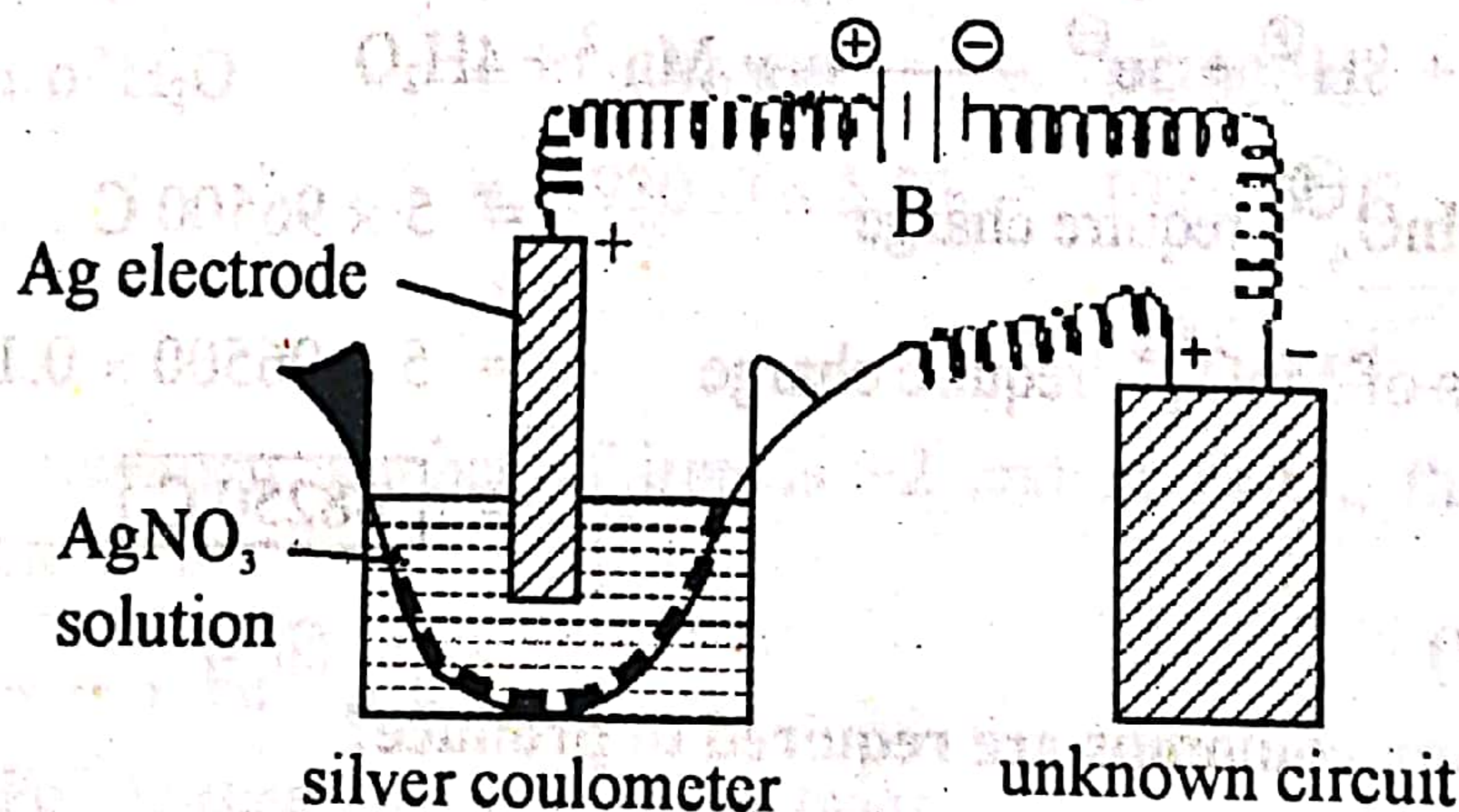The following arrangement (6) can help us to understand the process.

Fig. (6) *Use of silver coulometer to study the Faraday's laws.*

Solution of $AgNO_3$ is taken in the coulometer and is connected in series to the unknown circuit. Current is passed and Ag is deposited at silver cathode. After some times, the passage of electricity is stopped and the silver electrode of silver coulometer is washed and weighed. From the difference of the weight, the weight of Ag deposited is calculated. The quantity of electricity 'q' passed through the unknown circuits can be calculated by following equation

$$w = Z \times q$$

$$q = \frac{w}{Z}$$

EXAMPLE (6)

How many coulomb's of electricity are required for the reduction of :

(i)   0.02 moles of Al^{+3} to Al^0

(ii) 0.3 moles of Cu^{+2} to Cu^0

(iii) 0.1 moles of MnO_4^{-1}

SOLUTION:

When the Avogadro's number of electrons are transferred then 96500 coulombs of charge is dissipated.

To solve these problems write the equations.

(i) 1 mole of $Al^{\oplus}$ requires 3 moles of electrons or three Faraday's of charge

$$Al^{\oplus} + 3e^{\ominus} \longrightarrow Al^0$$
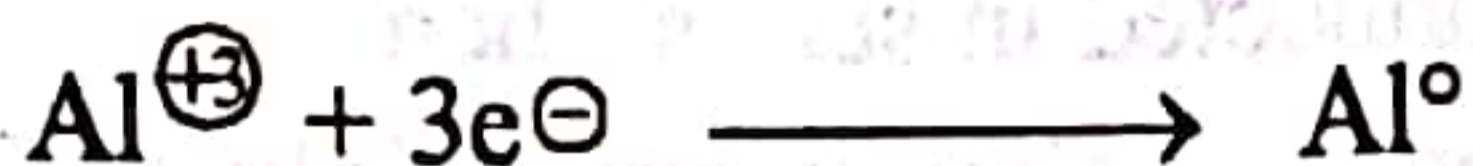
$$1 \text{ mole of } Al^{\oplus} \text{ requires charge} = 3 \times 96500 \text{ C}$$

$$0.02 \text{ moles of } Al^{\oplus} \text{ required charge} = 3 \times 96500 \times 0.02 \text{ C}$$

$$= \boxed{5790 \text{ C}} \quad \text{Ans.}$$

(ii) $$Cu^{\oplus 2} + 2e^{\ominus} \longrightarrow Cu^0$$

$$1 \text{ mole of } Cu^{\oplus 2} \text{ requires charge} = 2 \times 965500 \text{ C}$$

$$0.3 \text{ moles of } Cu^{\oplus 2} \text{ require charge} = 2 \times 96500 \text{ C} \times 0.3 \text{ C}$$

$$= \boxed{57900 \text{ C}} \quad \text{Ans.}$$

(iii) $$MnO_4^{\ominus} + 8H^{\oplus} + 5e^{\ominus} \longrightarrow Mn^{+2} + 4H_2O$$

$$1 \text{ mole } MnO_4^{\ominus} \text{ require charge} = 5 \times 96500 \text{ C}$$

$$0.1 \text{ moles of } MnO_4^{\ominus} \text{ require charge} = 5 \times 96500 \times 0.1 \text{ C}$$

$$= \boxed{48250 \text{ C}}$$

EXAMPLE (7)

How many coulombs are required to produce?

(i)   4 g of Na from molten NaCl.

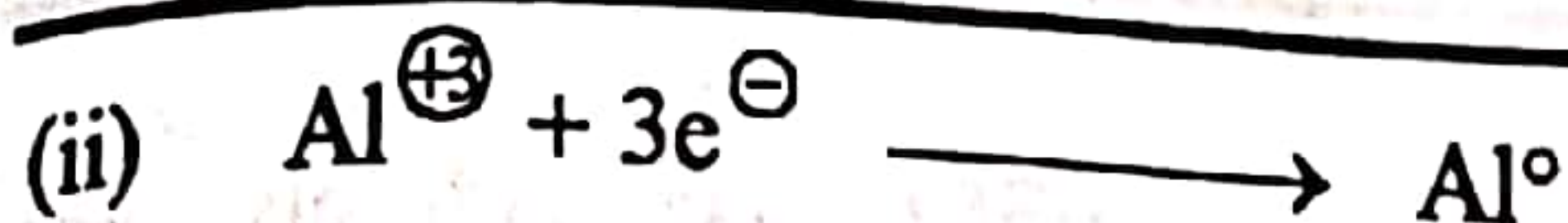(ii) 10 g of aluminum from molten Al_2O_3

SOLUTION:

(i) $$Na^{\oplus} + 1e^{\ominus} \longrightarrow Na^0$$

1 mole of Na is 23 g of sodium

$$23 \text{ g of } Na^{\oplus} \text{ require charge} = 96500 \text{ C}$$

$$4 \text{ g of } Na^{\oplus} \text{ require charge} = \frac{96500}{23} \times 4$$

$$= \boxed{16782.6 \text{ C}} \quad \text{Ans.}$$

(ii) $Al^{\oplus} + 3e^{\ominus} \longrightarrow Al^{\circ}$

1 mole of Al is 27 g of Al

27 g of $Al^{\oplus}$ requires charge $= 3 \times 96500$ C

1 g of Al require charge $= \dfrac{3 \times 96500}{27} \times 10$ C

$= \boxed{10722.22 \text{ C}}$ Ans.
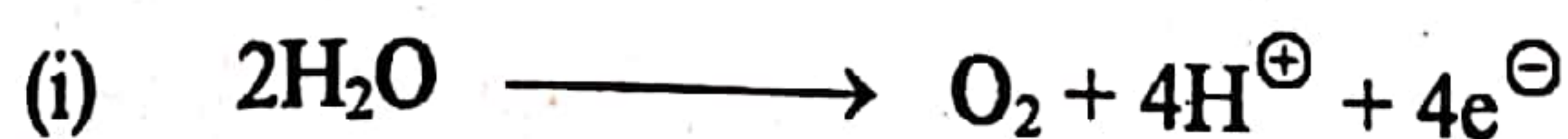
EXAMPLE (8)

How many coulombs are required for the following processes:

(i)   100 g of H_2O to O_2

(ii) 1 kg of FeO to Fe_2O_3

SOLUTION:

First of all write down the equation for conversion of H_2O to O_2

(i) $2H_2O \longrightarrow O_2 + 4H^{\oplus} + 4e^{\ominus}$

So, $H_2O \longrightarrow \dfrac{1}{2} O_2 + 2H^{\oplus} + 2e^{\ominus}$ (For 1 mole of H_2O)

No. of moles of water $= \dfrac{100}{18} = 5.55$

One mole of H_2O releases 2 moles of electrons

Charge required for	$= 2$ Faradays	
1 moles of H_2O	$= 2 \times 96500$	$= 193000$ C
5.5 " " "	$= 193000 \times 5.55$	$= 1071150$ C

$= \boxed{1.07 \times 10^{+6} \text{ C}}$ Ans.

In FeO, the oxidation number of iron is +2 and in Fe_2O_3, the oxidation number of iron is +3.

(ii) $Fe^{\oplus 2} \longrightarrow Fe^{\oplus 3} + e^{\ominus}$
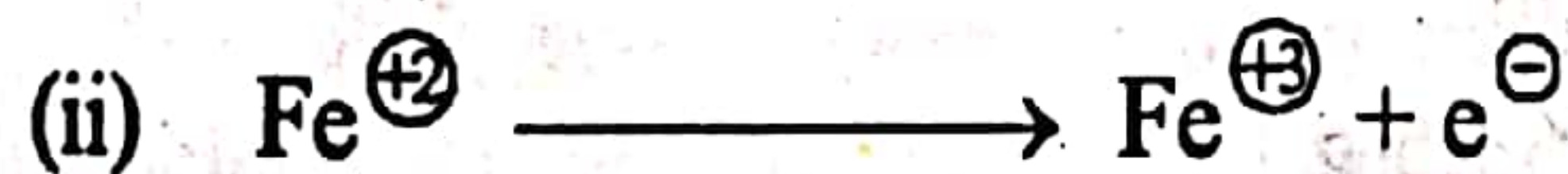
One mole of Fe^{+2} releases one mole of electrons

No. of moles of FeO $= \dfrac{1000}{72} = 13.88$

Hence   no. of moles of Fe $= \dfrac{1000}{72} = 13.88$

Charge required for one mole of FeO $= 1$ Faraday $= 96500$ C

Charge required for 13.88 moles of FeO $= 96500 \times 13.88$

$= 13402778$

$= \boxed{1.34 \times 10^{+7} \text{ C}}$ Ans.

EXAMPLE (9)

Three solutions of $ZnSO_4$, $AgNO_3$ and $CuSO_4$ respectively are connected in series. A steady current of 4.50 amperes is passed through them until 4.35 g of Ag are deposited at the cathode. Calculate the time for the flow of current? What weight of copper and of zinc are deposited?

SOLUTION:

As $Ag^{\oplus}$ ion will take up one $e^{\ominus}$ and so 1 mole of $Ag^{\oplus}$ will require N_A number of electrons

(i) $Ag^{\oplus} + e^{\ominus} \longrightarrow Ag$ (1 mole of 108 g)

Thus, 108 g of Ag is deposited by   = 96500 C

4.35 g of Ag is deposited by $= \dfrac{96500}{108} \times 4.35$ C

                                 = 3886.8 C

Formula:

It means that 3886.8 C of charge has passed through every cell.

     Charge   = Current × time in second

     Time $= \dfrac{\text{Charge}}{\text{Current}}$

Putting values

     Time $= \dfrac{3386.8 \text{ C}}{4.5 \text{ amp.}}$

     Time $= 863.73 \dfrac{C}{amp} = 863.735$ sec.

(ii) $Zn^{\oplus 2} + 2e^{\ominus} \longrightarrow Zn^0_{(s)}$ (1 mole or 65 g)
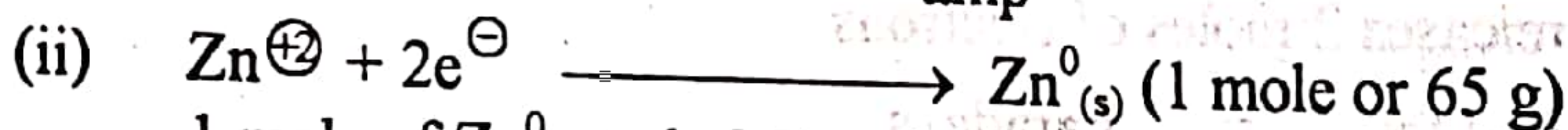
1 mole of Zn^0 needs 2 Faradays of charge

     2 × 96500 C can deposit   = 65 g of Zn

     3886.8 C can deposit Zn^0 $= \dfrac{65 \times 3886.8}{2 \times 96500}$

                             $= \boxed{1.31 \text{ g}}$ Ans.

(iii) $Cu^{\oplus 2} + 2e^{\ominus} \longrightarrow Cu^0_{(s)}$ (1 mole or 63.5 g)
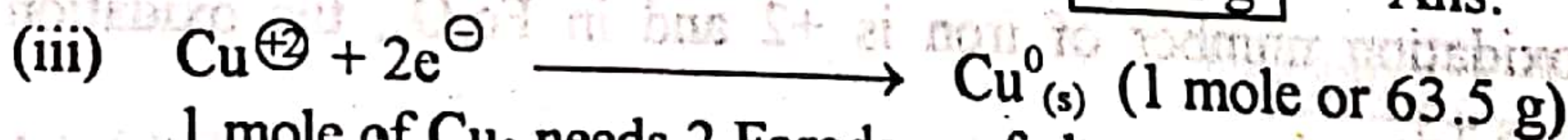
1 mole of Cu_0 needs 2 Faradays of charge

     2 × 96500 C can deposit Cu   = 63.5 g

     3886.8 C can deposit $Cu^0 = \dfrac{63 \times 3886.8}{2 \times 96500}$

                             $= \boxed{1.278 \text{ g}}$ Ans.

9.5.0 DEBYE-HUCKLE THEORY OF STRONG ELECTROLYTES

9.5.1 Introduction:

As we have discussed earlier, that the equivalent conductance increases with dilution in the case of weak electrolytes. This can be explained on the basis of

Arrhenius theory. This theory suggests that the conductance increases because the dissociation of weak electrolytes increases with dilution. Strong electrolytes are completely dissociated even at moderate concentrations. The increase in equivalent conductances for such electrolytes with dilution may be due to some other factors.

In this theory, we have to explore those factors which increase the conductance of strong electrolytes on dilution. These two major factors are:

    (i)   Relaxation effect or asymmetry effect

    (ii)   Electrophoretic effect.

9.5.2 Relaxation effect or asymmetry effect:

Electrolytes dissociate into solutions state to give positive and negative ions. Each ion is surrounded by an ionic atmosphere of opposite charge. This ionic atmosphere is spherically symmetrical. When a current is passed through the solution, the center of ion of the ionic atmosphere moves towards the oppositely charged electrode. During this movement it has to rebuild an ionic atmosphere of opposite charge around it. At the same time the old ionic atmosphere dies out. These two processes do not take place simultaneously. There is a some time lag which is called time of relaxation. During this time, old ionic atmosphere pulls the moving ion backward and so its motion is retarded. Following diagram (7) makes the idea clear.
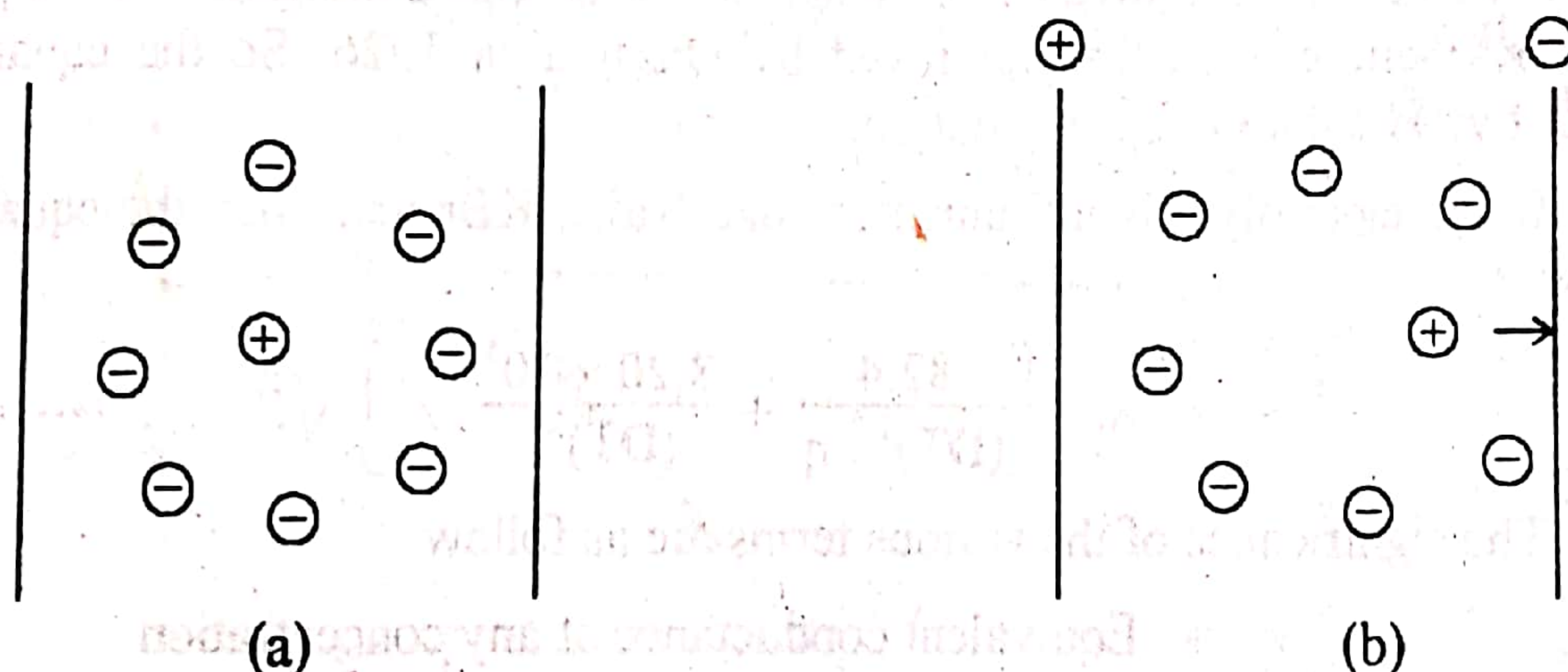

Fig. (7) Asymmetry effect or relaxation effect: (a) Ionic atmosphere is symmetrical (b) Ionic atmosphere is not symmetrical.

For this reason, this effect is called relaxation effect. Same thing can be explained in another way. When the central ion moves, then the symmetry of the ionic atmosphere is lost. More ions of the ionic atmosphere are left behind, than are present on the front. The excess ions of atmosphere present behind the moving ions pull it in the backward direction and its motion is retarded. This effect develops because of asymmetry of the ionic atmosphere of the moving ion, so it is called asymmetry effect.

9.5.3 Electrophoretic effect:

During the application of electromotive force, the central ions moves in one direction and the oppositely charged ions present in their ionic atmosphere move in opposite direction. Solvent molecules are also there in the ionic atmosphere. It means that the central ion is moving against the stream, hence the motion of the central ion is retarded. Following diagram (8) makes the idea clear.
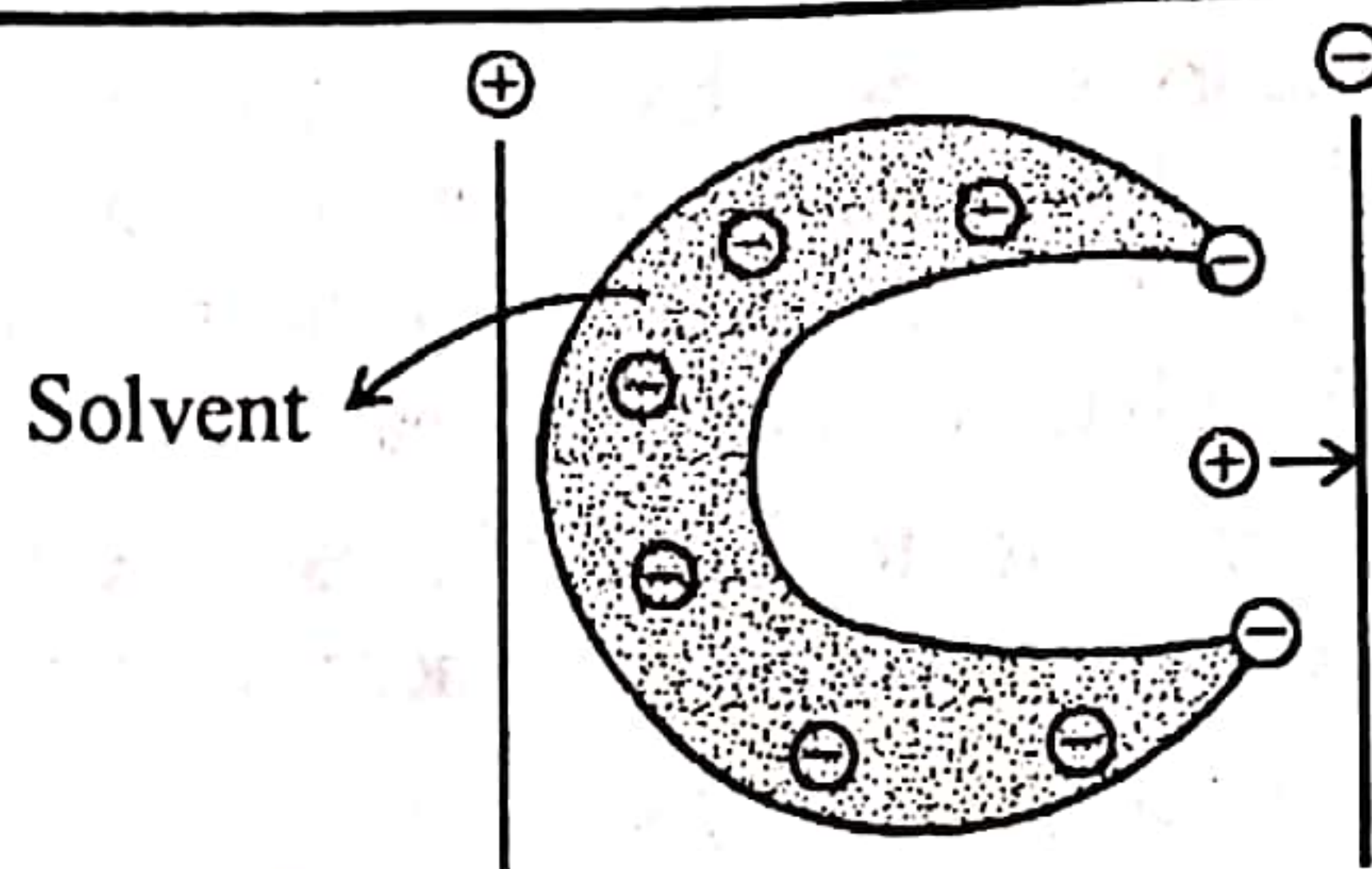
Fig. (8) The movement of the central ion in opposite direction to that of ionic atmosphere and that of associated molecules.

This effect is called electrophoretic effect.

9.5.4 Frictional resistance of the medium:

Whenever an ion with its ionic atmosphere travels in the solution, then the medium of the solution offers the frictional resistance. This force depends upon viscosity of the medium and its dielectric constant.

9.5.5 Mathematical explanation:

Keeping these three factors in view Debye and Huckle, derived a mathematical expression in 1923. Actually, they derived relationship by keeping in view the variation of equivalent conductance with concentrations. The equation derived by them was further improved by Onsagar in 1926. So the equation is called Debye-Huckle-Onsagar equation.

If the electrolyte is uni-univalent like NaCl, KBr, etc. then the equation is as follows:

$$\Lambda = \Lambda_o - \left[\frac{82.4}{(DT)^{1/2}\,\eta} + \frac{8.20 \times 10^5}{(DT)^{3/2}} \cdot \Lambda_o \right] \sqrt{C} \qquad \ldots\ldots (1)$$

The significance of the various terms are as follow:

Λ = Equivalent conductance at any concentration

Λ_o = Equivalent conductance at infinite dilution

D = Dielectric constant of the medium

η = Viscosity of the medium

T = Temperature of solution

C = Concentration of solution in moles dm^{-3}.

The values of dielectric constant of the medium and the viscosity of the medium are constant for a particular solvent at a given temperature. So, D, T and η are constants. For this reason.

We put

$$\frac{82.4}{(DT)^{1/2} \cdot \eta} = A \qquad \ldots\ldots (2)$$

$$\frac{8.2 \times 10^5}{(DT)^{3/2}} = B \qquad \ldots\ldots (3)$$

So, equation (1) can be written as

$$\Lambda = \Lambda_o - (A + B\Lambda_o)\sqrt{C} \qquad \ldots\ldots (4)$$

'Λ' is always found to be less than Λ_o. This is due to the both asymmetry and electrophonatic effect. The first term in the brackets given by equation (2) refers to be electrophoratic effect and it is inversely proportional to the viscosity of the medium. The second term given by equation (3) is the measure of asymmetry effect.

When solution is infinitely dilute, then 'C' approaches zero, and when C = 0 in equation (4), then

$$\Lambda = \Lambda_o \qquad \ldots\ldots (5)$$

It means that the factor 'A' and 'B' are responsible to create a difference between 'Λ' and 'Λ_o'. Greater the values of these factors, lesser the value of 'Λ' as compared to 'Λ_o'.

9.5.6 Experimental verification:

If we plot a graph between 'Λ' and '$\sqrt{C}$', for a number of uni-univalent electrolytes, then straight lines are obtained. The reason is that equation (4) is the equation of straight line. Anyhow, the straight line is obtained for dilute solutions upto 0.02 normality. At higher concentrations i.e. above 0.02 normal, deviations have been observed. These deviations are due to the reasons that certain approximation are introduced in the derivatives of equation (4). Following graphs (9) can make the ideas clear.
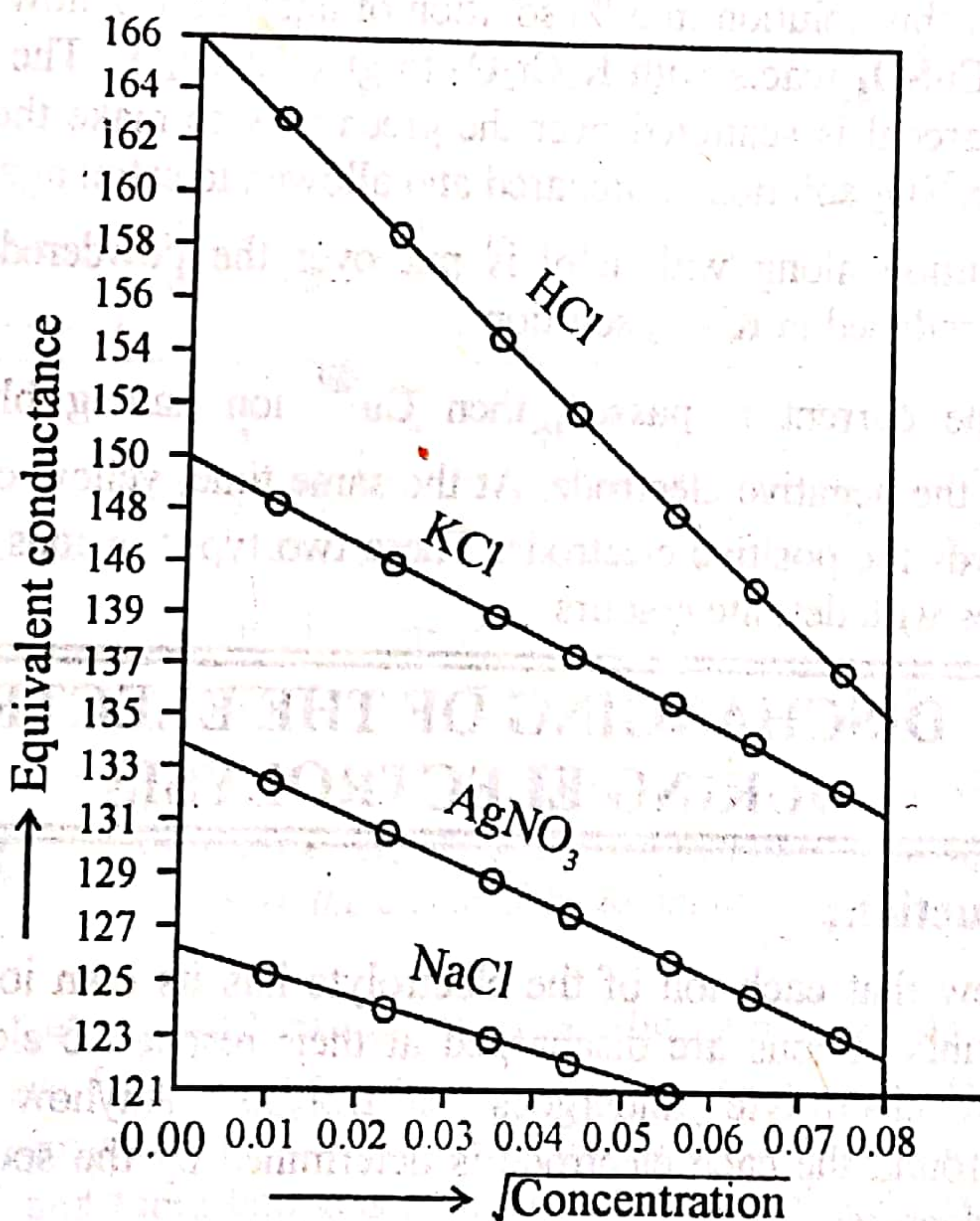

Fig. (9) Variation of equivalent conductance with concentration for some strong electrolytes.

9.5.7 Experiment to demonstrate the migration of ions:

In order to investigate the movement of ions under the influence of applied electrical field, we take up the arrangement as shown in the following diagram (10).
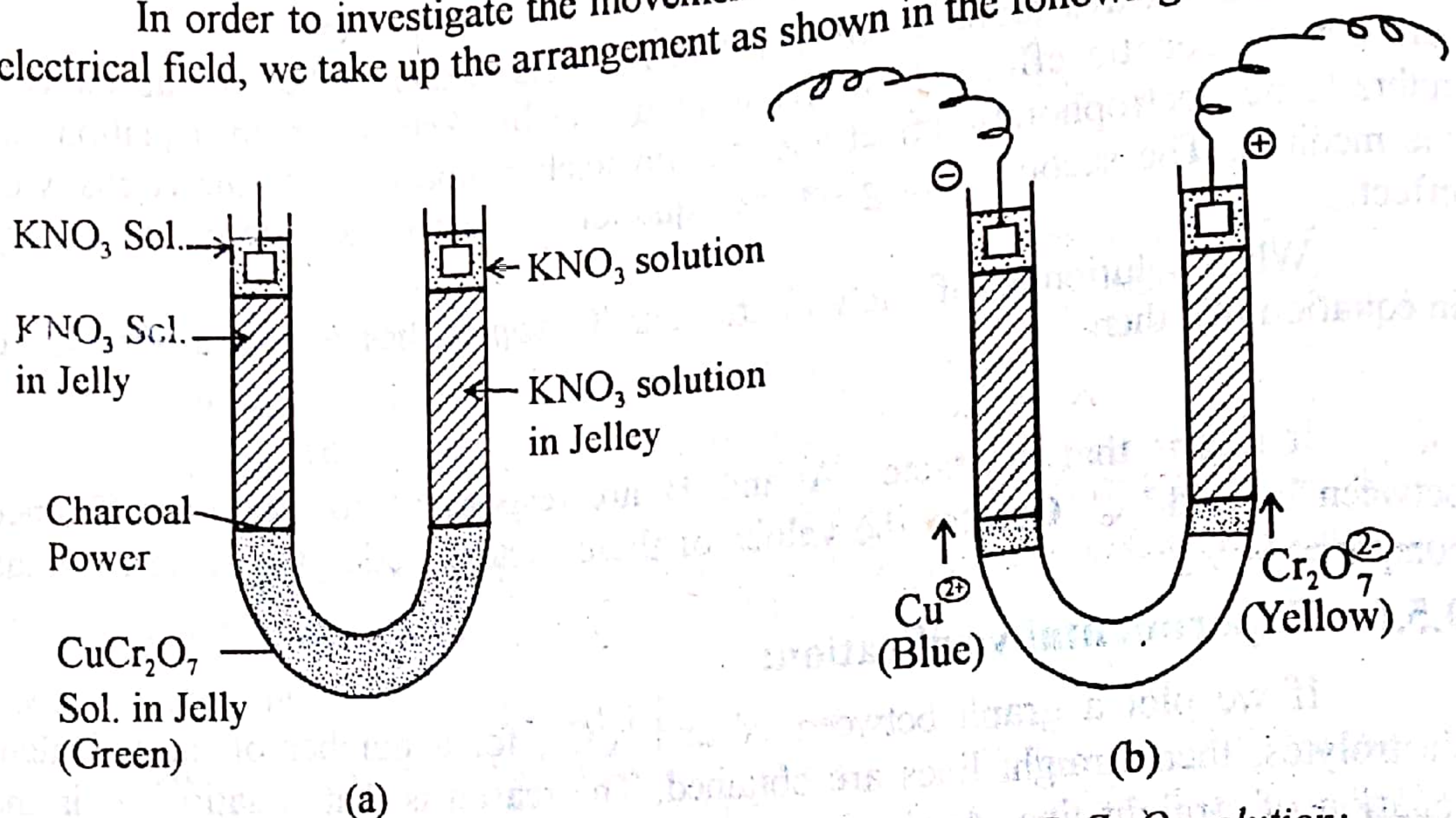

Fig. (10) Demonstration of the migration of ions, using $CuCr_2O_7$ solution:
(a) situation when current is not applied
(b) situation when current is applied and the respective ions move.

Take a U-shaped tube, and fill its lower portion with the mixture of $CuSO_4$ and $K_2Cr_2O_7$. Fill this solution in 5 % solution of agar-agar. Allow this jelly to set. The solution of $CuSO_4$ reacts with $K_2Cr_2O_7$ to give $CuCr_2O_7$. The jelly is green in colour. Some charcoal is scattered over the green jelly to make the position of the jelly distinctive. KNO_3 solution is prepared and allowed to set in agar-agar.

This solution along with jelly is put over the powdered charcoal. Two electrodes are introduced in KNO_3 solution.

When the current is passed, then Cu^{2+} ion having blue colour seem moving towards the negative electrode. At the same time, yellow coloured $Cr_2O_7^{2-}$ ions move towards the positive electrode. These two types of ions develop the well defined boundries with definite colours.

9.6.0 DISCHARGING OF THE ELECTRONS DURING ELECTROLYSIS

9.6.1 Introduction:

We know that each ion of the electrolyte has its own ionic mobility. The equivalent amounts of ions are discharged at their respective electrodes when the solution of an electrolyte undergoes electrolysis. Anyhow, the change in concentration around the each electrode is determined by the speed of the ion and the type of the electrode.

This phenomenon has been explained by Hittorf by means of a theoretical device.

9.6.2 Hittorf's explanation:

Take a hypothetical tank which contains equal number of positive and negative ions of the same valency. The tank is divided into three compartments by diaphrangms permeable to the ion. The electrodes of platinum are denoted by 'A' and 'C' for anode and cathode respectively. The compartment 1 is anode compartment III is the cathode compartment and II is the central compartment. ⊕ and ⊖ signs represent the cations and anions respectively.

Let us suppose first of all that there are (13) pairs of positive and negative ions. Five pairs are in the middle compartments while the eight are in the anodic and cathodic compartments. Now we will study three cases one by one.

9.6.3 When the electrodes are not attackable:

Case-I:

When only anions move. Suppose two anions leave cathodic compartment and enter the anodic compartment. So we get the position 'b'. Although the cations have not moved still we see that the number of ions liberated is two at both electrodes. But we see that the concentration in the anodic chamber has not altered while that in the cathodic chamber has fallen by two molecules. In the same way we can show that if cations are capable of movement and two of them enter the cathodic compartment from anodic compartment, then there will be fall in the concentration of two molecules in the anodic compartment. So we see that the fall of concentration in a compartment is proportional to the speed of the ion leaving that chamber. Following diagram (11) shows this movement of charges.
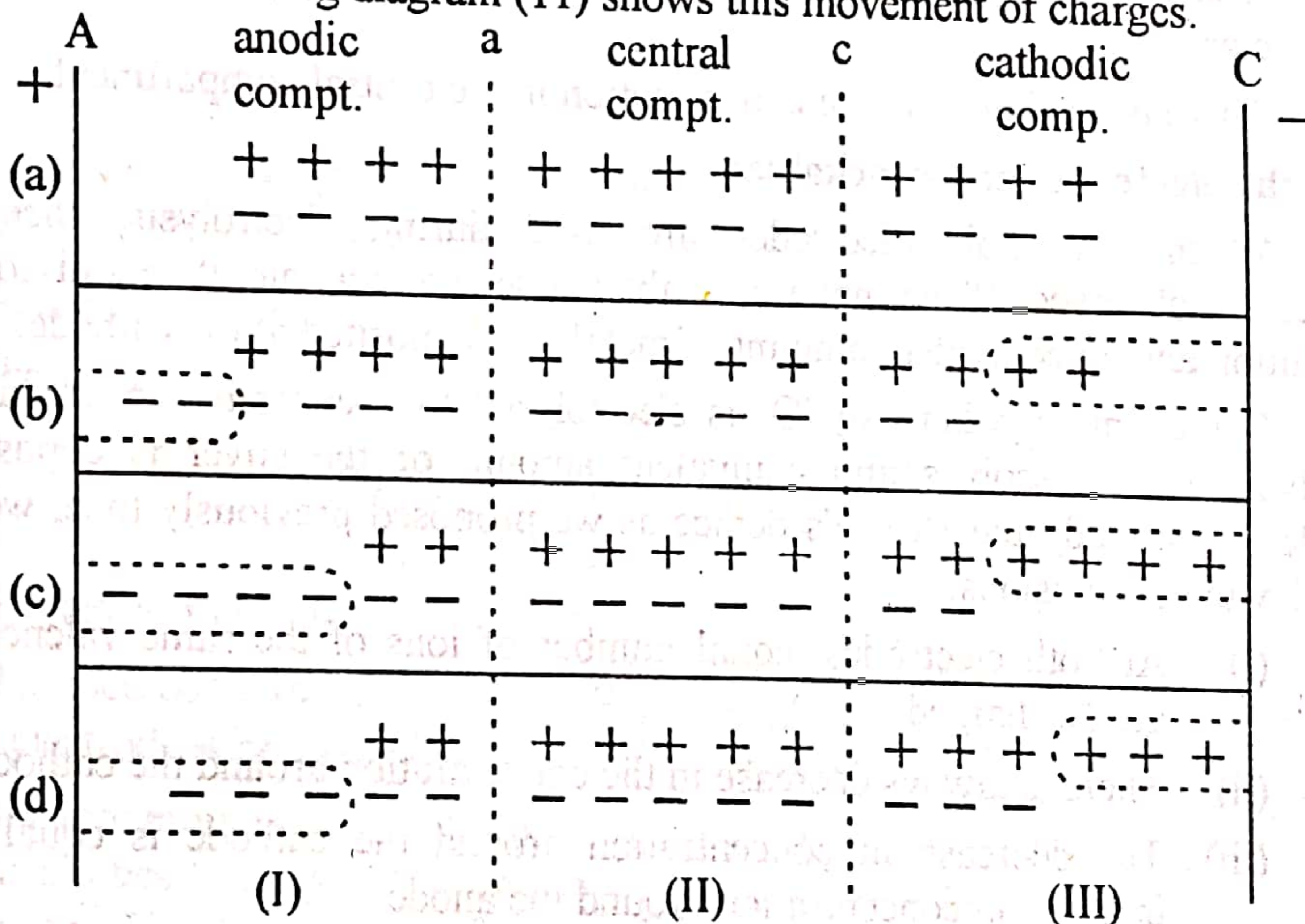

Fig. (11) Migration velocity of ions and change in concentration when the electrodes are not attacked.

Case-II:

When cations and anions move at the same velocity. Now suppose that two cations move from anodic compartment to the cathodic compartment and two anions move from cathodic compartment to anodic compartment. In this way, we get position 'c' and there happens a fall in concentration of two molecules in each compartment.

But we find that number of ions liberated at both electrodes, is same and that is four.

Case-III:

When cations move with double the velocity of anions. Now, let us suppose that two cations from anodic compartment leave and enter the cathodic compartment. Since, the speed of the anion is half the speed of cations. So, only one anion enters the anodic compartment. This position is shown in 'd'. We also observe that the fall in concentrations in anodic and cathodic departments are two and one molecules respectively. But the number of ions discharged is gain the same that is three on each electrode.

9.6.4 Conclusions:

Three conclusions can be drawn from this discussion:

(i)   Fall in the concentration around cathode is directly proportional to the speed of the anion.

(iii)   Fall in the concentration around anode is directly proportional to the speed of the cations.

Fall in concentration around anode:

(i)   Fall in concentration around cathode $= \dfrac{\text{speed of cation}}{\text{speed of anion}}$

(ii)   Irrespective of the speed of the ion, the number of ions liberated on both electrodes is equal.

(iii)   There is no change in the concentration in the central compartment.

When the electrodes are attackable:

When attackable electrodes are used during electrolysis, then some changes are observed. If the material of the anode is attackable, it gets dissolved in the solution and an equivalent amount of metal gets deposited at the cathode.

For example, when $AgNO_3$ is electrolysed by using silver electrode, then the silver anode dissolves and equivalent amount of the silver is deposited at cathode. If we study the Hittorf's device as we proposed previously then, we reach the following conclusions.

(i)   At both electrodes, equal number of ions of the same valence types are discharged.

(ii)   There is always decrease in the concentration around the cathode.

(iii)   The decrease in concentration around the cathode is equal to the increase in concentration around the anode.

(iv)   The concentration of the middle compartment does not change.

9.6.5 Transport number:

"The transport number is the fraction of the total current carried by an ion." Transport number is also called transference number or Hittorf number. It is the property of anions and cations and may be denoted by t_+ and t_- for cations and anions respectively. Greater the speed of the ions, greater the amount of the current carried by it and greater will be transport number.

Let,

Speed of the cation $= u_c$

Speed of the anion $= u_a$

Current carried by cation $\propto u_c = k\,u_c$ ...... (1)

Current carried by the anions $u_a = k\,u_a$ ...... (2)

Total current carried $= k\,u_c + k\,u_a$

$= k(u_c + u_a)$ ...... (3)

Transport number of cation $t_+ = \dfrac{ku_c}{ku_c + ku_a}$

or $t_+ = \dfrac{u_c}{u_c + u_a}$ ...... (4)

Transport number of anion $(t_-) = \dfrac{ku_a}{ku_c + ku_a}$

or $t_- = \dfrac{u_a}{u_c + u_a}$ ...... (5)

According to equation (4) and (5), the value of transport number of the ion is a quantity less than unity and sum of the transport numbers should be equal to unity.

$$t_\oplus + t_\ominus = 1 \qquad\qquad ...... (6)$$

The transport number of an ion is not a constant quantity. It depends upon the second ion which is present in the salt.

9.6.6 Determination of transport number:

These are two methods for the determination of transport number:

(1) Hittorf's method

(2) Moving boundary method.

9.6.7 Hittorf's method:

This method is based upon the principle that the decrease in concentration around an electrode is proportional to the speed of the ion moving away from it.

The apparatus is consisted of U-shaped tube, joined at its two sides to two vertical glass tubes having bulbs. The U-tube and two bulbs have got the stop cork at the bottom. The left glass tube contains the cathode and is called cathodic compartment. The right tube contains the anode, and is called anodic compartment. The electrodes are made up of suitable metal and are sealed in a narrow glass tube. The middle compartment prevents the intermixing of the solution in the anodic and cathodic compartment. Fig. (12)

The concentration of the solution in the middle compartment remains unchanged at the end of the experiment.

If we want to determine the transport number of the silver ion in $AgNO_3$ solution, then the electrodes are either made up of Pt or silver. Platinum electrodes are inert but silver electrode are attacked during the process.

N/5 solution of $AgNO_3$ is taken in the glass tube A, B and C. This apparatus is connected in series with a copper silver coulometer. The number of equivalents of copper and silver deposited in the coulombmeter give the measurement of total current passed. This also gives the total fall in the concentration around anode and cathode.

During electrolysis, 10 – 20 milliamperes of the current is usually passed for 2 – 3 hours. In this time, an appreciable change in concentration around the electrode takes place. After electrolysis, the solution from the anodic compartment 'A' is taken out and change in its concentration is determined by titration. Concentration of the middle compartment is also analysed and there should be no change in that.

Calculations:

We can do the calculations for the determination of transport number of $Ag^\oplus$ ion by two ways:

    (i)   When electrodes are not attacked

    (ii) When the electrode are attacked.

(i)   **When electrodes are not attacked:**

In this case, we use the platinum electrode:

(I)   **After electrolysis:**

'X' grams of anode solution contain $AgNO_3$ = Y grams

Weight of water   = X – Y grams

Gram equivalent of $AgNO_3$ $= \dfrac{Y}{170}$

It means that (X – Y) grams of H_2O, contains $Ag^\oplus$ ions $= \dfrac{Y}{170}$ gram

equivalent = A.

(II)   **Before electrolysis:**

Suppose 'L' grams of the anodic solution contains $AgNO_3$ = M grams

Weight of H_2O in solution   = (L – M) gram

So, (L – M) grams of H_2O contains $AgNO_3$ = N grams

Therefore, (X – Y) grams of H_2O contains

$$= \frac{M}{(L-M)} \cdot (X-Y) \text{ g of } AgNO_3$$

$$= \frac{M}{(L-M)} \cdot \frac{(X-Y)}{170} \text{ g. eq. of } AgNO_3$$

$$= \frac{M}{(L-M)} \cdot \frac{(X-Y)}{170} \text{ g eq. of } Ag^\oplus$$

$$= B$$

So, the fall in the concentration around the anode, due to migration of $Ag^{\oplus}$ ions = (B – A), gram equivalent. Suppose that the weight of copper deposited in the Cu colometer in the same time is 'W' grams. Then the gram equivalent of 'Cu' deposited on the cathode in the colometer = $\dfrac{W}{31.75}$ = C.

'C' represents the total fall in concentration around the cathode and the anode.

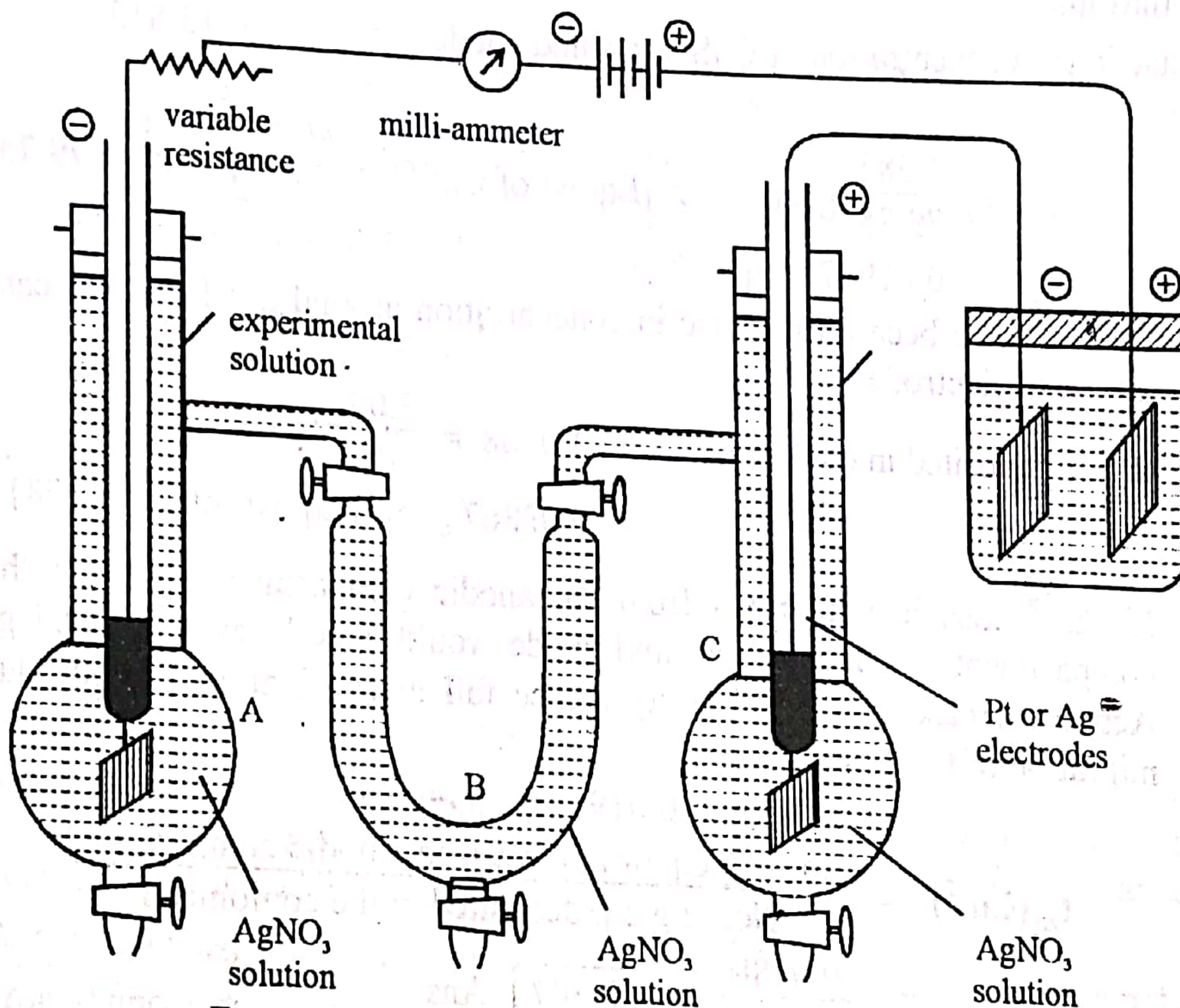Transport number of $Ag^{\oplus}$ ion = $\dfrac{(B - A)}{C}$

Fig. (12) Apparatus for the determination of transport
number of Hittorf's method.

Similarly, calculation of transport number can be done, if we consider that electrodes are attacked.

EXAMPLE (10)

A solution containing 10.09 g of $CuSO_4$ in 189.9 g of water was electrolysed. After electrolysis 275.4 g of the solution around the anode was found to contain 15.4 g of $CuSO_4$ and 3.096 g silver was deposited in a coulometer placed in series. Calculate the Hittorf's numbers of Cu^{2+} and SO_4^{-2} ions.

SOLUTION:

Data:

After electrolysis

Weight of the anode solution   = 275.4 g
Weight of $CuSO_4$ present   = 15.4 g
∴   Weight of water present   = 275.4 – 15.4 g = 260 g

Before electrolysis

    Weight of water   = 189.9 g

    Weight of $CuSO_4$ = 10.09 g

i.e. 189.9 g of water are associated with $CuSO_4$ = 10.09 g

$\therefore$ 260 g water is associated with $CuSO_4$ $= \dfrac{10.01}{189.9} \times 260$

                                 = 13.815 g

Calculations:

Increase in the concentration of $CuSO_4$ around anode   = 15.4 − 13.815

                                                   = 1.585 g

$$= \frac{1.585}{79.75} \text{ g eq.} \quad \because \left\{ \text{Eq. wt of } CuSO_4 = \frac{60.5+32+64}{2} = 79.75 \right\}$$

$$= 0.01987 \text{ g eq.}$$

As there has been an increase in concentration around anode, it is a case of attack of electrode.

Silver deposited in coulometer $= 3.0968 = \dfrac{3.096}{108} \text{ g eq.}$

                              $= 0.02867 \text{ g eq.} \quad \{\text{Eq. wt. of } Ag = 108\}$

If Cu^{+2} ions had migrated from the anodic compartment to the cathodic compartment, the increase around anode would have been $= 0.02867$ g eq. Actual increase $= 0.01987$ g eq. Hence fall in conc. around anode due to migration of Cu^{+2} ions

         $= 0.02867 - 0.01987 = 0.0088 \text{ g eq.}$

$$t_{\oplus}(Cu^{+2}) = \frac{\text{No. of g eq. of ion lost from anodic compartment}}{\text{No. of g eq. deposited in the coulometer}}$$

$$= \frac{0.0088}{0.02867} = \boxed{0.307} \text{ Ans.}$$

$$t_{\ominus}(SO_4^{-2}) = 1 - 0.307 = \boxed{0.693} \text{ Ans.}$$

EXAMPLE (11)

A solution of silver nitrate was electrolysed between silver electrodes. Before electrolysis 10 g of the solution contains 0.01788 g of silver nitrate. After the experiment 20.09 g of the anodic solution contained 0.06277 g of silver nitrate and 0.00947 g of copper was deposited in copper coulometer placed in series. The atomic weights of Ag and Cu are 108 and 63.6 respectively. Calculate the transport number of $Ag^{\oplus}$ and $NO_3^{\ominus}$.

SOLUTION:

Data:

    After Electrolysis

        Weight of the anodic solution = 20.09 g

        Weight of $AgNO_3$ present   = 0.06277 g

        Weight of water present   = 20.09 − 0.06277 = 20.02723 g

Before electrolysis

Weight of solution	=	10 g
Weight of AgNO₃ present	=	0.01788 g
∴ Weight of water present	=	10 − 0.1788 = 9.98212 g

Thus 9.98212 g of water in associated with AgNO₃ = 0.01788 g

Calculations:

20.02723 g of water is associated with $AgNO_3$.

$$= \frac{0.01788}{9.98212} \times 20.02723 = 0.03587$$

Increase in conc. of $AgNO_3$ around anode $= 0.06277 - 0.03587 = 0.02690$ g

$$= 0.0269 \text{ g} \quad \{\text{Eq. wt. of } AgNO_3 = 170\}$$

$$= \frac{0.0269}{170} \text{ g eq.}$$

$$= 0.0001582 \text{ g eq.}$$

Copper deposited in the coulometer

$$= 0.00947 \text{ g} \quad = \frac{0.00947}{31.8} \text{ g eq.} \quad \text{Eq. wt of } Cu = \frac{63.6}{2} = 31.8$$

$$= \boxed{0.0002977 \text{ g eq.}} \quad \text{Ans.}$$

Thus if no. $Ag^{\oplus}$ ion had migrated from the anodic compartment to the cathodic compartment, the increase in concentration of the anodic compartment would have been $= 0.0002977$ g eq.

Actual increase in conc. $= 0.0001582$ g eq. Hence fall in concentration around anode due to migration of $Ag^{\oplus}$ ions from the anodic compartment.

$$= 0.0202977 - 0.00015827 \text{ g eq.}$$

$$= 0.0001395 \text{ g eq.}$$

∴ $t_+(Ag^{\oplus}) = \dfrac{\text{No. of g eq. lost from the anodic compartment}}{\text{No. of g eq. deposited in the coulometer}}$

$$= \frac{0.0001395}{0.0002977} = \boxed{0.469} \quad \text{Ans.}$$

∴ $t_-(NO_3^{\ominus}) = 1 - t_{(-)} = 1 - 0.469 = \boxed{0.531}$ Ans.

9.6.8 Moving boundary method:

Principle:

The basic principle for the measurement of transport number by moving boundary method is based upon the fact that the transport number of the ions depend upon the velocities of cations and anions. So, if we know the speeds of cations and anions, then the transport numbers can be calculated.

Procedure:

The apparatus which is used for the determination of transport number is shown in the following diagram (13).
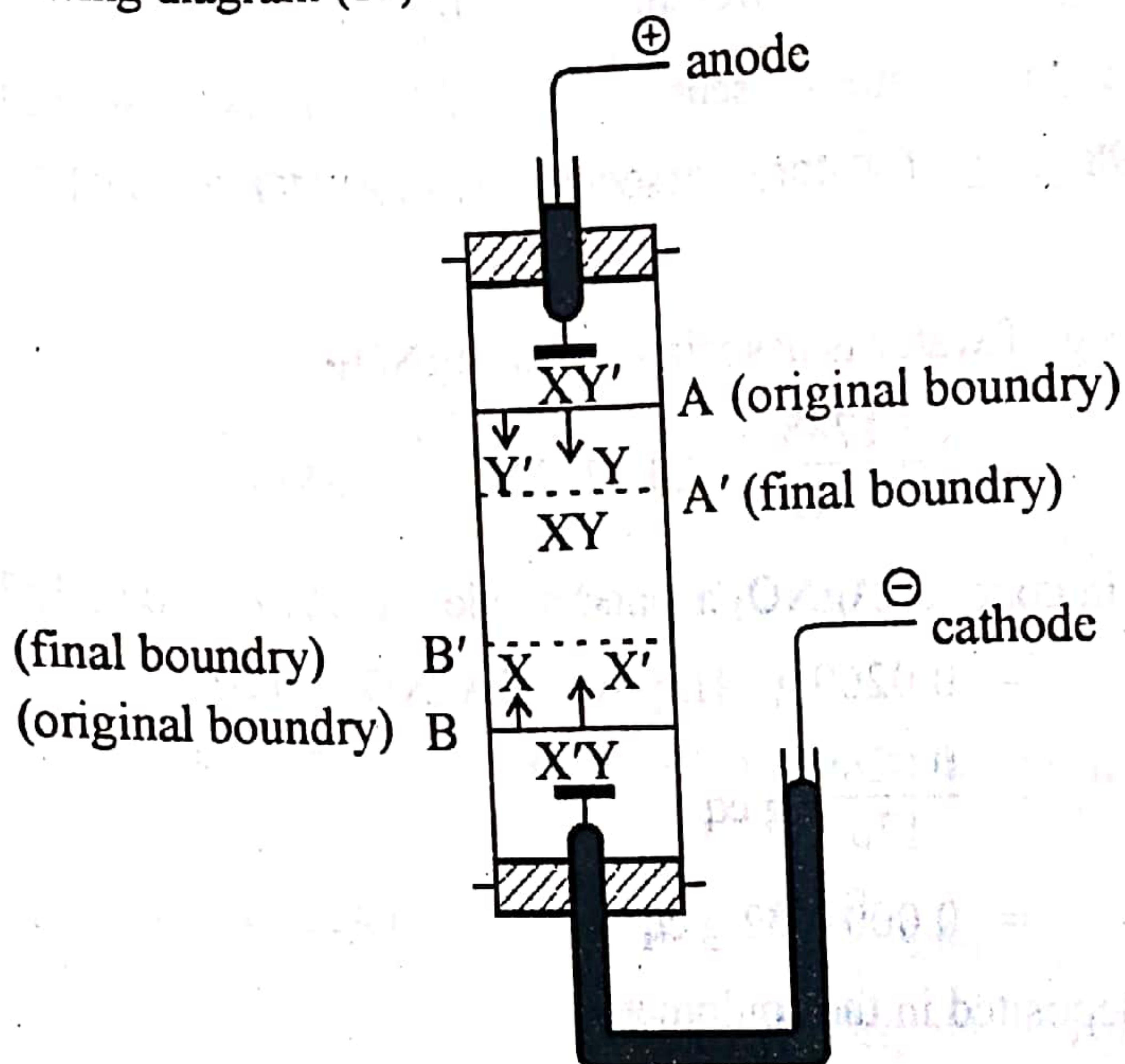

Fig. (13) Moving boundary method for determination of transport number.

It is consisted of long tube. This tube is mounted vertically and fitted with platinum electrodes on both sides. Salt XY, which is under investigation is dissolved in water. This solution is placed between the solutions of two other salts X'Y and Y'X. These two solutions have two common ions with XY. For example, if XY is NaCl then X'Y may be LiCl and XY' may be CH_3COONa. These three solutions are arranged in such a way that the solution of greater density is lower than the other.

Suppose that the original boundaries are A and B. The solution may be colourless but the distinction between the boundaries will be there because of the differences in refractive indice of the solution. If we want that the boundaries may remain sharp throughout the experiment, then X' and Y' must have smaller velocities than X and Y. When the current is passed, then the boundaries move to new positions A' and B'.

Hence

Velocity of the cation $X^{\oplus}$,

$u_c \propto$ length AA'

Velocity of the anion $Y^{\ominus}$,

u_a length BB'

$$t_{\oplus} = \frac{AA'}{AA' + BB'}$$

$$t_{\ominus} = \frac{BB'}{AA' + BB'}$$

It means that the measuring the displacement of the boundaries, the transport numbers can be calculated.

Factors which affect the transport number of the ion:

We know that the transport number depends upon the velocity of the ion. The velocity of the ion is influenced by following factors.

(1)   Nature of ion:

The size of the ion determines the speed of the ion under the given potential difference. Small sized ion like $H^{\oplus}$ in 0.1 M HCl has greater velocity than $Na^{\oplus}$ ion in 0.1 M NaCl. So, the transport number of $H^{\oplus}$, is greater than that of $Na^{\oplus}$.

(2)   Nature of the other ion present:

The transport number is the ratio of velocities of ion to the sum of the velocities of both ions. So, if the nature of the companion ion changes, then the transport number changes.

For example, $t_{Cl}\ominus$ in HCl is different from $t_{Cl}\ominus$ in NaCl.

$$t_{Cl}\ominus \text{ (HCl)} = \frac{\mu_{Cl}\ominus}{\mu_H + \mu_{Cl}\ominus}$$

$$t_{Cl}\ominus \text{ (NaCl)} = \frac{\mu_{Cl}\ominus}{\mu_{Na}\oplus + \mu_{Cl}\ominus}$$

Since $u_H\oplus$ and $u_{Na}\oplus$ are different, so the transport numbers are different. Due to greater value of $u_H\oplus$ than $u_{Na}\oplus$, the $t_{Cl}\ominus$ from HCl is smaller than $t_{Cl}\ominus$ from NaCl.

(3)   Hydration of ions:

Greater the possibility of hydration of a particular ion, lesser the velocity of that ion and lesser the transport number. For example, $Li^{\oplus}$, ions are smaller in size than $Na^{\oplus}$, so we expect that the transport number of $Li^{\oplus}$, will be greater than $Na^{\oplus}$. But, actually reverse is true. The reason is that $Li^{\oplus}$ ions are more hydrated than $Na^{\oplus}$ ion, due to greater charge density.

(4)   Concentration:

When the concentration of a solution changes, then the transport number of the ion changes. But, it is observed that the changes are very small. Mostly it is observed that the transport number falls down with the increase of concentration.

(5)   Temperature:

The increase of temperature increases the transport number. It is observed that with increasing temperatures, the ions tend to approach a transport number value of 0.5. It means that equal fraction of current is carried by cations and anions. If the transport number is less than 0.5 at ordinary temperature, then it increases with increase of temperature. If the transport number is greater than 0.5 at ordinary temperature, it approaches 0.5 with the increase of temperature.
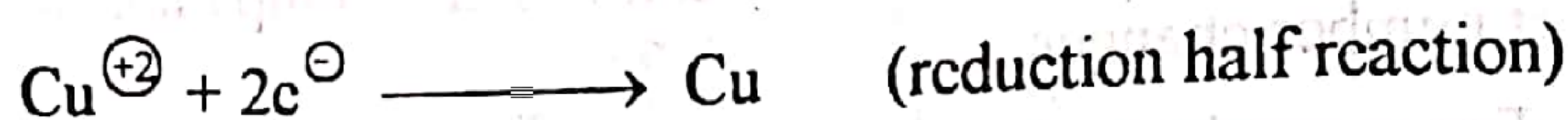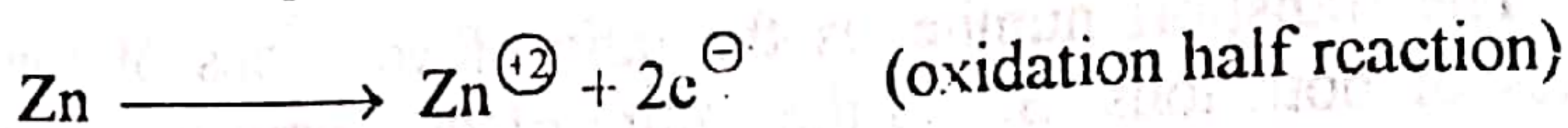
9.7.0 ELECTROCHEMICAL CELLS

9.7.1 Introduction:

In order to understand the electrochemical cells, consider a reaction between Zn and $CuSO_4$. When Zn powder is added in $CuSO_4$, solution, then blue colour of $CuSO_4$ solution vanishes and copper metal settles down.

$$Zn + CuSO_4 \longrightarrow ZnSO_4 + Cu$$
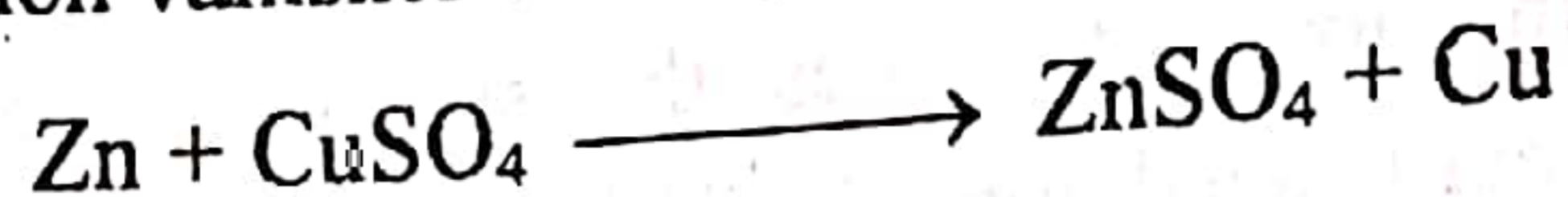
It is an oxidation reduction reaction

$$Zn^° + Cu^{+2} \longrightarrow Zn^{+2} + Cu^0$$

This reaction can be splitt up into two half reactions

$$Zn \longrightarrow Zn^{+2} + 2e^{\ominus} \qquad \text{(oxidation half reaction)}$$

$$Cu^{+2} + 2e^{\ominus} \longrightarrow Cu \qquad \text{(reduction half reaction)}$$

The overall reaction is obtained from the addition of these two reactions.

9.7.2 How to make the electrochemical cell:

Arrange the two solutions by taking Zn rod in $ZnSO_4$ solution and Cu rod in $CuSO_4$ solution and join the two rods as shown in the following diagram (14). The solutions are connected by a salt bridge.

The oxidation half reaction takes place in the left beaker and reduction half reaction in the right beaker.
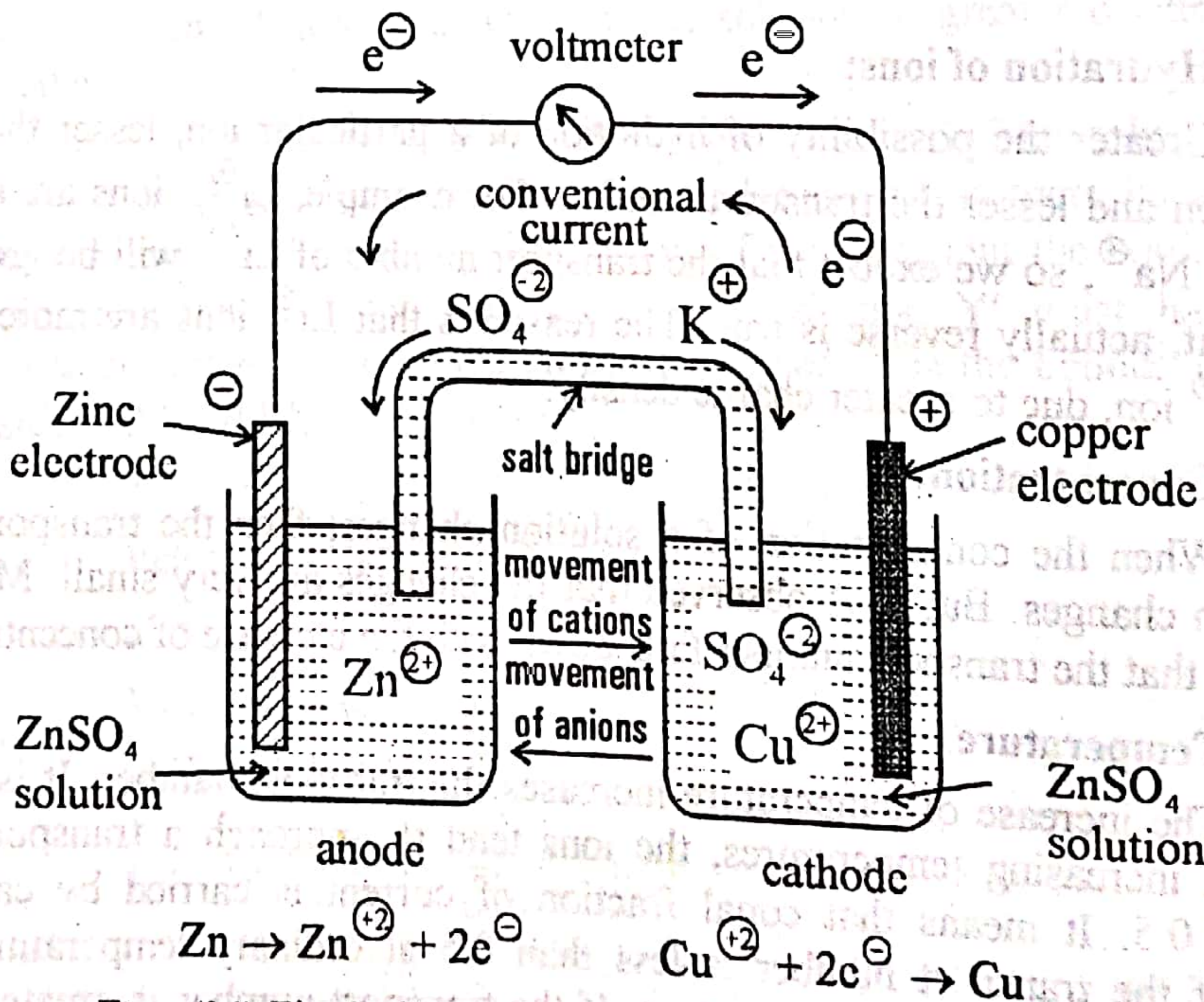
Fig. (14) Electrochemical cell based on the redox reaction

$$Zn + CuSO_4 \longrightarrow ZnSO_4 + Cu$$

The electrons are given out by zinc rod and they are taken by the copper rod.

The salt bridge is a U-shaped tube containing a concentrated solution of a strong electrolyte as KCl, or K_2SO_4. This bridge makes the contact of two solutions for the movement of the ions without the mixing of the two solutions. This arrangement shown in the above diagram allows the electrons to move in the outer circuit and the ions through the salt bridge.

9.7.3 Some important points:

Some important features of the above arrangement which construct a cell are as follows:

(i)   Oxidation takes place at zinc electrode and it is called anode. Reduction takes place at the copper electrode and it is called cathode.

(ii) Zinc rod is rich in electrons, so it is called the negative pole. Copper rod is poor of electrons and it is called positive pole.

(iii) The electrons flow from negative pole to positive pole in the external circuit, but the conventional current is said to flow in opposite direction.

(iv) The zinc electrode releases the zinc ions and electrons are set free. Zinc ions become excess in the left beaker and sulphate ion from the salt bridge compensate these ions to make the solution neutral.

(v)   When Cu^{+2} ions are deposited at the right electrode, then the SO_4^{-2} become excess in this beaker. $K^{\oplus}$ from the salt bridge travel towards this beaker and solution becomes neutral.

(vi) The net result is that the weight of the Cu electrode increases and that of zinc electrode decreases.

(vii) The tendency of the net flow of the electrons through the outer circuit decreases due to the changing concentration of Cu^{+2} ion and of Zn^{+2} ion in both the beakers separately.

9.7.4 Some other electrochemical cells:

Just like the above arrangement of a zinc and copper, we can have the arrangement of any two suitable metal electrodes. It depends upon the nature of electrode that what will be the direction of the flow of the current.

When copper dipped in $CuSO_4$ solution is connected with Ag dipped in $AgNO_3$ solution, then the current flows from Cu to Ag as shown in the following diagram (15).
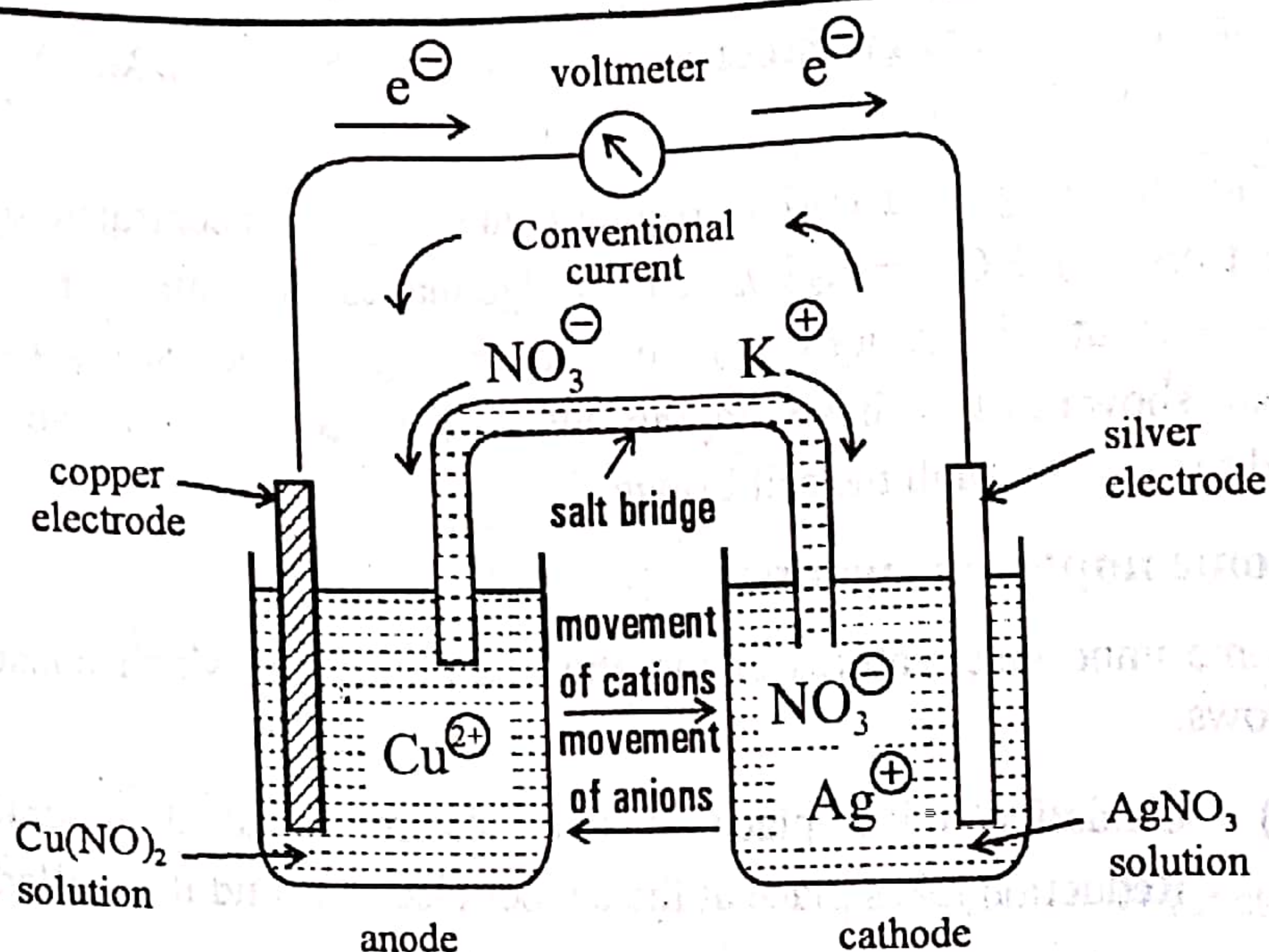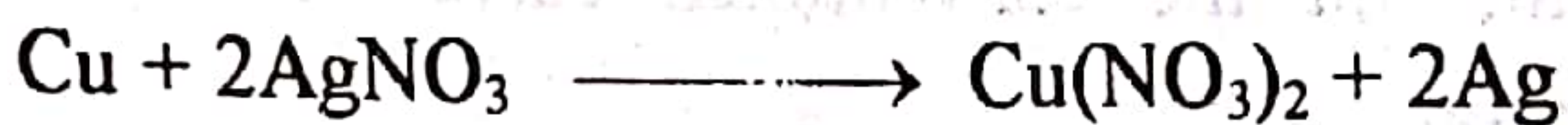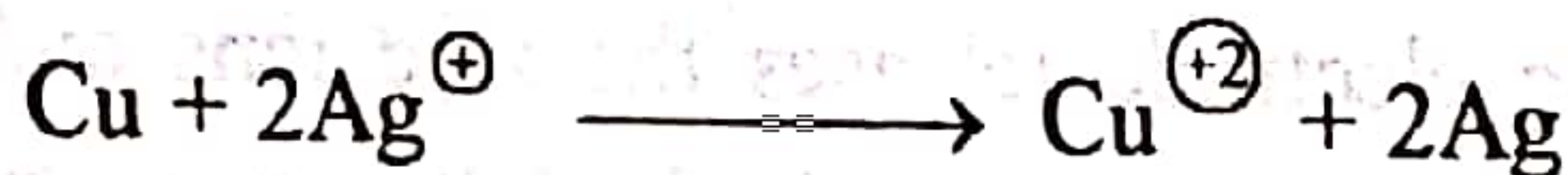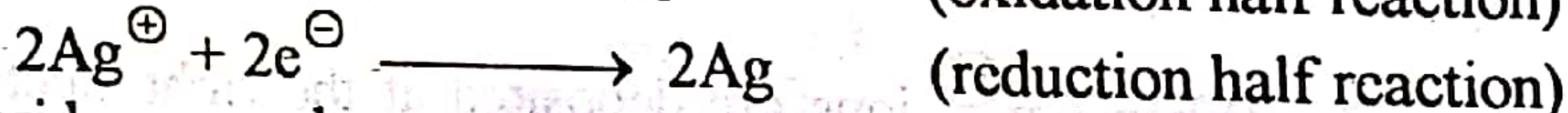
$$Cu \rightarrow Cu^{+2} + 2e^{\ominus} \qquad\qquad Ag^{\oplus} + e^{\ominus} \rightarrow Ag$$
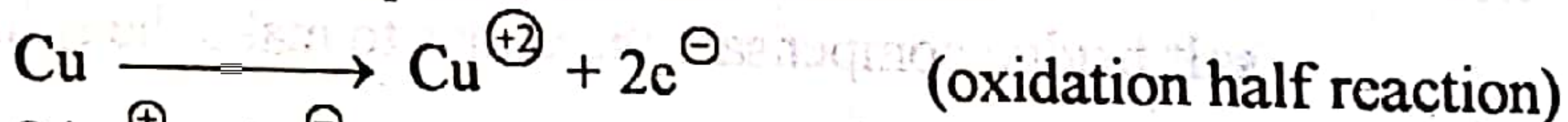
Fig. (15) Electrochemical cell based on the redox reaction

$$Cu + 2AgNO_3 \longrightarrow Cu(NO_3)_2 + 2Ag$$

The cell redaction is

$$Cu + 2AgNO_3 \longrightarrow Cu(NO_3)_2 + 2Ag$$

The ionic reaction is

$$Cu + 2Ag^{\oplus} \longrightarrow Cu^{+2} + 2Ag$$

The reaction can be split up into two half reactions

$$Cu \longrightarrow Cu^{+2} + 2e^{\ominus} \qquad \text{(oxidation half reaction)}$$

$$2Ag^{\oplus} + 2e^{\ominus} \longrightarrow 2Ag \qquad \text{(reduction half reaction)}$$

The salt bridge may be prepared by taking a concentrated solution of KNO_3. The important points are as follows:

(i)　Oxidation takes place at copper electrode and it is called anode.

(ii)　Reduction takes place at Ag electrode and it is called cathode.

(iii)　The electrical neutrality of the solution is maintained by the migration of $K^{\oplus}$ and $NO_3^{\ominus}$ ions.

(iv)　The conventional current flows from Ag to Cu.

9.7.5　Comparison of two cells:

In the first arrangement of zinc and copper, the current flows from Zn to the Cu and Zn acts as anode. In the second arrangement of Cu and Ag, the Cu acts an anode and Ag as cathode. It means that it is the relative tendency of one of the electrodes as compared to the other companion, whether it will be loser or gainer of electrons.

9.7.6　Electrolytic cell:

"This is an arrangement in which the electrical energy is supplied to bring about the reaction, which is otherwise non-spontaneous."

When we pass electrical current through molten NaCl, then sodium deposits at the cathode and Cl_2 is deposited at the anode. The following arrangement (16) shows the movements of the ions towards the respective electrodes.
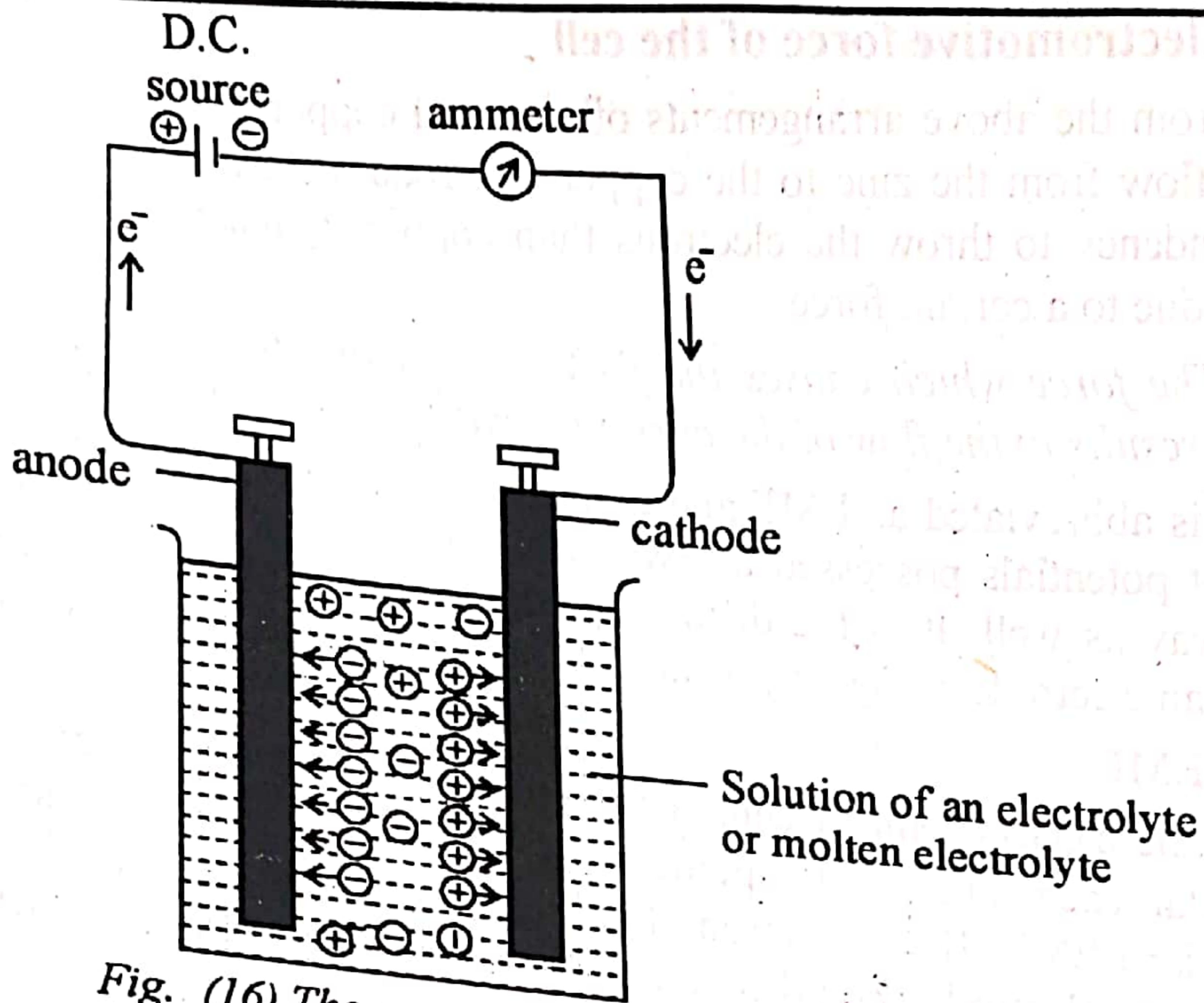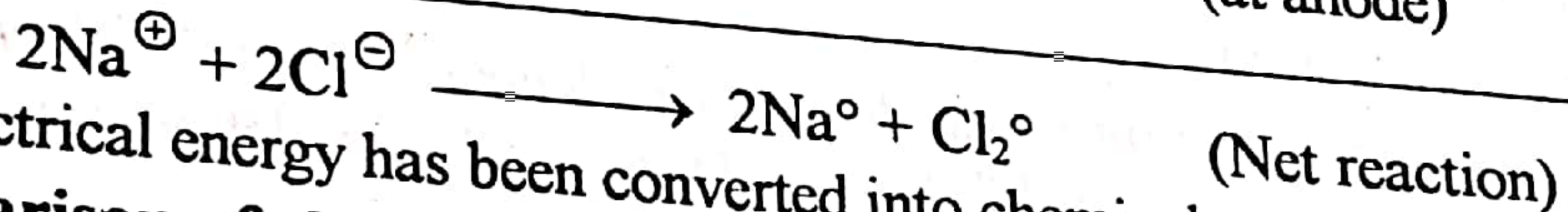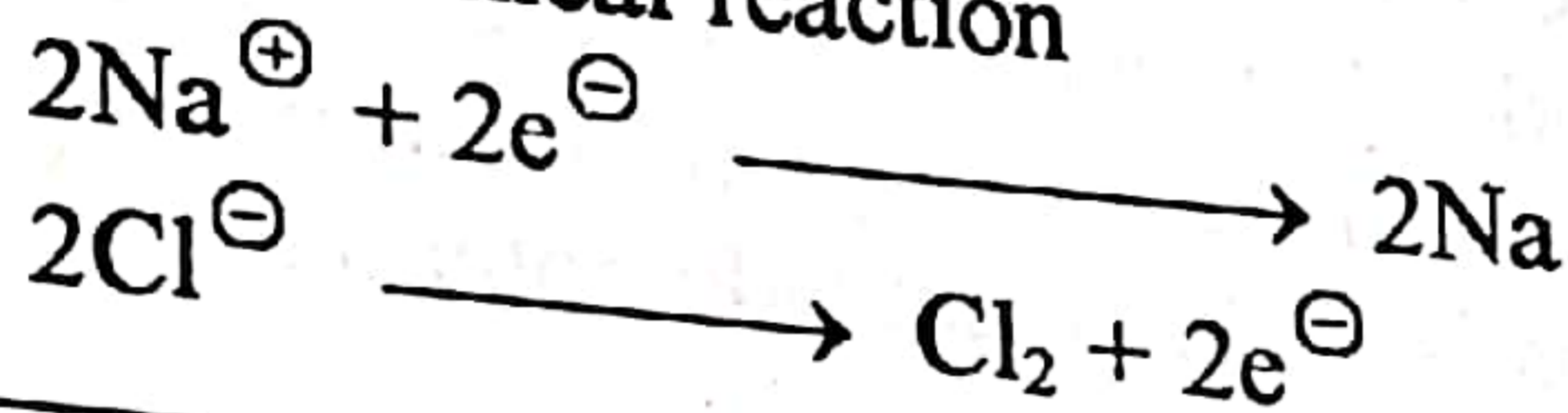
Fig. (16) The movement of ions towards the respective electrodes in electrolytic cell

In this arrangement, the external source of potential difference is applied which brings about a chemical reaction

$$2Na^{\oplus} + 2e^{\ominus} \longrightarrow 2Na \quad \text{(at cathode)}$$
$$2Cl^{\ominus} \longrightarrow Cl_2 + 2e^{\ominus} \quad \text{(at anode)}$$

$$\overline{2Na^{\oplus} + 2Cl^{\ominus} \longrightarrow 2Na° + Cl_2° \quad \text{(Net reaction)}}$$

The electrical energy has been converted into chemical energy.

9.7.7 Comparison of electrochemical and electrolytic cell:

Following are the some important points, in which these two types of cells differ from each other:

Electrochemical cell		Electrolytic cell	
1.	Chemical energy is converted into electrical energy.	1.	Electrical energy is converted into chemical energy.
2.	Spontaneous reactions complete this cell.	2.	Redox reactions are mostly non-spontaneous.
3.	We can set up two electrodes in the solutions of same or different electrolytes.	3.	The two electrodes are set up in same electrolytic solution.
4.	That electrode on which oxidation takes place is called the anode and that electrode on which reduction takes place is called cathode.	4.	That electrode which is connected to the negative terminal of battery is called cathode.
5.	In electrochemical cell we need a salt bridge to maintain the internal flow of the ions.	5.	There is no need of any salt bridge.

9.7.8 Electromotive force of the cell

From the above arrangements of zinc and copper, we have noticed that the electrons flow from the zinc to the copper electrode. It means that the zinc has the greater tendency to throw the electrons than copper. It means electrical current is generated due to a certain force.

"The force which causes the flow of electrons from one electrode to the other and results in the flow of the current is called electromotive force of the cell."

It is abbreviated as EMF and is measured in volts. This force develops due to different potentials possessed by two electrodes. So, we can define the EMF in an other way as well. It is the difference of potential which causes the current to flow from an electrode at higher potential to an electrode at lower potential.

Standard EMF:

In the electrochemical cell, if the solutions are arranged at concentrations of one molar each, and the temperature is 25°C, then the EMF so produced is called standard EMF. If the electrode is gaseous in nature, then the pressure of the gas working as electrode should be one atmosphere to give a standard EMF to the cell.

Electrode potential:

In the electrochemical cells, oxidation occurs at one electrode and the reduction occurs at other electrode. It means that one electrode has a tendency to loose electrons while the other has tendency to gain electrons. This tendency of an electrode to loose or gain electrons is called electrode potential.

Oxidation potential:

"If the oxidation takes place at an electrode, then the electrode potential is called oxidation potential." In the Daniel cell, oxidation takes place at zinc electrode.

Reduction potential:

"If the reduction takes place at one of the electrodes, then the electrode potential is called reduction potential." In the Daniel cell, reduction takes place at copper electrode.

"If the half cell or the metal rod is suspended in a solution of 1 M concentration or unit activity and the temperature is maintained at 25 C°, then it is called standard electrode potential and is denoted by E°."

If a gaseous substance is involved in making an electrode, then the pressure maintained should be one atmosphere along with other standard conditions to have the standard electrode potential.

Absolute value of electrode potential:

Be careful that the absolute value of the electrode potential can not be determined. The reason is that, neither oxidation nor reduction can take place independently. No half reaction works alone. The electrode potential of any electrode is always determined with respect to a standard electrode. Moreover, the change of the concentration of the solution and the change of pressure and temperature also change the electrode potential.

9.7.9 Source of emf in galvanic cell:

The source of EMF in a Galvanic cell is the chemical reaction which happens in the cell. Oxidation happens at one electrode and the reduction at the other.

Why there is oxidation at one electrode and reduction at the other?

Its answer can be given when we understand the potential difference, which is developed when a metal rod is dipped in its own ions.

Nernst in 1889, put forward a theory to explain this phenomenon. Following diagram (17) shows that a metal 'M' is dipped in a solution of its own ions 'M$^{\oplus}$'. There are two tendencies which are operative in the solution.

(i) The tendency for the metal atom to ionize and go into the solution in the form of 'M$^{\oplus}$'. This is called solution pressure of metal.

(ii) The tendency for the ions in the solution to give up their charge and to become metal atoms on the metal surface. This is called osmotic pressure of ions.

Following diagram (17) shows these two tendencies:

solution pressure of metal

osmotic pressure of ions
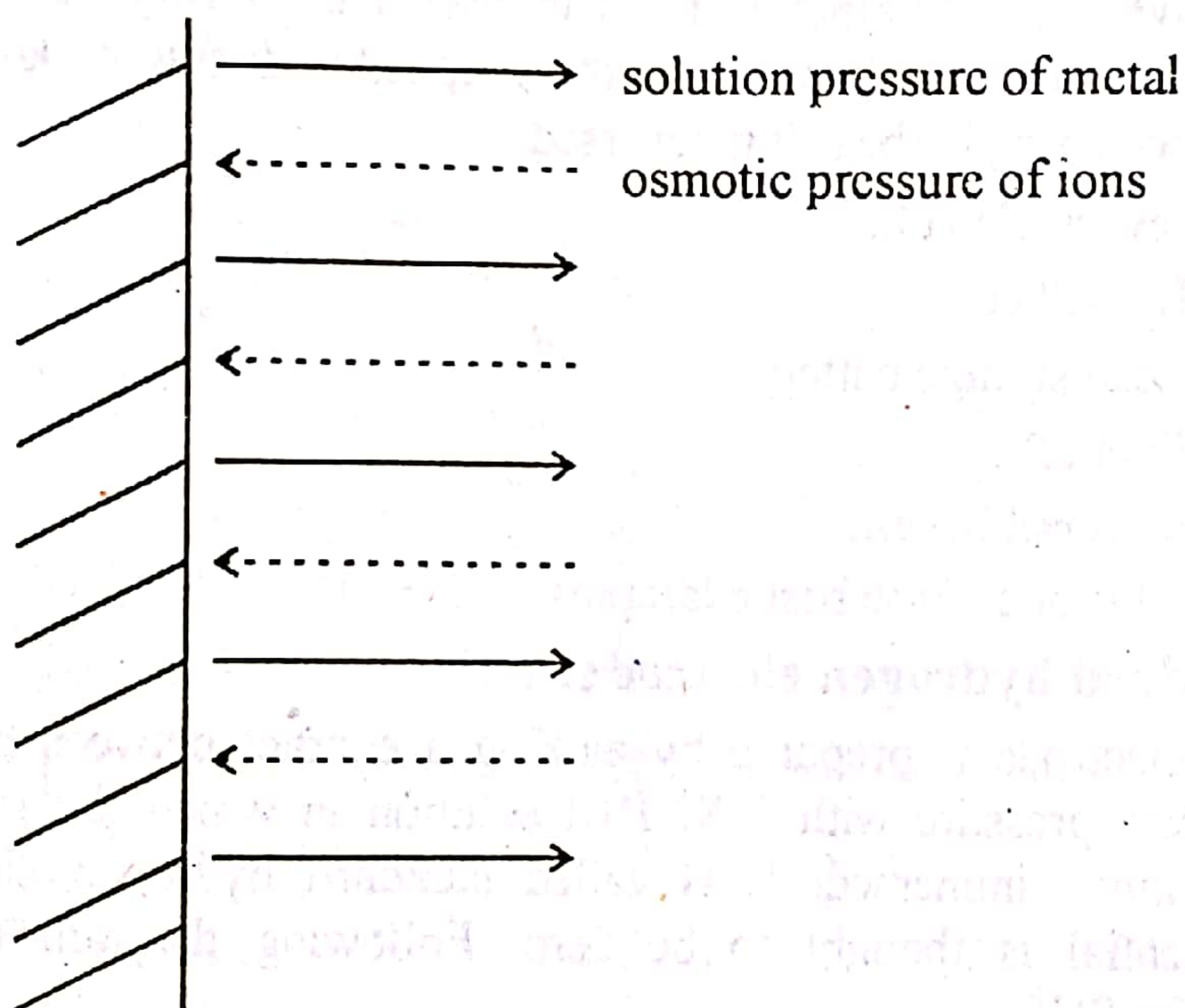
Fig. (17) Metal / solution interface.

Nernst says that an equilibrium is set up instantly between these two tendencies. If any one of the tendencies is dominant, then the metal and the solution will take on different potentials. If the solution pressure exceeds the osmotic pressure of the ions in the solution, then the metal atom goes to the solution and the electrons are deposited at the rod.

$$M \longrightarrow M^{\oplus} + 1e^{\ominus}$$
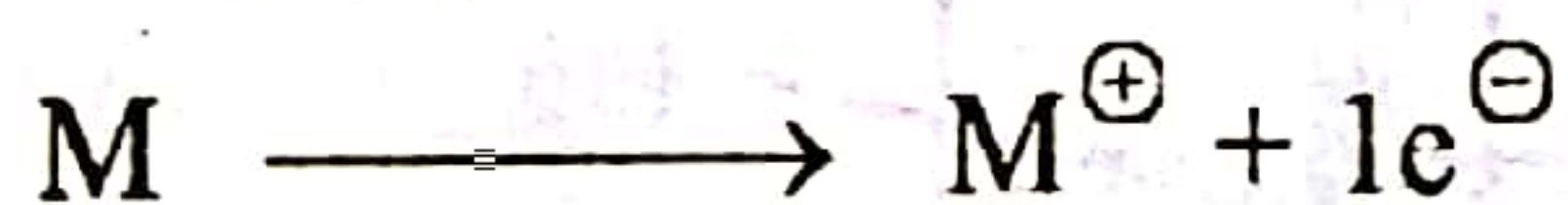
If the solution pressure is less than the osmotic pressure of the ion, then the M$^{\oplus}$ ions goes to the metal rod and rod becomes positive.

$$M^{\oplus} + 1e^{\ominus} \longrightarrow M$$
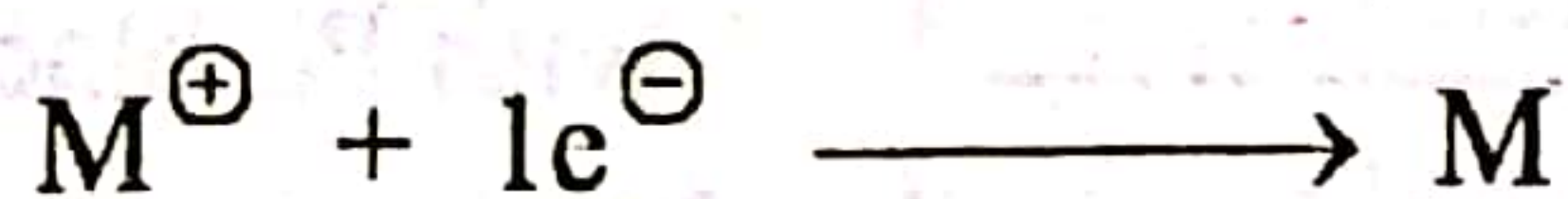
So, in galvanic cell each electrode acquires a certain potential due to the difference in the rate of migration and return of the cations. It depends upon the nature of the metal and the concentration of the solution that which sign and the value of the potential is developed.

If both metals have the same tendencies to be ionized, then each electrode will have the same number of free electrons. There will be no difference of potential and there will be no flow of electrons. Anyhow, if there is difference of potential, it will cause a current to flow from the electrode at higher potential to one at lower potential. This difference of potential is called EMF.

9.7.10 Difference between reversible and irreversible cells:

Reversible cell must satisfy the following conditions:

(i)   When the cell is connected to an external source of EMF, equal to that of the cell, then no current flows and no chemical reaction takes place.

(ii) When the external EMF is decreased by a very very small amount, then the current will flow from the cell and chemical change will takes place.

(iii) When the external EMF is increased by a very very small amount, then current passes in the opposite direction and the process occurring in the cell is reversed.

Examples of reversible cell:

(1) Daniell cell
(2) Lead storage battery
(3) Fuel cell.

Example of irreversible cell:

Dry cell is one of the best examples.

9.7.11 Standard hydrogen electrode:

This electrode is prepared by making a contact between hydrogen gas at one atmospheric pressure with 1 M HCl solution in which the foil of platinized platinum remains immersed. It is called standard hydrogen electrode and its electrode potential is thought to be zero. Following diagram (18) shows the arrangement for SHE.


T = 25°C

H$_2$ Gas (1 atm. P)
copper wire
Hg
1 M HCl solution
platinum foil coated with Pt. black
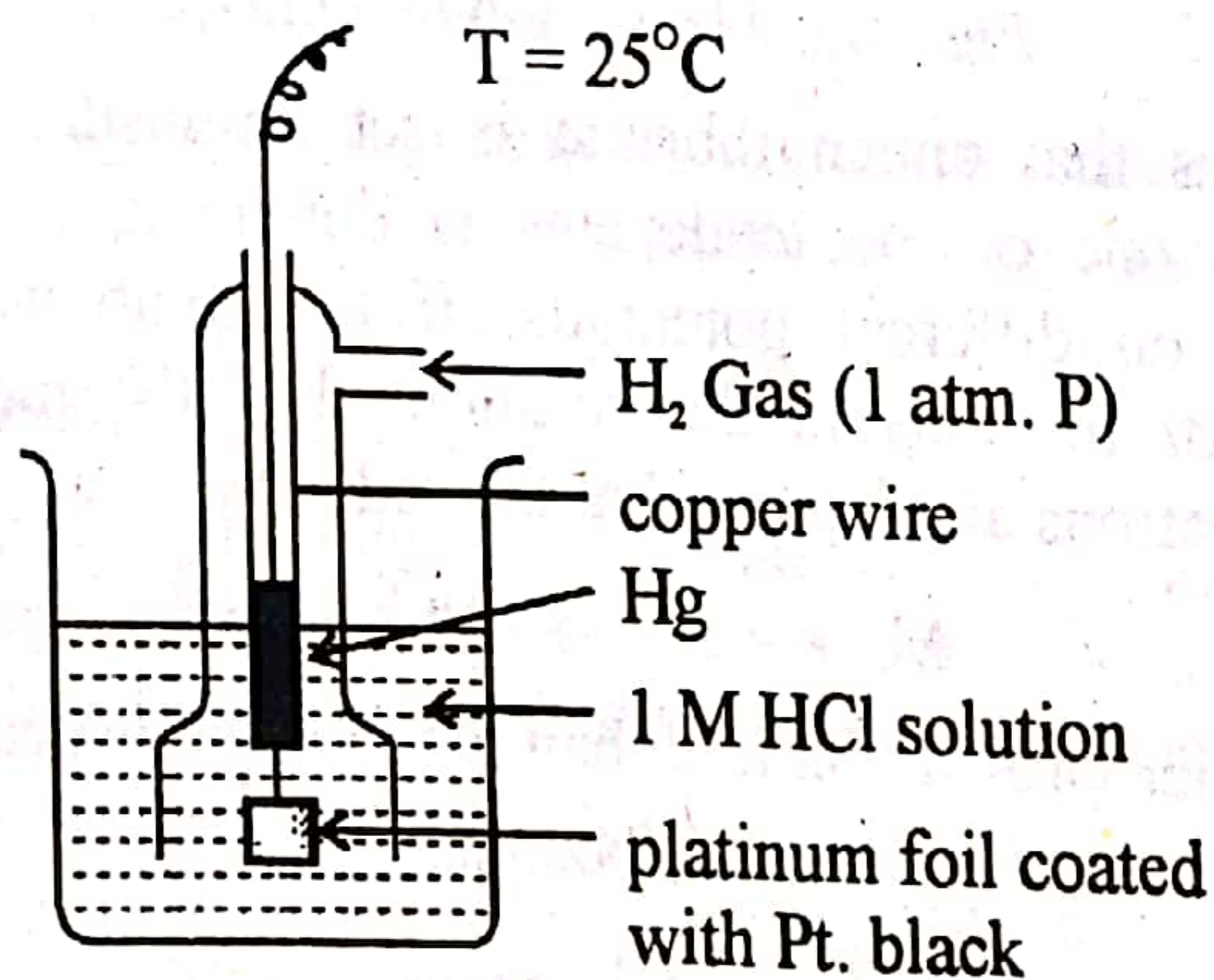
Fig. (18) Standard hydrogen electrode (SHE).

SHE can act as cathode and anode both depending upon the nature of the electrode with which it is connected to complete a electrochemical cell.
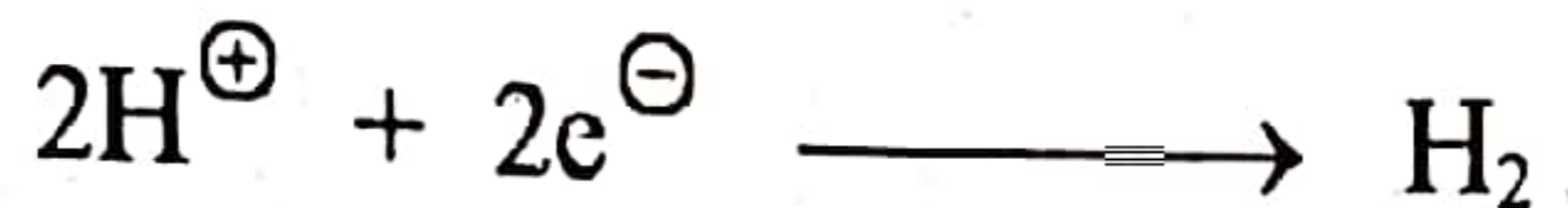
SHE as anode:

It can act as anode by delivering its electrons to the other electrode. The H_2 gas which is supplied is converted into $H^\oplus$ ions and electrons are set free. $H^\oplus$ ions join the solution
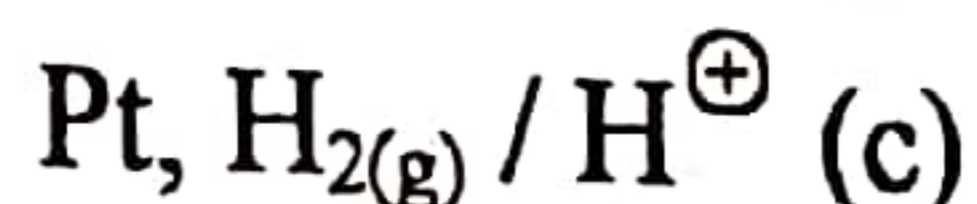
$$H_2 \longrightarrow 2H^\oplus + 2e^\ominus$$
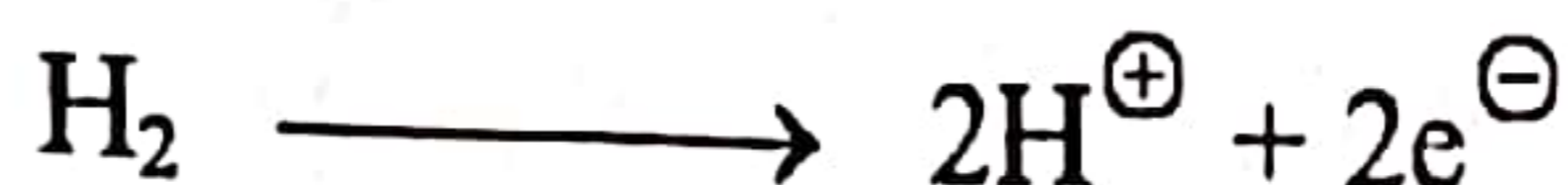
SHE as cathode:

When the hydrogen ions present in the solution accept the electrons from other electrode, then hydrogen gas is produced from the solution.

$$2H^\oplus + 2e^\ominus \longrightarrow H_2$$

It means that the SHE is reversible electrode with respect to $H^\oplus$.

This electrode is usually represented as

$$Pt, H_{2(g)} / H^\oplus \text{ (c)}$$

9.7.12 Determination of standard electrode potential of zinc electrode:

In order to have understanding about the value of standard electrode potential of the zinc, following arrangement is there in the diagram (19)

Anode: $Zn \longrightarrow Zn^{+2} + 2e^\ominus$ Cathode: $H^{+2} + 2e^- \longrightarrow 2H_2$
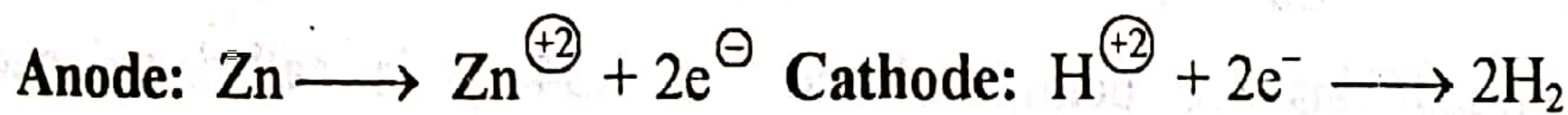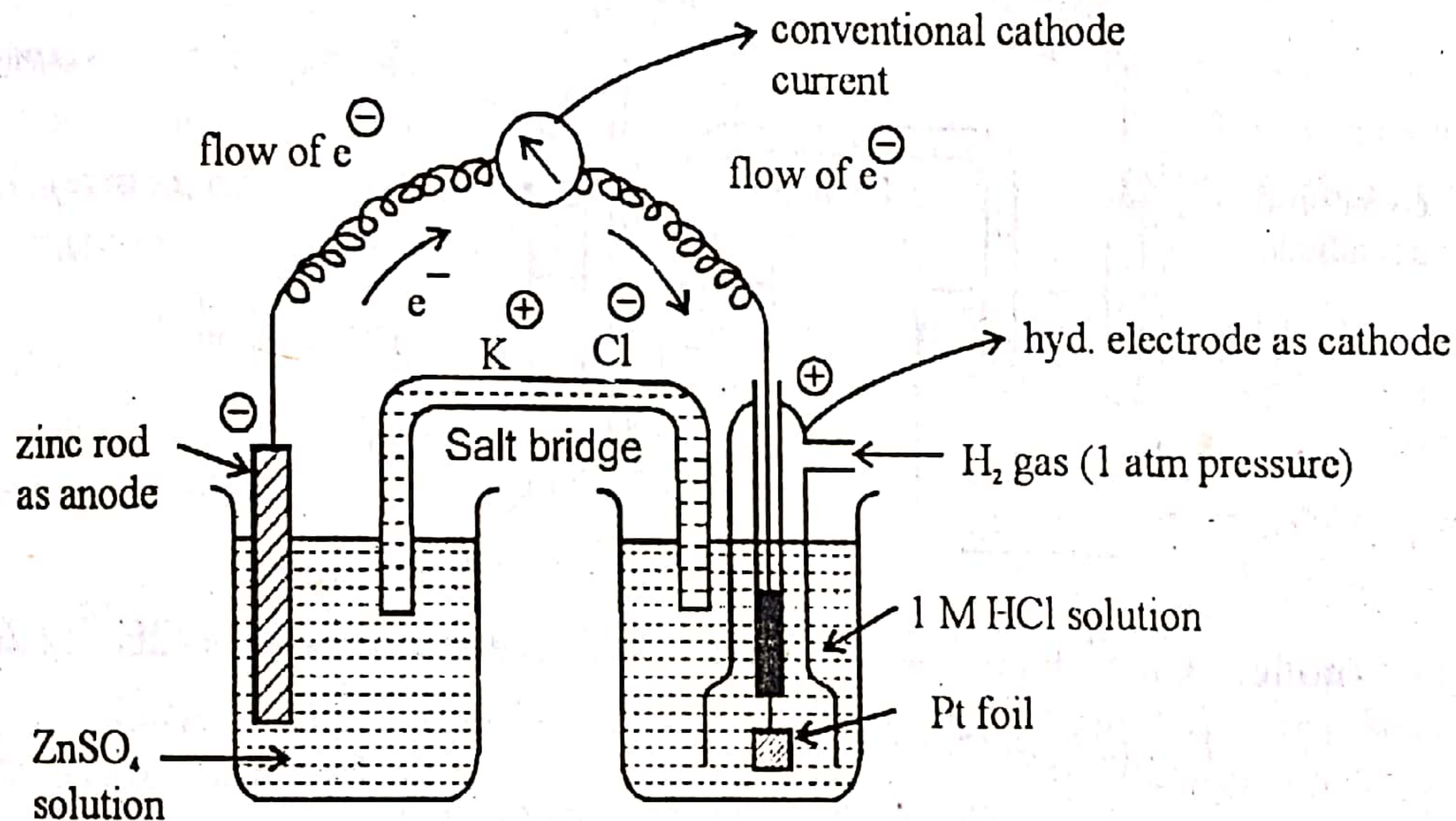
Fig. (19) Measurement of standard electrode potential of Zn / Zn^{+2} electrode using (SHE)

The net flow of electrons takes place from zinc to SHE and the EMF of the cell under standard conditions comes out to be 0.76 volts. Since the standard electrode potential of hydrogen electrode is zero. So, 0.76 volts is the standard electrode potential of zinc. It is written as,

$$Zn / Zn^{+2} \text{ (electrode)} = 0.76 \text{ V}$$

$$Zn \longrightarrow Zn^{+2} + 2e^- \text{ (anode)}$$

$$2H^\oplus + 2e^\ominus \longrightarrow H_2 \text{ (cathode)}$$
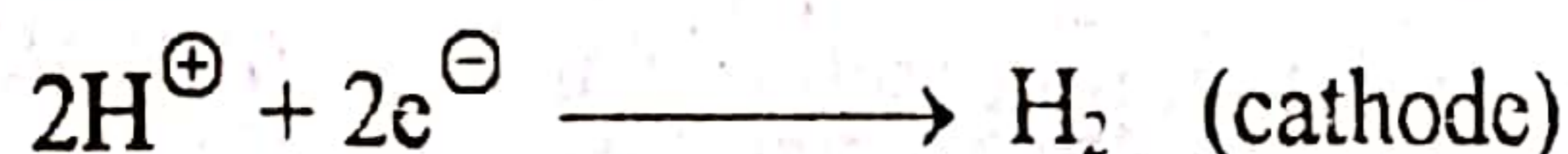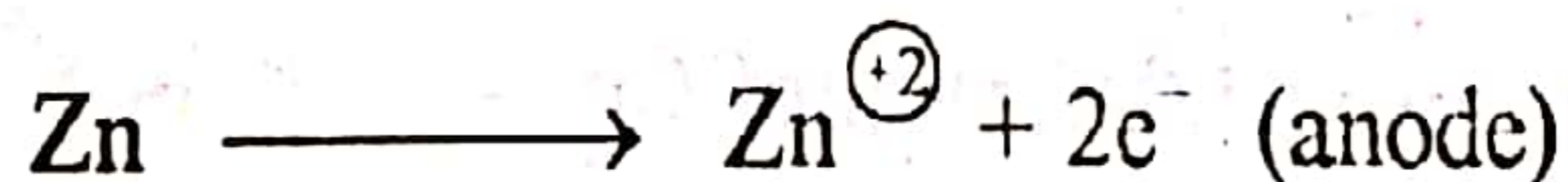
Since, the zinc has been oxidized in this arrangement, so it is called standard oxidation potential.

So, the oxidation potential of Zn / Zn^{+2} electrode = 0.76 V.

9.7.13 Determination of standard electrode potential of copper electrode:

For this measurement look at the following arrangement in which copper electrode under standard conditions is connected with SHE. SHE loses the electrons and copper ions gain the electrons. Following reaction takes place

$$H_2 \longrightarrow 2H^{\oplus} + 2e^{\ominus} \qquad \text{(anode)}$$

$$Cu^{+2} + 2ed^{\ominus} \longrightarrow Cu^{\circ} \qquad \text{(cathode)}$$
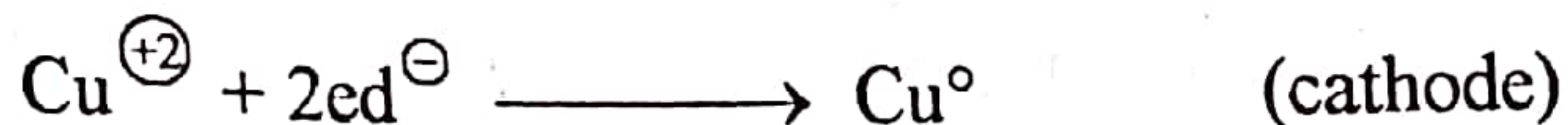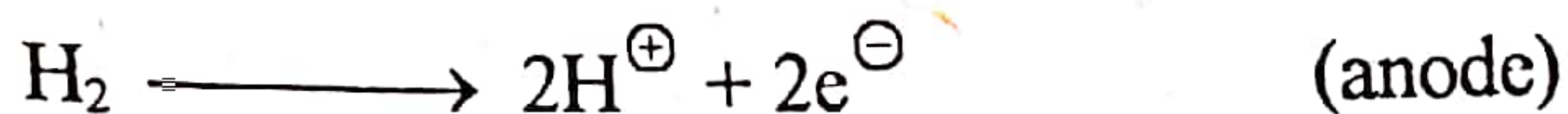
The EMF of the cell for the following arrangement (20) comes out to be 0.34 V.

anode: $Cu^{+2} + 2e^{\ominus} \longrightarrow Cu$ cathode: $H_2 \longrightarrow 2H^{\oplus} + 2e^{\ominus}$
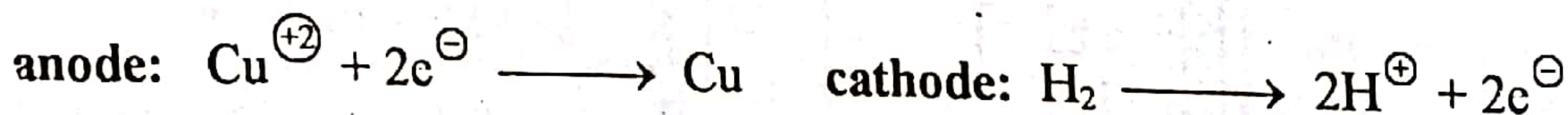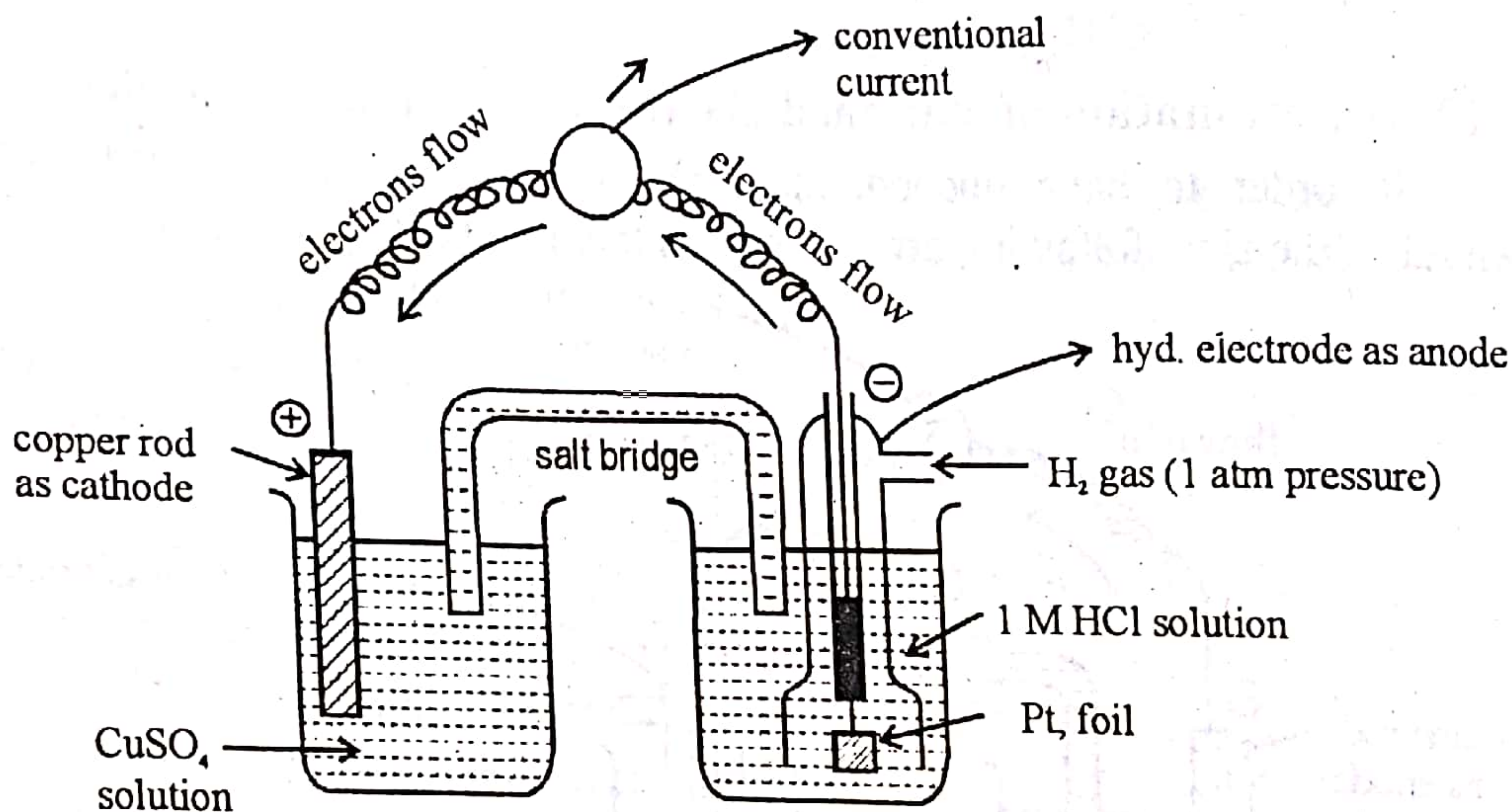
Fig. (20) *Measurement of standard electrode potential of* Cu / Cu^{+2} *electrode using (SHE)*

Since, copper ions are being reduced, so 0.34 V is called reduction potential of copper.

Reduction potential of copper electrode, $Cu^{+2}/Cu = 0.34$ V

When we change the sign of the oxidation potential of zinc, then it becomes reduction potential of zinc.

Standard oxidation potential of Zn = + 0.76 V

Standard reduction potential of Zn = − 0.76 V

Standard reduction potential of Cu = + 0.34 V

Standard oxidation potential of Cu = − 0.34 V

9.7.14 Weston standard cell:

This cell is made up of mercury, cadmium, Hg_2SO_4, and $CdSO_4$. Platinum electrode acts as inert electrode in the cell. Following diagram (21) shows the arrangements of the chemicals of this cell.
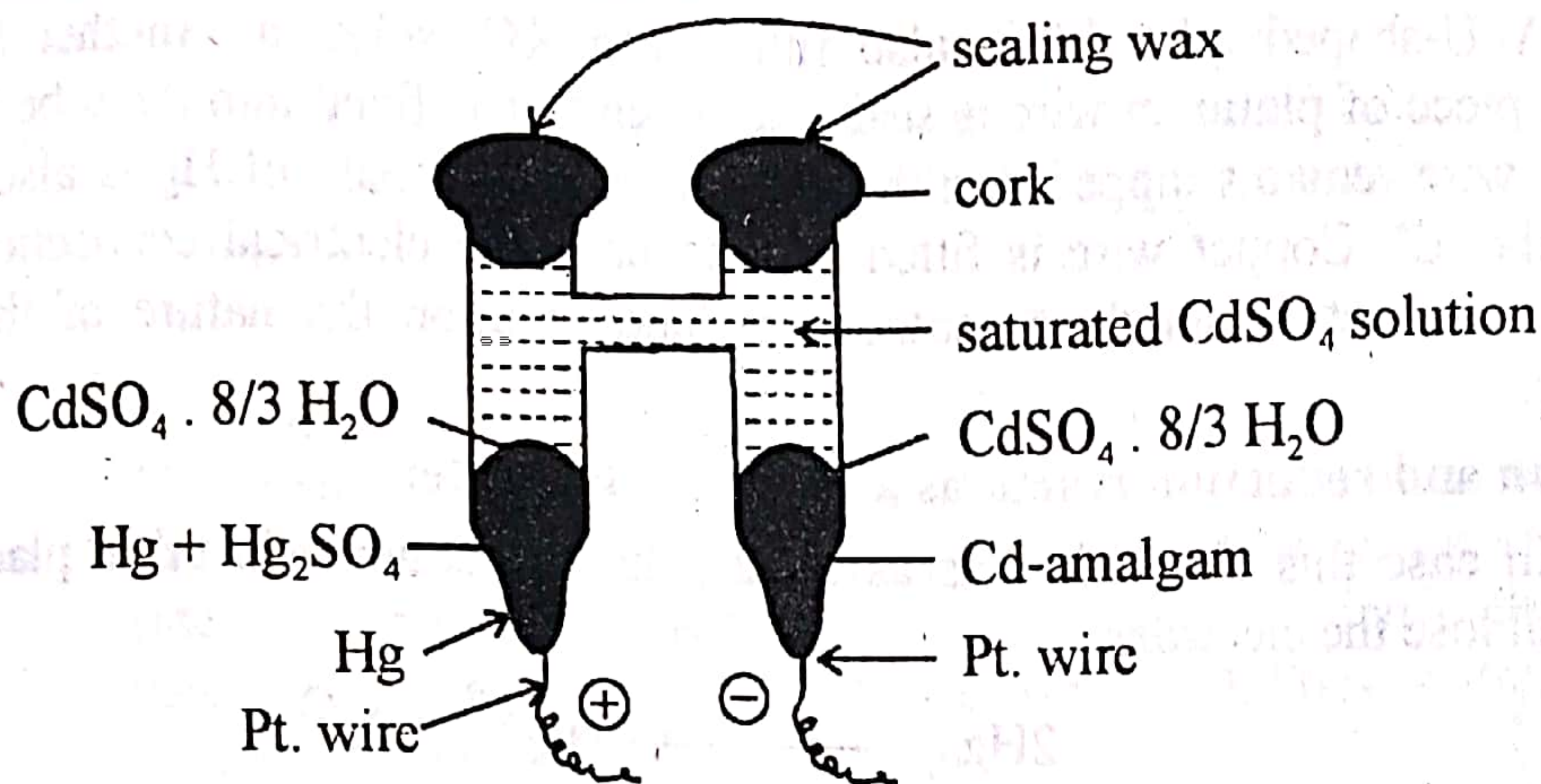

Fig. (21) Weston standard cell.

It is a H-shaped glass vessel. The positive electrode contains mercury, which is covered with a paste of Hg_2SO_4 and Hg. Crystals of $CdSO_4$ with 8/3 water molecules are also placed in the past. This solid material is covered with a solution of $CdSO_4$. The cathode contains cadmium amalgum containing 12. – 14 % of cadmium by weight. It is covered with crystals of $CdSO_4$. 8/3 H_2O and then saturated solution of $CdSO_4$. Both limbs of H-shaped tube are finally closed with corks and sealing wax. The crystal of $CdSO_4$ 8/3 H_2O make the $CdSO_4$ solution saturated every time at all temperatures.

The EMF of this cell does not change with time. The effect of temperature on the cell is very minor which means that the temperature co-efficient of EMF of the cell is very low. The EMF of this cell is 1.018 V at 15 C° and is 1.0181 V at 25°C. Following reaction takes place in the cell.

$$Cd + Hg_2SO_{4(aq)} \longrightarrow CdSO_4 . 8/3\ H_2O + 2Hg$$
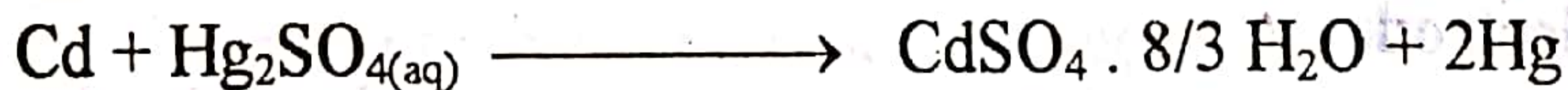
9.7.15 Calomel electrode:

This is also a reference electrode and is made up of $Hg - Hg_2 Cl_2 - KCl$. The arrangement to prepare this electrode is as shown in the diagram (22).
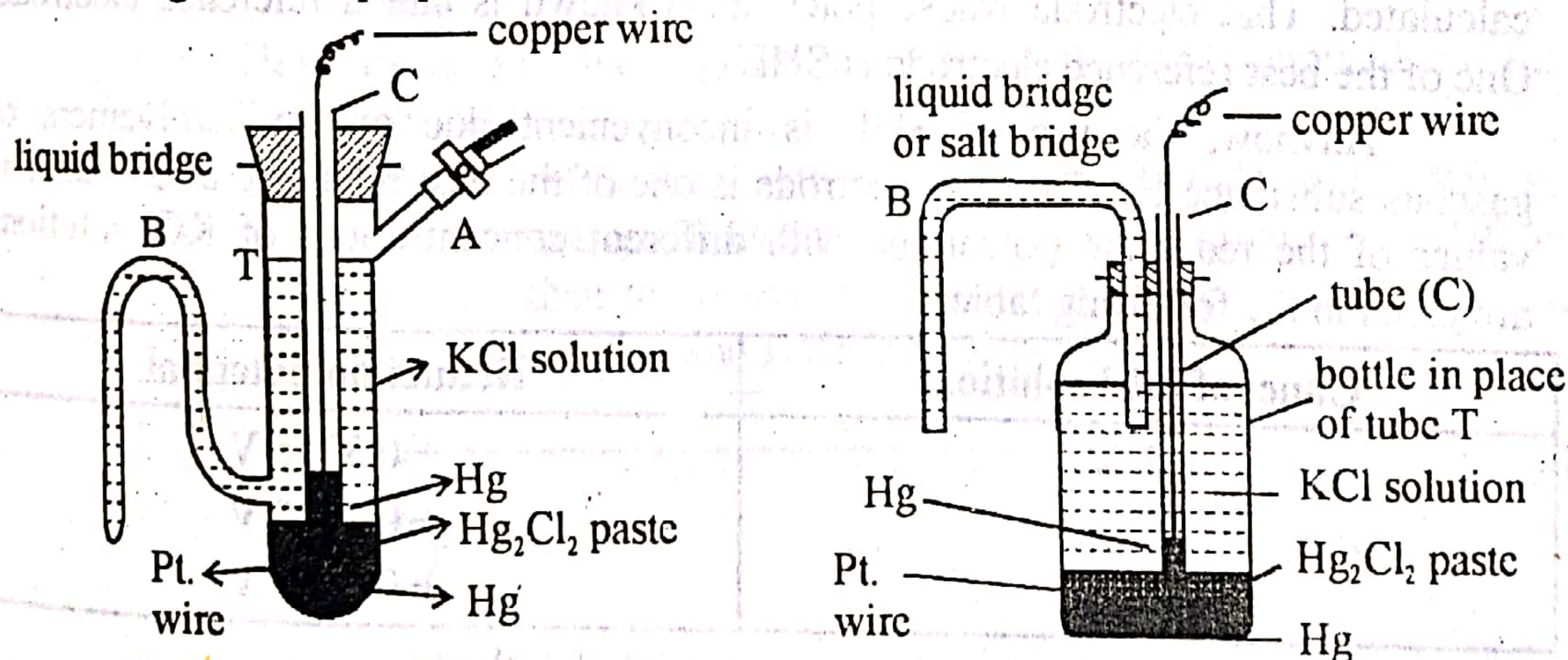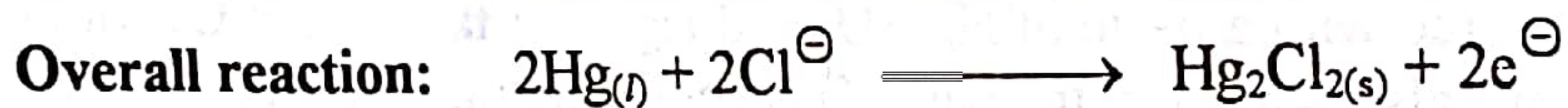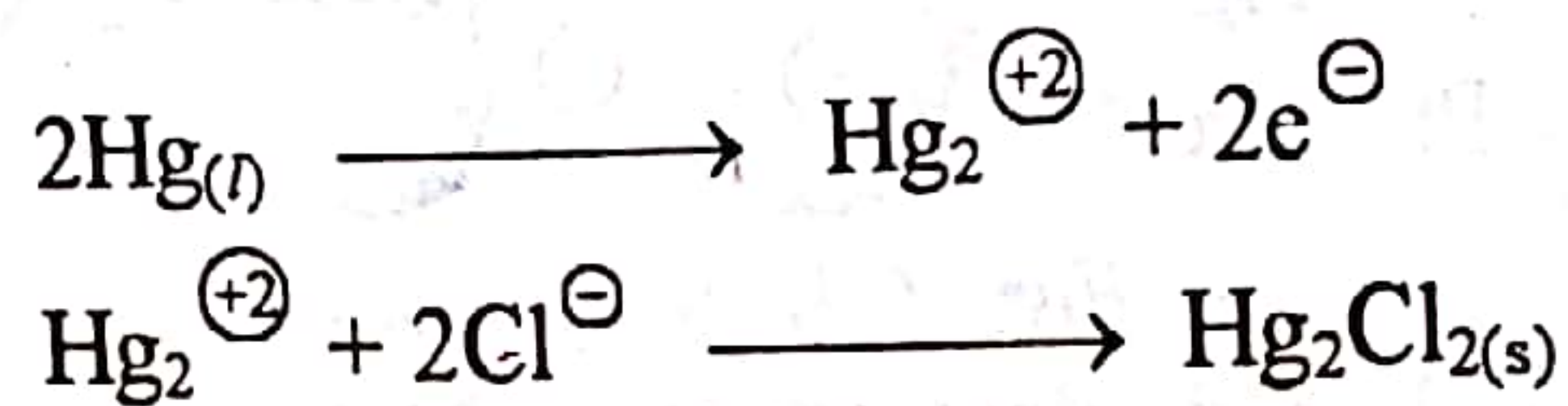

Fig. (22) Two shapes of calomel electrodes which are mostly used as reference electrodes.

The electrode is consisted of a tube having pure mercury at the bottom. This layer of Hg is covered with a paste of Hg_2Cl_2. This Hg_2Cl_2 is called calomel. Now, the rest of the tube is filled with 0.1 N or 1 N or saturated solution of KCl from the side tube.
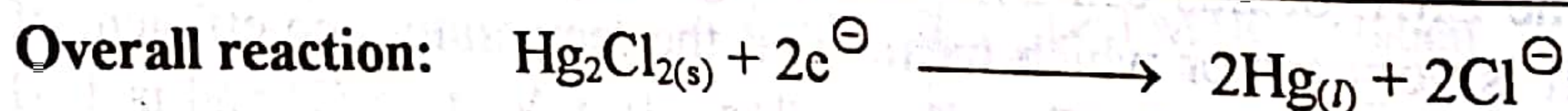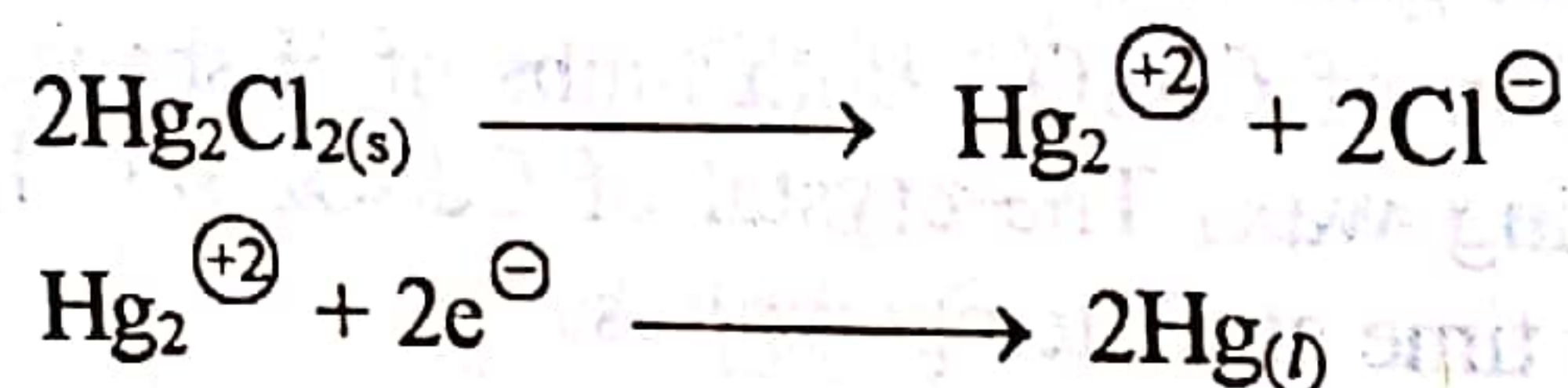
A U-shaped tube, 'B' is also filled with KCl solution, Another tube 'C' having a piece of platinum wire is sealed at its end. It is fixed into the tube 'T'. The platinum wire remains dipped into the Hg. The small amount of Hg is also placed in the tube 'C'. Copper wire is fitted to it to have the electrical connection. This electrode can act as anode or cathode depending upon the nature of the other electrode.

Oxidation and reduction reactions at calomel electrode:

In case this electrode acts as anode, then oxidation will takes place at it, and it will lose the electrons

$$2Hg_{(l)} \longrightarrow Hg_2^{\oplus 2} + 2e^{\ominus}$$

$$Hg_2^{\oplus 2} + 2Cl^{\ominus} \longrightarrow Hg_2Cl_{2(s)}$$

Overall reaction: $\quad 2Hg_{(l)} + 2Cl^{\ominus} \longrightarrow Hg_2Cl_{2(s)} + 2e^{\ominus}$

In case this electrode acts as cathode then reduction will take place and calomel electrode will gain the electrons. The reactions are as follows:

$$2Hg_2Cl_{2(s)} \longrightarrow Hg_2^{\oplus 2} + 2Cl^{\ominus}$$

$$Hg_2^{\oplus 2} + 2e^{\ominus} \longrightarrow 2Hg_{(l)}$$

Overall reaction: $\quad Hg_2Cl_{2(s)} + 2e^{\ominus} \longrightarrow 2Hg_{(l)} + 2Cl^{\ominus}$

Calomel electrode is reversible electrode with respect to the chloride ion.

Reference electrode:

The electrode potential of an electrode can be only determined, if we combine it with an electrode of known potential to make a cell. The EMF of the cell is determined and then the electrode potential of unknown electrode is calculated. That electrode whose potential is known is called reference electrode. One of the best reference electrode is SHE.

Anyhow, the use of SHE is inconvenient due to the involvement of gaseous substance H_2. Calomel electrode is one of the best reference electrode. The values of the reduction potentials, with different concentrations of KCl solutions are given in the following table.

| Conc. of KCl solution	Reduction potential
0.1 N	+ 0.3338 V
1 N	+ 0.2800 V
saturated	+ 0.2415 V

EMF of the cell = reduction potential of cathode
– reduction potential of anode
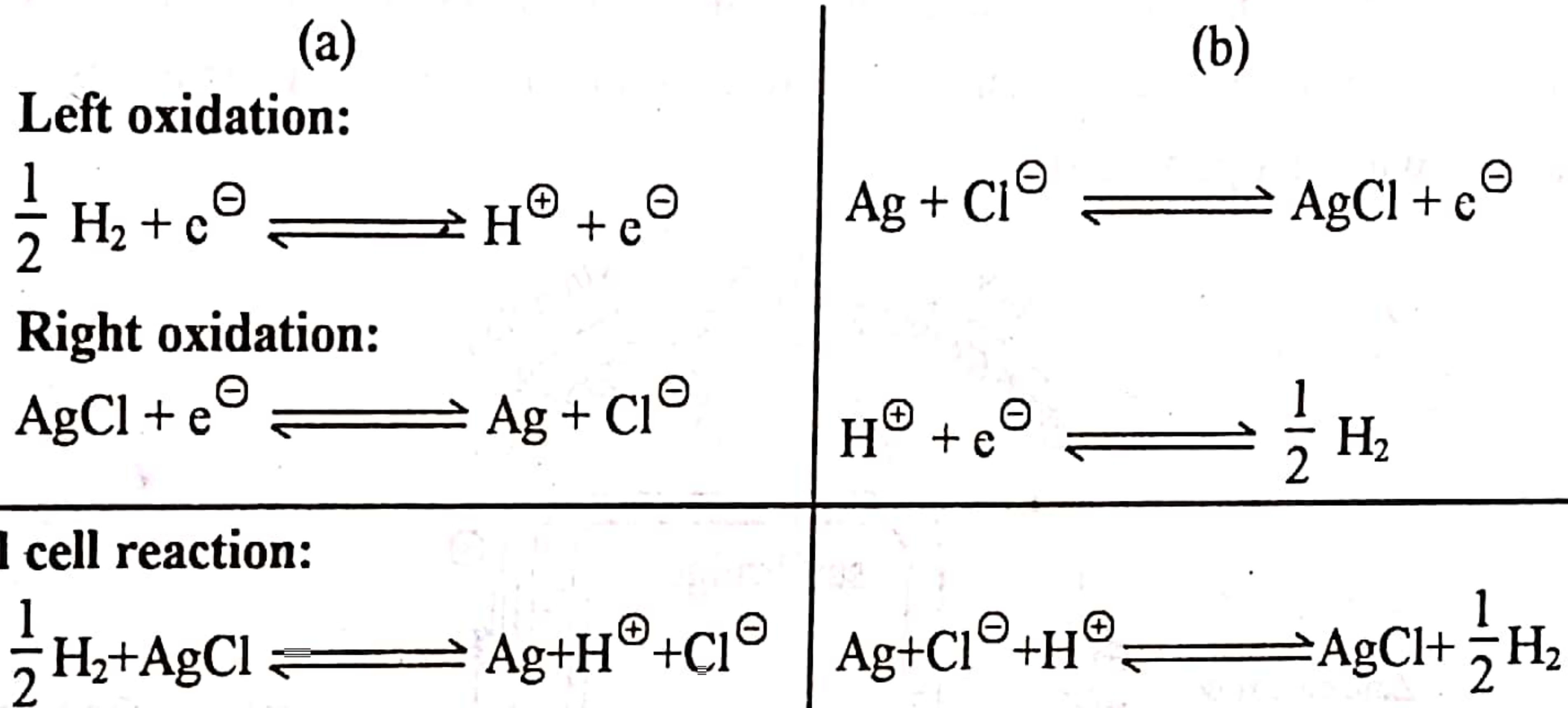
9.8.0 SIGN CONVENTIONS TO REPRESENT A CELL

We should use the accepted conventions for electrode potentials in a particular cell.

The rules are stated as follows:

(i) Arrange the two half cells, so as to form a complete cell. Suppose we are connecting SHE with Ag/AgCl electrode. This arrangement can be written in two ways:

(a) Pt / H_2 (1 atm.) HCl ($a = 1$) $\parallel AgCl / Ag$

(b) $Ag / AgCl // HCl$ ($a = 1$) $/ H_2$ (1 atm) $/ Pt$
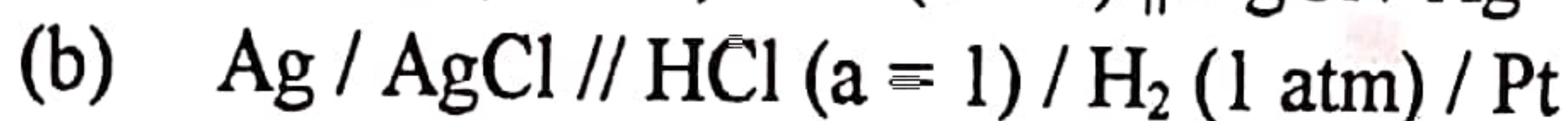
(ii) That reaction which takes place at the left electrode is arbitrarily written as an oxidation reaction and that which is on the right hand side is the reduction reaction. The overall cell reaction is the sum of these two electrode reactions. Above two possibilities is step number 1 and is written as follows:

(a)	(b)
Left oxidation:	
$\frac{1}{2} H_2 + e^{\ominus} \rightleftharpoons H^{\oplus} + e^{\ominus}$	$Ag + Cl^{\ominus} \rightleftharpoons AgCl + e^{\ominus}$
Right oxidation:	
$AgCl + e^{\ominus} \rightleftharpoons Ag + Cl^{\ominus}$	$H^{\oplus} + e^{\ominus} \rightleftharpoons \frac{1}{2} H_2$

Overall cell reaction:

$\frac{1}{2} H_2 + AgCl \rightleftharpoons Ag + H^{\oplus} + Cl^{\ominus}$	$Ag + Cl^{\ominus} + H^{\oplus} \rightleftharpoons AgCl + \frac{1}{2} H_2$

(iii) The cell voltage is the algebraic sum of both single electrode potentials, provided that the electrode potentials are fixed with a sign corresponding to the reaction at each electrode.

$$E_{cell} = E_{oxidation\ potential} + E_{reduction\ potential}$$

i.e. $E_{cell_{(a)}} = E_{H_2/H^{\oplus}} + E_{AgCl/Ag}$

$E_{cell_{(b)}} = E_{Ag/AgCl} + E_{H^{\oplus}/H_2}$

(iv) How to decide the sign convention? Try to understand in the following way:

(a) If the cell is written with the negative electrode on the left, so that the electrons flow through the external circuit from left to the right, then the reaction will be spontaneous. It will occur in the following way and EMF will be positive.
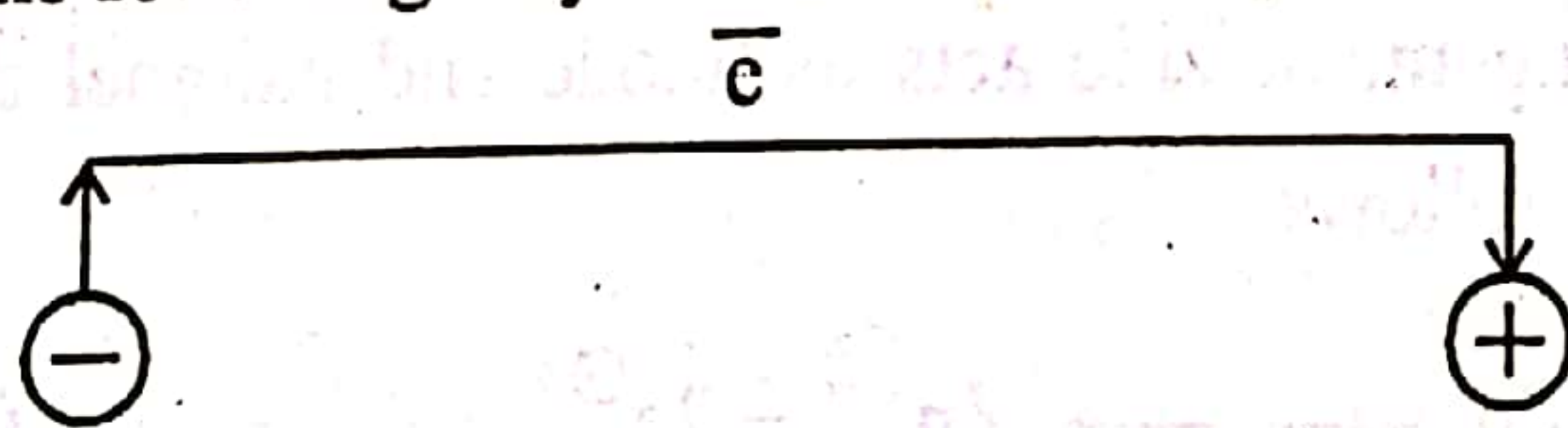
Pt / H_2 (1 atm) $/ HCl$ ($a = 1$) $/ AgCl / Ag$

Cell (a)

(b) If the cell is written down with the positive electrode on the left, then the cell EMF will be negative and the reaction is non-spontaneous. In order to obtain the spontaneous reaction, the reaction is reversed and the sign of EMF is changed without changing its magnitude.

$$\overline{e}$$

$$\oplus \quad \ominus$$

$$Ag\,/AgCl\ \ (a = 1)\,/\,H_2\ atm\,/\,Pt$$

Cell (b)
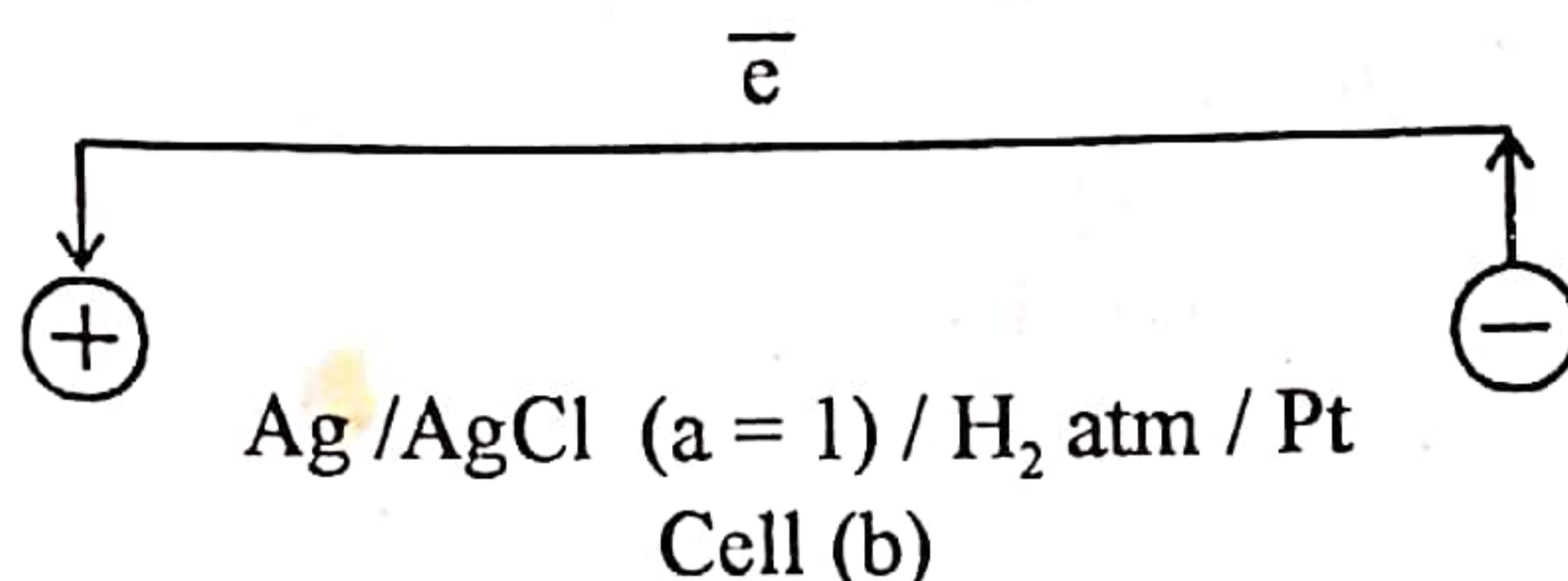
9.8.1 Determination of electrod potential of zinc using calomel electrode:

For this purpose, zinc is dipped in 1 M $ZnSO_4$ solution and is connected with calomel electrode by using 1 N KCl solution. The arrangement is shown in the following diagram (23).
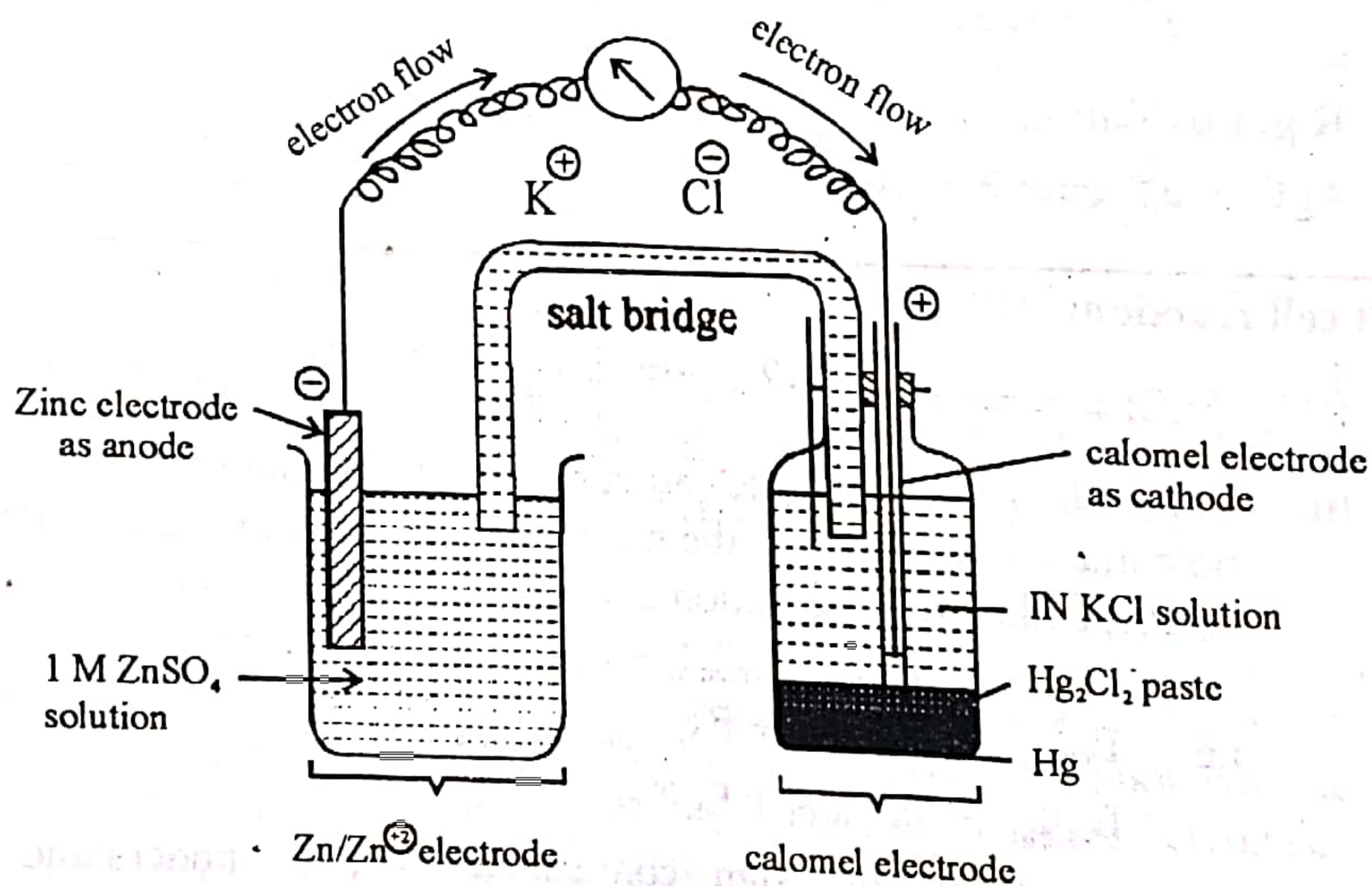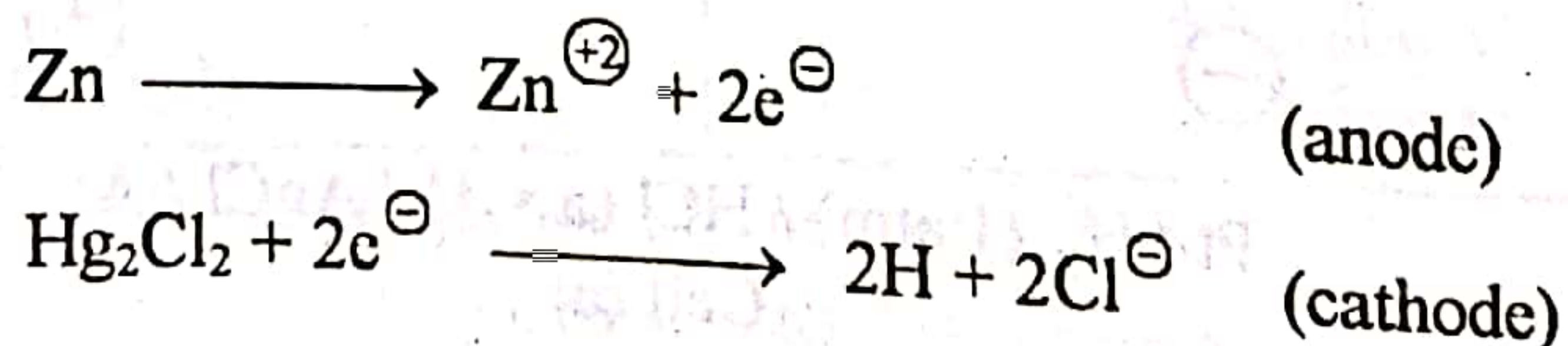

Anode: $Zn \rightleftharpoons Zn^{+2} + 2e^{\ominus}$ Cathode: $Hg_2Cl_2 + 2e^{\ominus} \longrightarrow 2Hg + Cl^{\ominus}$
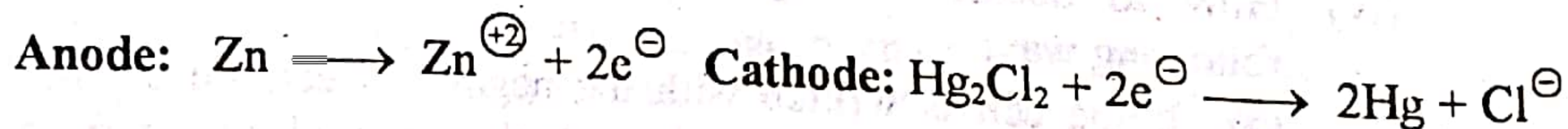
Fig. (23) Measurement of standard electrode potential of Zn/Zn^{+2} electrode using calomel electrode as the reference electrode.

In this arrangement, zinc acts as anode and calomel electrode as cathode. The reactions are as follows:

$$Zn \longrightarrow Zn^{+2} + 2e^{\ominus} \qquad \text{(anode)}$$

$$Hg_2Cl_2 + 2e^{\ominus} \longrightarrow 2H + 2Cl^{\ominus} \qquad \text{(cathode)}$$

The cell potential or the EMF of this cell at 25°C is 1.040 V.

$$\text{Cell EMF} = \text{reduction potential of calomel}$$
$$- \text{reduction potential of zinc}$$

$$1.040 \text{ V} = 0.28 \text{ V} - \text{reduction potential of Zinc}$$

Reduction potential of Zn $= 0.28$ V $- 1.040$ V $= -0.76$ V

Oxidation potential of Zn $= +0.76$ V.

Determination of electrode potential of copper using calomel electrode:

For this purpose, copper is dipped in 1 M $CuSO_4$ solution and is connected with calomel electrode by using 1 N KCl solution. This arrangement is shown in the following diagram (24).
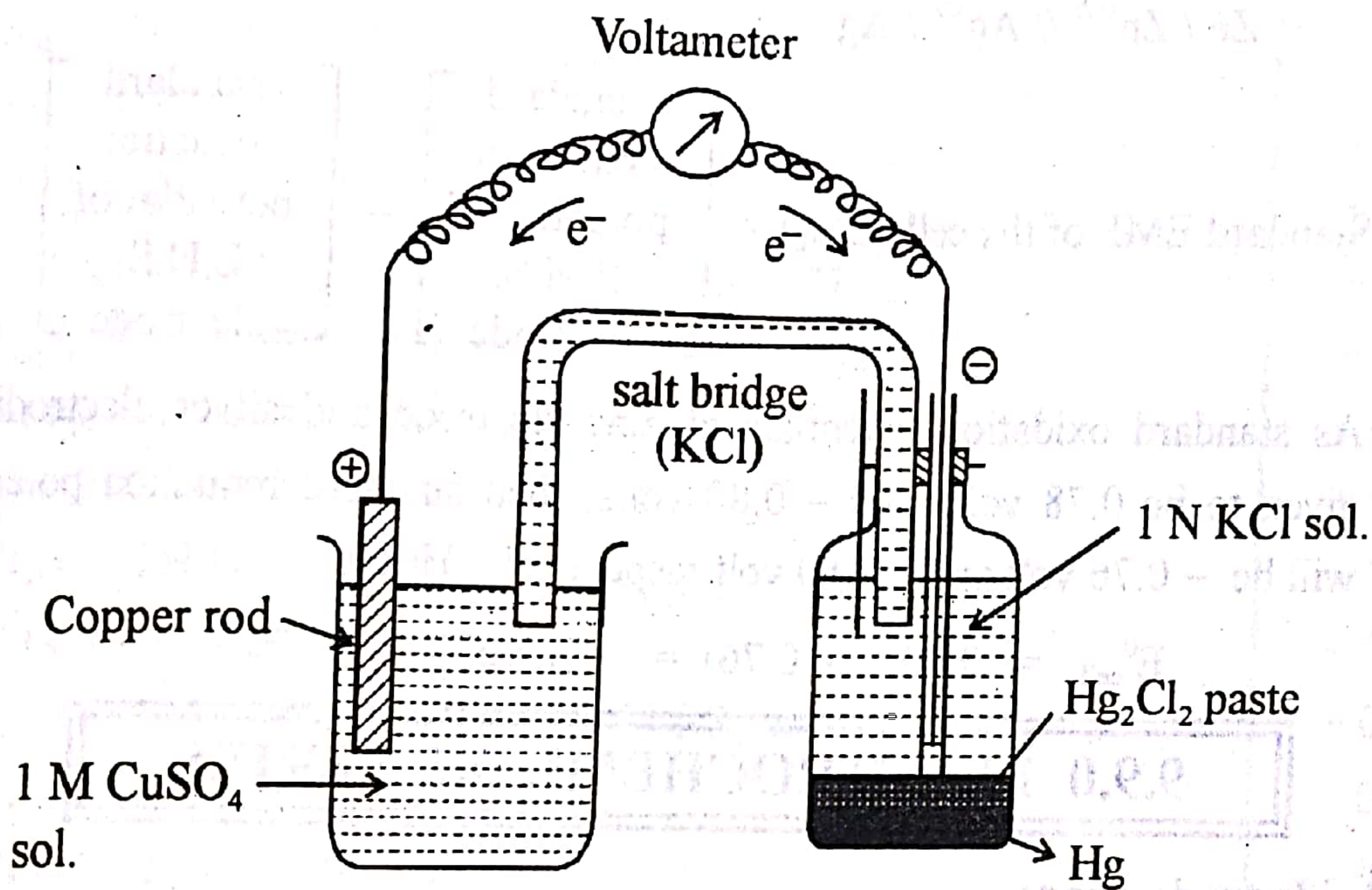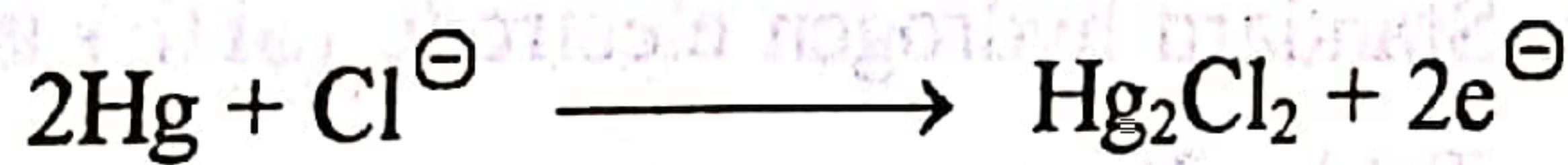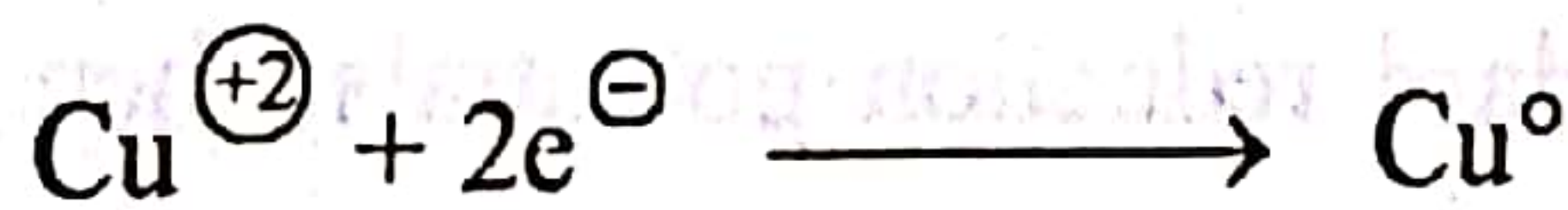

Fig. (24) *Standard electrode potential of Cu/Cu^{+2} electrode by using calomel electrode.*

In this arrangement, copper rod acts as the cathode and calomel electrode as anode. The electrode reactions are as follows:

$$Cu^{+2} + 2e^{\ominus} \longrightarrow Cu^{\circ}$$
$$2Hg + Cl^{\ominus} \longrightarrow Hg_2Cl_2 + 2e^{\ominus}$$

The EMF of this arrangement comes out to be 0.060 volts.

$$\text{EMF of cell} = \text{reduction potential of copper}$$
$$- \text{reduction potential of calomel}$$

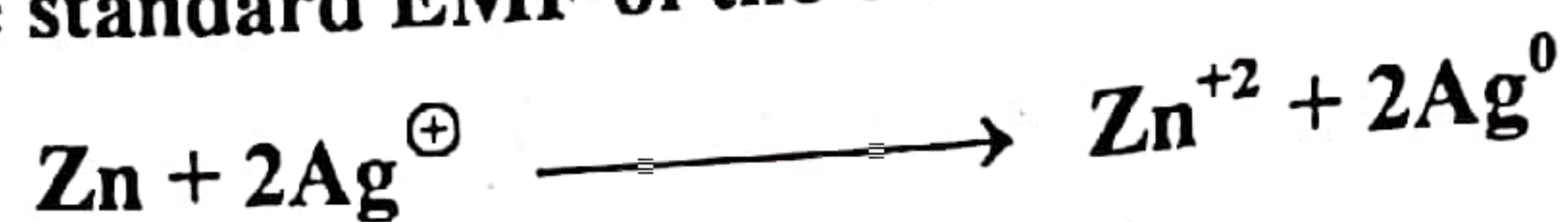$$0.060 \text{ V} = \text{reduction potential of copper} - 0.28 \text{ V}$$

$$\text{Reduction potential of copper} = 0.060 \text{ V} + 0.28 \text{ V}$$
$$= 0.34 \text{ V}$$

$$\text{Oxidation potential of copper} = -0.34 \text{ V}$$

EXAMPLE (12)

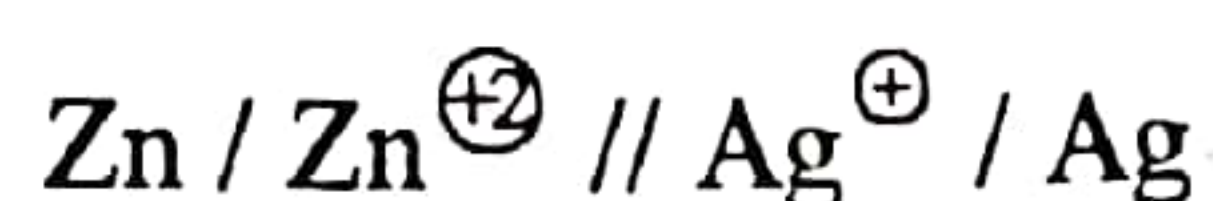Calculate the standard EMF of the cell reaction

$$Zn + 2Ag^{\oplus} \longrightarrow Zn^{+2} + 2Ag^0$$

Given that:

$$E^0_{Zn/Zn^{+2}} = 0.76 \text{ volts} \quad \text{and} \quad E^0_{Ag/Ag^{\oplus}} = -0.80 \text{ volts}$$

SOLUTION:

Oxidation takes place at the zinc electrode and reduction at silver electrode. By convention the cell may be represented as

$$Zn / Zn^{\oplus 2} // Ag^{\oplus} / Ag$$

$$\text{Standard EMF of the cell } (E^0_{cell}) = \begin{bmatrix} \text{standard} \\ \text{reduction} \\ \text{potential of} \\ \text{R.H.S.} \\ \text{electrode} \end{bmatrix} - \begin{bmatrix} \text{standard} \\ \text{reduction} \\ \text{potential of} \\ \text{L.H.S.} \\ \text{electrode} \end{bmatrix}$$

As standard oxidation potentials of zinc electrode and silver electrode are given to be 0.78 volts and − 0.80 volts, then standard reduction potentials will be − 0.76 volt and + 0.80 volt respectively. Hence

$$E^0_{cell} = 0.80 - (-0.76) = 1.56 \text{ volts}$$

9.9.0 ELECTROCHEMICAL SERIES

9.9.1 Introduction:

The electrode potentials of various electrodes are arranged in a definite order. They should be arranged by keeping in view the reduction potentials or oxidation potentials. If the various electrodes are arranged in the order of their increasing values of standard reduction potentials, then this arrangement is called electrochemical series. Standard hydrogen electrode (SHE) is almost somewhere in the middle of the series Table (2).

According to the following table (2), lithium electrode is at the top with a standard reduction potential of − 3.05 volts. Fluorine electrode is at the bottom having a maximum positive oxidation potential among the whole series. The electrodes above SHE have negative reduction potentials and positive oxidation potentials. The electrodes below SHE have positive reduction potentials and negative oxidation potentials.

Table: (2) Standard reduction potentials at 25 C°. (Electrochemical series)
Standard reduction potentials in aqueous solution

| Half Reaction	E° (V)
$F_2(g) + 2e^- \rightleftharpoons 2F^-(aq)$	+ 2.87
$PbO_2(s) + SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \rightleftharpoons PbSO_4(s) + 2H_2O$	+ 1.69
$2HOCl(aq) + 2H^+(aq) + 2e^- \rightleftharpoons Cl_2(g) + 2H_2O$	+ 1.63
$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightleftharpoons Mn^{2+}(aq) + 4H_2O$	+ 1.49
$PbO_2(s) + 4H(a) + 2e^- \rightleftharpoons Pb^{2+}(aq) + 2H_2O$	+ 1.46
$BrO_3^-(aq) + 6H^+(aq) + 6e^- \rightleftharpoons Br^-(aq) + 3H_2O$	+ 1.44
$Au^{3+}(aq) + 3e^- \rightleftharpoons Au(s)$	+ 1.42
$Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-(aq)$	+ 1.36
$O_2(g) + 4H^+(aq) + 4e^- \rightleftharpoons 2H_2O$	+ 1.23
$Br_2(aq) + 2e^- \rightleftharpoons 2Br^-(aq)$	+ 1.07
$NO_3^-(aq) + 4H^+(aq) + 3e^- \rightleftharpoons NO(g) + 2H_2O$	+ 0.96
$Ag^+(aq) + e^- \rightleftharpoons Ag(s)$	+ 0.80
$Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq)$	+ 0.77
$I_2(s) + 2e^- \rightleftharpoons 2I^-(aq)$	+ 0.54
$NiO_2(s) + 2H_2O + 2e^- \rightleftharpoons Ni(OH)_2(s) + 2OH^-(aq)$	+ 0.49
$Cu^{2+}(aq) + 2i^- \rightleftharpoons Cu(s)$	+ 0.34
$SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \rightleftharpoons H_2SO_3(aq) + H_2O$	+ 0.17
$2H^+(aq) + 2e^- \rightleftharpoons H_2(g)$	0.00
$Sn^{2+}(aq) + 2e^- \rightleftharpoons Sn(s)$	− 0.14
$Ni^{2+}(aq) + 2e^- \rightleftharpoons Ni(s)$	− 0.25
$Co^{2+}(aq) + 2e^- \rightleftharpoons Co(s)$	− 0.28
$PbSO_4(s) + 2e^- \rightleftharpoons Pb(s) + SO_4^{2-}(aq)$	− 0.36
$Cd^{2+}(aq) + 2e^- \rightleftharpoons Cd(s)$	− 0.40
$Fe^{2+}(aq) + 2e^- \rightleftharpoons Fe(s)$	− 0.44
$Cr^{3+}(aq) + 3e^- \rightleftharpoons Cr(s)$	− 0.74
$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)$	− 0.76
$2H_2O + 2e^- \rightleftharpoons H_2(g) + 2OH^-(aq)$	− 0.83
$Al^{3+}(aq) + 3e^- \rightleftharpoons Al(s)$	− 1.66
$Mg^{2+}(aq) + 2e^- \rightleftharpoons (Mg(s)$	− 2.37
$Na^+(aq) + e^- \rightleftharpoons Na(S)$	− 2.71
$Ca^{2+}(aq) + 2e^- \rightleftharpoons Ca(s)$	− 2.76
$K^+(aq) + e^- \rightleftharpoons K(s)$	− 2.92
$Li^+(aq) + e^- \rightleftharpoons Li(s)$	− 3.05

9.9.2   Salient features of electrochemical series:

Following are some salient features of electrochemical series:

(i)   The electrodes are arranged in the deceasing order of reduction potentials and they are all written in the reduction mode.

(ii)   All the electrodes above SHE can accept the electrons from SHE, creating the cell voltage equal to the standard electrode potential given in the series.

(iii)   All the electrodes below SHE, when connected with SHE create the cell voltage equal to the reduction potential written in the series.

(iv)   When an electrode is connected to SHE and that electrode gives the electrons to SHE, then electrode acts as anode and SHE acts as cathode. So, $H^{\oplus}$ ions are reduced in SHE.

(v)   When an electrode is connected with SHE and it accepts the electron from SHE, then that electrode acts as a cathode, and SHE as anode. Hydrogen gas is converted to hydrogen ions. Whenever, two electrodes are connected with each other, then the electrons flow from lower to the higher, and the EMF of the cell is determined from the electrode potentials of the two.

(vi)   If both the electrodes are above SHE then current flows from lower to the higher with the difference of the two.

(vii)   When both electrodes are below SHE then electrons flow from lower to the higher with the difference of the two.

(viii)   If an electrode is above SHE and the other is below that of SHE in electrochemical series, then current flows from lower to the higher with the sum of the two standard reduction potentials.

9.9.3   Applications of electrochemical series:

(1)   We can predict the relative ease of oxidation or reduction of various elements. Greater the reduction potential, more easily is the substance reduced. F_2 has the highest reduction potential while $Li^{\oplus}$ has the lowest reduction potential.

It means that fluorine is reduced more easily, whereas $Li^{\oplus}$ ion are reduced with greater difficult.

$$F^{\oplus} + 1e^- \longrightarrow F^- \text{ (very easy)}, \quad Li^+ + 1e^- \longrightarrow Li^{\ominus} \text{ (very difficult)}$$
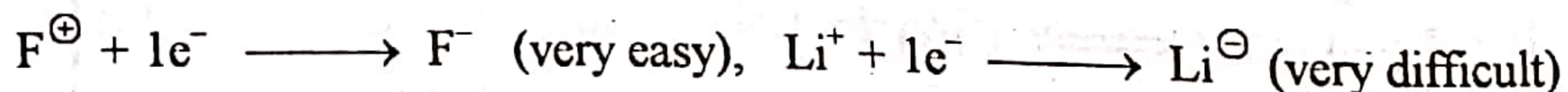
(2)   From the values of standard reduction potentials, we can choose the strongest oxidizing agents and the weakest oxidizing agents. F_2 is the strongest oxidizing agent while $Li^{\oplus}$ is the weakest oxidizing agent.

(3)   From the electrochemical series, we can predict, whether a metal reacts with an acid to give hydrogen gas or not. According to electrochemical series the metal having negative reduction potential which are above SHE can displace hydrogen from acids, because $H^{\oplus}$ ions have to get the electrons from them. So the metal like Li, K, Na, Al, Zn etc. can displace $H^{\oplus}$ from acid. But Ag, Cu and Au cannot do so.

(4) We can calculate the standard EMF of any electrochemical cell. Actually, electrochemical cell is based on redox reaction which can be split into two half reactions.

    (i)   Oxidation half reaction

    (ii) Reduction half reaction

When we represent a cell, then the electrodes on which oxidation takes place is written on the L.H.S. and the other is written on the R.H.S.

(5) We can predict the spontaneity of reaction. If we want to find out, whether a reaction is feasible or not, then the EMF of the cell which is based upon the given redox reaction is calculated. If the EMF comes out to be positive, then the reaction is feasible and if it comes out to be negative, then reaction is not feasible.

9.9.4 Relationship between electrical energy and chemical energy:

When a cell produces a current, then the current can be used to do the work. The principles of thermodynamics can be employed to derive a relationship between electrical energy and the maximum amount of the work which is obtained from the cell.

It was observed that for a large number of reactions, the electrical energy produced was not equal to the chemical energy. It was suggested by Gibbs in 1875 and Helmohltz in 1882, that the electrical energy produced in the reversible cell is equal to the decrease of free energy accompanying the cell reaction.

The electrical energy produced in a cell is the product of quantity of electricity that passes through the cell and the EMF of the cell.

$$\text{Electrical energy} = \text{Quantity of electricity} \times \text{EMF} \quad \cdots\cdots \text{ (1)}$$

From Faraday's law of the electrolysis, we know that for every one mole of the electrons transferred in the cell reaction, the quantity of electricity that flows through the cell is one Faraday (1F = 96,500 C). So, if 'n' moles of electrons are transferred in any cell reaction, then the quantity of the electricity passing through the cell is nF Faradays.

If E is the EMF of the cell, then

$$\text{Electrical energy} = nFE \quad \cdots\cdots \text{ (2)}$$

If ΔG represents the change in the free energy and that is the useful work done by the system. Then,

$$-\Delta G = nEF \quad \cdots\cdots \text{ (3)}$$

A well known equation from thermodynamics is Gibb's-Helmohltz equation.

$$\Delta G = \Delta H + T\left[\frac{\partial(\Delta G)}{\partial T}\right]_P \quad \cdots\cdots \text{ (4)}$$

Putting the value of ΔG from the equation (3) into equation (4), we get

$$- nEF = \Delta H + T\left[\frac{\partial(-nEF)}{\partial T}\right]_p$$

$$nEF = -\Delta H + nFT\left[\frac{\partial E}{\partial T}\right]_p \qquad \cdots\cdots (5)$$

Because E is variable while 'n' and 'F' are constants.

According to the equation (5), it is clear that the enthalpy change ΔH or the chemical energy of the reaction depend upon the temperature co-efficient of EMF i.e. $\frac{\partial E}{\partial T}$. Temperature co-efficient is the rate of change of e.m.f. of the cell with respect to temperature. So, we can draw the following important conclusions.

Dividing by equation (5) by nF

$$E = -\frac{\Delta H}{nF} + T\left[\frac{\partial E}{\partial T}\right]_p \qquad \cdots\cdots (6)$$

Conclusions:

(i)   When $\frac{\partial E}{\partial T}$ is extremely small, i.e. very close to zero then the electrical energy nEF is equal to the enthalpy change.

(ii) When $\frac{\partial E}{\partial T}$ is positive, then the electrical energy produced is greater than the heat of reaction at constant pressure. It means that the additional energy is being absorbed from the surroundings.

(iii) When $\frac{\partial E}{\partial T}$ is negative then the electrical energy produced is less than the heat of reaction and the additional energy is being absorbed by the surroundings.

Meaning of $\frac{\partial E}{\partial T}$:

This is the rate of change of EMF of the cell with respect to temperature. If the change of temperature does not effect 'E' then $\frac{\partial E}{\partial T}$ is zero. If the increase of temperature increases E, then $\frac{\partial E}{\partial T}$ is positive. If increase of temperature decreases E then $\frac{\partial E}{\partial T}$ is negative.

9.9.5   Relationships of ΔG, ΔH and ΔS with EMF of the cell:

As we has discussed above, that

$$\Delta G = -nEF \qquad \cdots\cdots (7)$$

We have derived equation (5), as

$$nEF = -\Delta H + nFT\left[\frac{\partial E}{\partial T}\right]_p$$

After rearrangement, this equation becomes,

$$\Delta H = nF\left[T\cdot\left(\frac{\partial E}{\partial T}\right)_p - E\right] \quad \cdots\cdots (8)$$

According to the equation (8), if we know the temperature, the EMF of the cell and $\frac{\partial E}{\partial T}$ of the system, then we can calculate ΔH.

From the above equation when we have calculated ΔG, from equation (7) and ΔH from equation (8), the ΔS can be calculated from the following relationship.

$$\Delta G - \Delta H = -T\Delta S \quad \cdots\cdots (9)$$

Gibbs-Helmohltz equation say that

$$\therefore \quad \Delta G - \Delta H = T\left[\frac{\partial(\Delta G)}{\partial T}\right]_p \quad \cdots\cdots (4)$$

Now compare equation (4) and (9)

$$\text{So} \quad -T\Delta S = T\left[\frac{\partial(\Delta G)}{\partial T}\right]$$

$$\therefore \quad \Delta G = -nEF$$

$$-T\Delta S = -nFT\left[\frac{\partial E}{\partial T}\right]_p$$

$$\Delta S = nF\left[\frac{\partial E}{\partial T}\right]_p \quad \cdots\cdots (10)$$

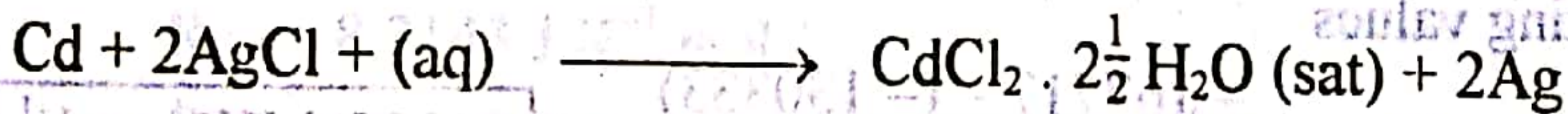So, the entropy change of the reaction is zero, when the temperature co-efficient of the cell is zero.

EXAMPLE (13)

The emf of the cell $Cd/CdCl_2 \cdot 2\frac{1}{2} H_2O$ (saturated) $// AgCl_{(s)} / Ag$ is found to be 0.6753 volts at 25°C and 0.6915 volt at 0°C. Calculate ΔG, ΔH and ΔS of the cell reaction at 25°C.

Solution:

Data:

The cell reaction is as follows:

$$Cd + 2AgCl + (aq) \longrightarrow CdCl_2 \cdot 2\frac{1}{2} H_2O \text{ (sat)} + 2Ag$$

or

$$Cd + 2Ag^{\oplus} \longrightarrow Cd^{+2} + 2Ag^0$$
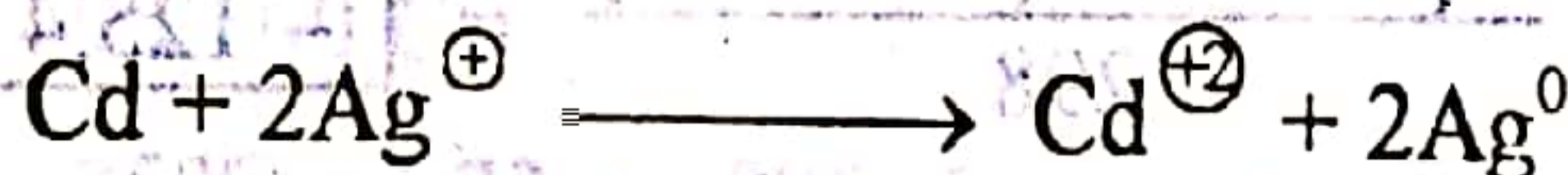
Two electron are being lost for one Cd atom, so n = 2.

(i) Calculation of free energy change (ΔG)

$E = 0.6753$ V

$F = 69500$ C

$n = 2$

Formula:

$$\Delta G = -nFE$$

Putting values

$$\Delta G = -2 \times 96500 \times 0.6753$$
$$= -130333 \text{ joules mol}^{-1}$$
$$\Delta G = \boxed{-130.33 \text{ kJ mol}^{-1}} \qquad \text{Ans.}$$

(ii)   Calculation of enthalpy change (ΔH)

Data:

At atmospheric pressure, the temperature coefficient of EMF in the range of $0° - 25°C$ will be

$$T_1 = 0°C + 273 = 273 \text{ K}$$
$$T_2 = 25°C + 273 = 298 \text{ K}$$

Putting values

$$\left(\frac{\partial E}{\partial T}\right) = \frac{E_2 - E_1}{T_2 - T_1} = \frac{0.695 - 0.6753}{273 - 298}$$
$$= \frac{0.0162}{25} = -0.00065 \text{ volts K}^{-1}$$

Formula:

Now using the relationship

$$E = \frac{\Delta H}{nF} + T\left[\frac{\partial E}{\partial T}\right]$$

$$\Delta H = -nFE + nTF\left(\frac{\partial E}{\partial T}\right)_p$$

Putting values

$$\Delta H = -2 \times 96500 \times 0.6753 \times 2 \times 298 \times 96500 \times (-0.00065)$$
$$\Delta H = -167717 \text{ joules mol}^{-1}$$
$$\Delta H = \boxed{-167.72 \text{ kJ mol}^{-1}} \qquad \text{Ans.}$$

(iii)   Calculation of entropy change (ΔS)

Formula:

$$\Delta S = \Delta H - T\Delta S$$
$$\Delta S = \frac{\Delta H - \Delta G}{T}$$

Putting values

$$\Delta S = \frac{-167717 - (-130333)}{298} = \boxed{-125.4 \text{ JK}^{-1} \text{mol}^{-1}} \qquad \text{Ans.}$$

The negative signs with ΔG, ΔH and ΔS indicates the decrease in these quantities.

9.10.0 NERNST EQUATION

Nernst equation is the quantitative relationship between EMF of the cell with the concentrations of reactants and products of the cell reaction at a given temperature.

In order to derive this equation, let us take the hypothetical cell reaction which is happening in any reversible cell.

$$aA + bB \rightleftharpoons cC + dD$$
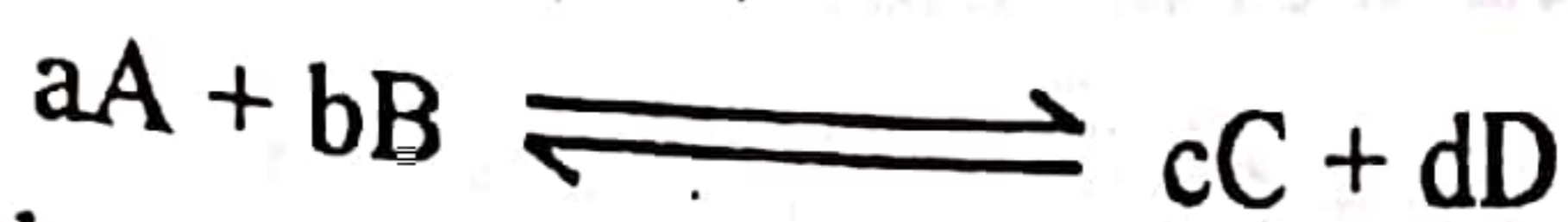
The free energy change of this reaction is given by the equation

$$\Delta G = \Delta G^\circ + RT \ln \frac{a_C^c \cdot a_D^d}{a_A^a \cdot a_B^b} \qquad \cdots\cdots (1)$$

ΔG = Free energy change

ΔG° = Standard free energy change

a_A, a_B, a_C, a_D = Activities in any state other than the standard state

Since, $-\Delta G = nEF$

and $-\Delta G^\circ = nE^\circ F$

E = EMF of the cell at any condition

E° = EMF of the cell under standard condition

Putting these expressions in equation (1)

$$-nEF = -nE^\circ F + RT \ln \frac{a_C^c \cdot a_D^d}{a_A^a \cdot a_B^b}$$

Dividing this equation with nF and rearranging the negative sign.

$$E = E^\circ - \frac{RT}{nF} \ln \frac{a_C^c \cdot a_D^d}{a_A^a \cdot a_B^b} \qquad \cdots\cdots (2)$$

If we know the cell reaction and the standard EMF as E°, then E can be calculated, by knowing the activities of the substances at a given temperature. This equation (2) is called Nernst equation for the calculations of EMF of the cell.

9.10.1 Nernst equation at low concentrations:

When the concentrations are not very high, then we can replace the activities in equation (2) by concentrations in moles. dm^{-3}. So [ ] will be used and Nernst equation can be written as

$$E = E^\circ - \frac{RT}{nF} \ln \frac{[C]^c [D]^d}{[A]^a [B]^b} \qquad \cdots\cdots (3)$$

Suppose the cell is working at 25°C, then

$R = 8.3143 \text{ J K}^{-1} \text{ mol}^{-1}$

$F = 96,500 \text{ C}$

$T = 25°C + 273 = 298 \text{ K}$
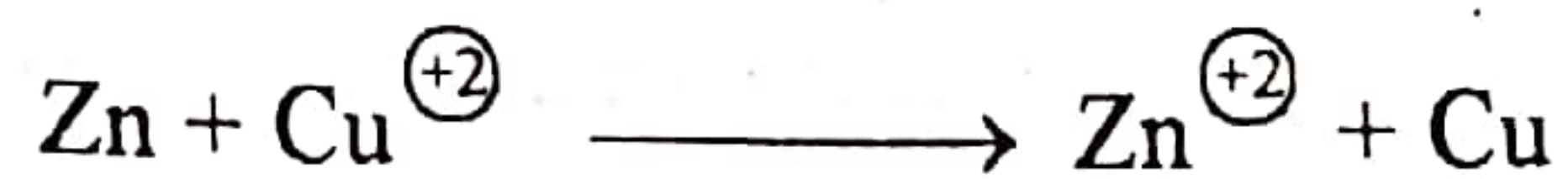
n = depends upon the nature of the reaction

Putting these values in equation (3)

$$E = E^\circ - \frac{8.3143 \times 298}{n \times 96500} \ln \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

$$E = E^\circ - \frac{0.0591}{n} \ln \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

9.10.2 Nernst equation and the Daniell cell:

The overall reaction of the Danicl cell is

$$Zn + Cu^{+2} \longrightarrow Zn^{+2} + Cu$$

$n = 2$ (because two electrons are being lost or gained for one atom of Zn)

Let us apply equation (2),

$$E = E° - \frac{RT}{2F} \ln \frac{a_{Zn^{+2}} \cdot a_{Cu}}{a_{Zn} \cdot a_{Cu^{+2}}} \qquad \ldots\ldots (4)$$

The activities of the solid substances are taken as unity

$$a_{Zn} = a_{Cu} = 1$$

$$E = E° - \frac{RT}{2F} \cdot \ln \frac{a_{Zn^{+2}}}{a_{Cu^{+2}}} \qquad \ldots\ldots (5)$$

If we substitute the activities by the concentrations in the case of dilute solutions

$$E = E°' - \frac{RT}{2F} \ln \cdot \frac{[Zn^{+2}]}{[Cu^{+2}]} \qquad \ldots\ldots (6)$$

Putting the value of R, T and F at 25°C, and converting the natural log into common log, the Nernst equation for the Daniel cell is

$$E = E° - 0.0295 \log \frac{[Zn^{+2}]}{[Cu^{+2}]} \qquad \ldots\ldots (7)$$

With the help of equation (7), we can calculate the EMF of the cell at 25°C at any concentration of Zn^{+2} and Cu^{+2}.

EXAMPLE (14)

Calculate the EMF of a zinc-silver cell at 25°C, the activity of Zn^{+2} ions is 0.8 and the activity of Ag^{+} ion is 10. Standard reduction potentials at 30°C are:

(i) Ag^{+} Ag electrode = + 0.799 volts

(ii) Zn^{+2} Zn electrode = – 0.76 volts.

SOLUTION:

Data:

The reduction potential of silver (0.799 v) is greater than that of zinc (– 0.760 v). This means that in the cell reaction, reduction take place at the silver electrode and oxidation at the Zn electrode. Hence the cell reaction will be

$$Zn + 2Ag^{+} \longrightarrow Zn^{+2} + 2Ag°$$
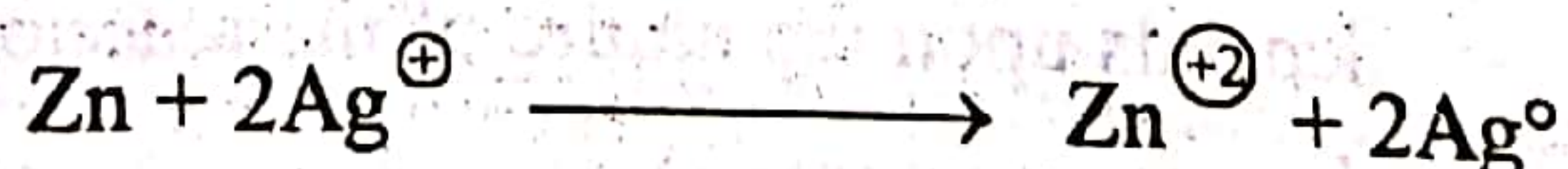
One atom of the Zn loses 2 electrons, so n = 2

The cell may be represented by convention, as

$$Zn / Zn^{+2} \ (a = 0.8) \ // \ Ag^{+} \ (a = 10) \ / \ Ag$$
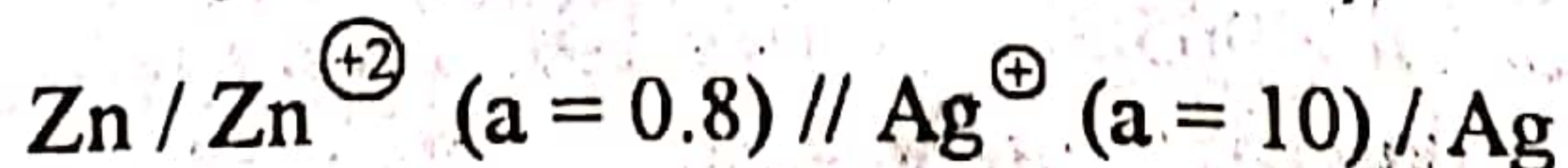
$$T = 25°C + 273 = 298 \ K$$

Standard EMF of the cell; $E^0 = E^0_{Ag^{\oplus}/Ag} - E^0_{Zn^{+2}/Zn}$

$E^0 = +0.799 - (-0.76)$ volt

$E^0 = 1.559$ volt

Formula:

Now, we calculate the EMF of the given cell E, by using Nernst equation

$$E = E^0 - \frac{RT}{nF} \ln \frac{a_{Zn}^{+2}}{a_{Ag}^{+2}}$$

Putting the values

$= 1.599 - \dfrac{8.314 \times 298 \times 2.303}{2 \times 96500} \log \dfrac{0.8}{(10)^2}$

$= 1.559 - 0.03006 \log (0.008)$

$= 1.559 - 0.03006(-2.0969)$

$E = 1.559 + 0.063 = \boxed{1.622 \text{ volts}}$ Ans.

9.10.3 Nernst equation and the effect of concentration of surrounding electrolyte on the electrode potential

The measurement of pH:

We know that an electrode is completed by dipping metal rod in the solution of its own ions. The concentration of the surrounding solution of the electrolyte determines the electrode potential. According to Nernst equation, we are able to calculate the electrode potential depending upon the concentration of that ion in the solution but we should know the temperature and the standard electrode potential of the electrode.

Let us take the example of different electrodes and construct the Nernst equation for them.

(i)   **Hydrogen electrode:**

Consider the hydrogen electrode which is consisted of hydrogen gas in equilibrium with $H^{\oplus}$ ion. The reaction of this electrode, when written as reduction reaction is

$$H^{\oplus} + 1e^{\ominus} \longrightarrow \frac{1}{2} H_2$$
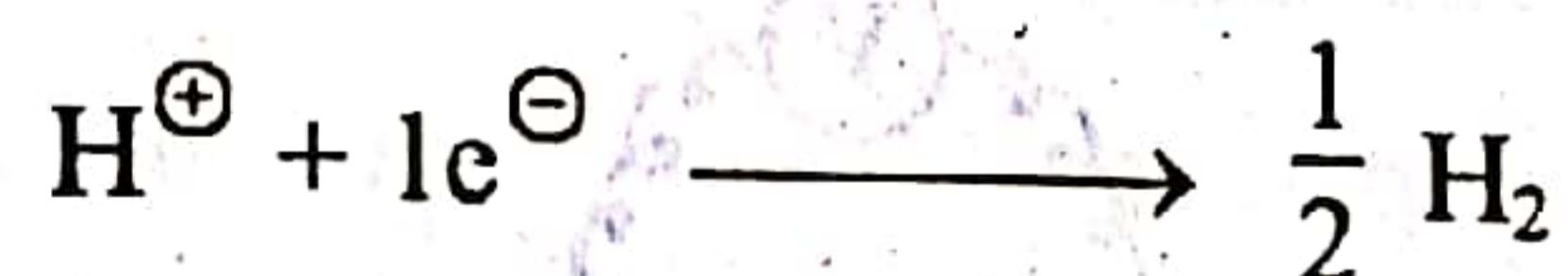
For this reaction n = 1, because one electron is being transferred for one ion of hydrogen. The Nernst equation can be written as

$$E_{H^{\oplus}/H_2} = E^{\circ}_{H^{\oplus}/H_2} - \frac{RT}{F} \ln \frac{a^{1/2}_{H_2}}{a_{H^{\oplus}}} \qquad \cdots\cdots (1)$$

When the pressure of hydrogen is one atmosphere, then the activity H_2 is unity. Then, $a_{H_2} = 1$

$$E_{H^{\oplus}/H_2} = E^{\circ}_{H^{\oplus}/H_2} - \frac{RT}{F} \ln \frac{1}{a_{H^{\oplus}}} \qquad \cdots\cdots (2)$$

Rearranging this equation by taking '$a_{H^{\oplus}}$' in the numinator.

$$E_{H^{\oplus}/H_2} = E^{\circ}_{H^{\oplus}/H_2} + \frac{RT}{F} \ln a_{H^{\oplus}} \qquad \cdots\cdots (3)$$

If we substitute the activity of $H^\oplus$ ion by molar concentration, then

$$E_{H^\oplus/H_2} = E^\circ_{H^\oplus/H_2} + \frac{RT}{F} \ln [H^\oplus] \qquad \ldots\ldots (4)$$

The standard electrode potential of hydrogen

$$E^\circ_{H^\oplus/H_2} = 0$$

So, $$E_{H^\oplus/H_2} = \frac{RT}{F} \ln [H^\oplus]$$

If the temperature is 25°C and F = 96,500 C, and natural log is converted to common log.

Then $$E_{H^\oplus/H_2} = 0.0591 \log [H^\oplus] \qquad \ldots\ldots (5)$$

This equation (5) is very useful because log $[H^\oplus]$, corresponds to the pH of the solution. So, we can determine the pH of the solution, when hydrogen electrode is set up.

9.11.0 CONCENTRATION CELLS

"Those cells in which the EMF is produced due to the difference in the concentrations of the electrode or electrolytes are called concentration cells." When there is a difference in the concentration of electrode, then the cells are called electrode concentration cells. If there is a difference in the concentration of electrolyte in the cells then they are called electrolyte concentration cells.

9.11.1 Electrode concentration cell:

One of the best examples in this reference is hydrogen electrode. If the pressure of the hydrogen at the two electrodes is different and the both electrodes are dipped in the same solution of $H^\oplus$ ion, then it becomes a electrode concentration cell. It will be represented as follows:

$$H_2 (p_{H_2} = p_1) / H^\oplus / H_2 (p_{H_2} = p_2)$$

Following diagram (25) shows this arrangement.

(H₂ at p_1 atm. pressure) →   ← (H₂ at p_2 atm pressure)
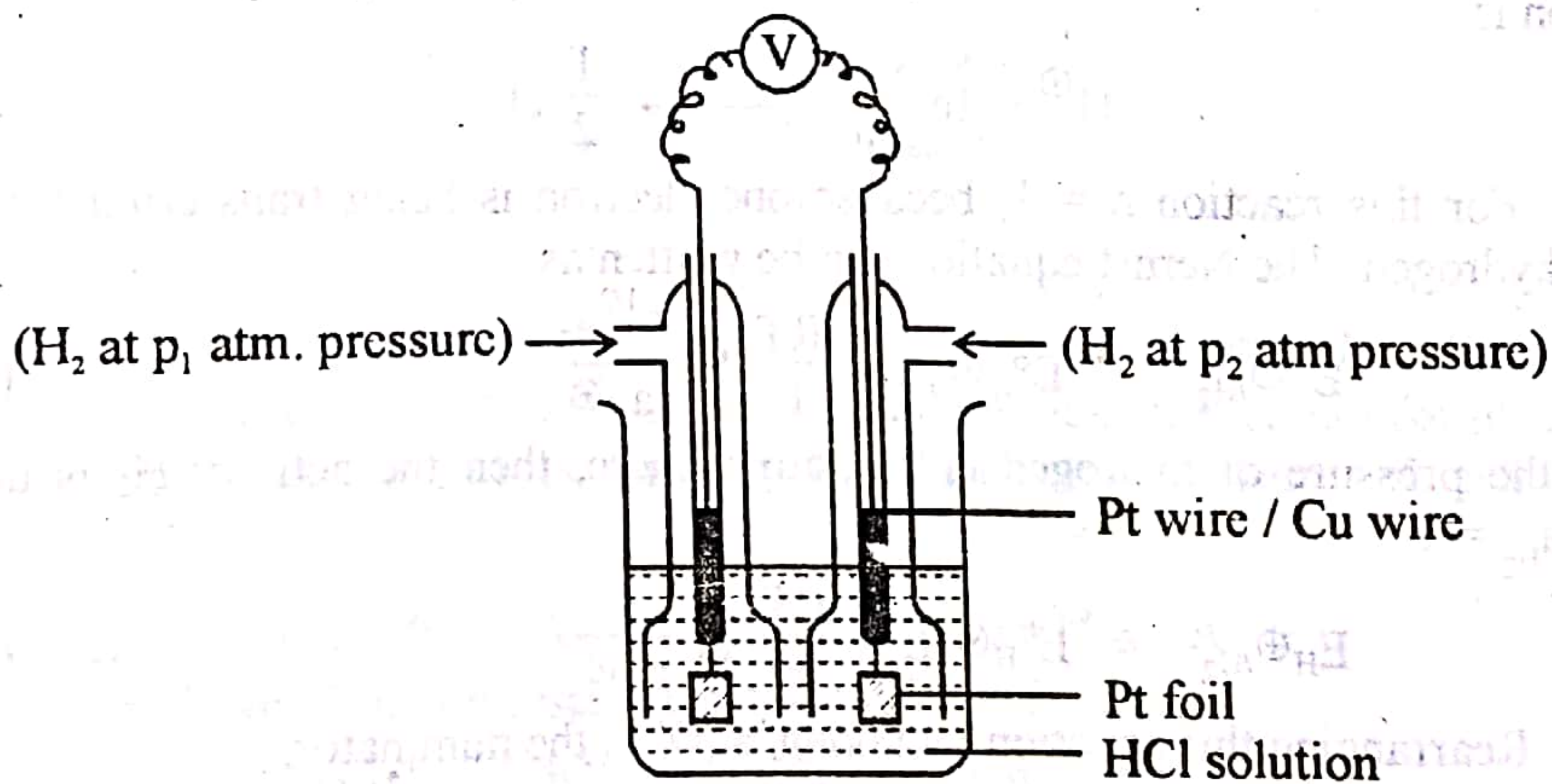
Pt wire / Cu wire

Pt foil

HCl solution

Fig. (25) *Electrode concentration cell consisting of hydrogen electrodes without transference.*

In this cell, there is no transference of electrolytes, and so this cell is called electrode concentration cell without transference.

9.11.2 Electrolyte concentration cell:

"That cell, in which the two electrodes are same and they have different concentrations of electrolytes and are connected by the salt bridge."

Examples:

(1) Hydrogen Electrode

We can take two hydrogen electrodes having same pressures of hydrogen, but the concentration of HCl in the two beakers may be different. Moreover, these two electrodes are connected by salt bridge Fig. (26). This cell can be represented as,

$$H_2 \text{ (1 atm)} \,|\, H^{\oplus} (a_1) \,\|\, H^{\oplus} (a_2) \,|\, H_2 \text{ (1 atm)}$$
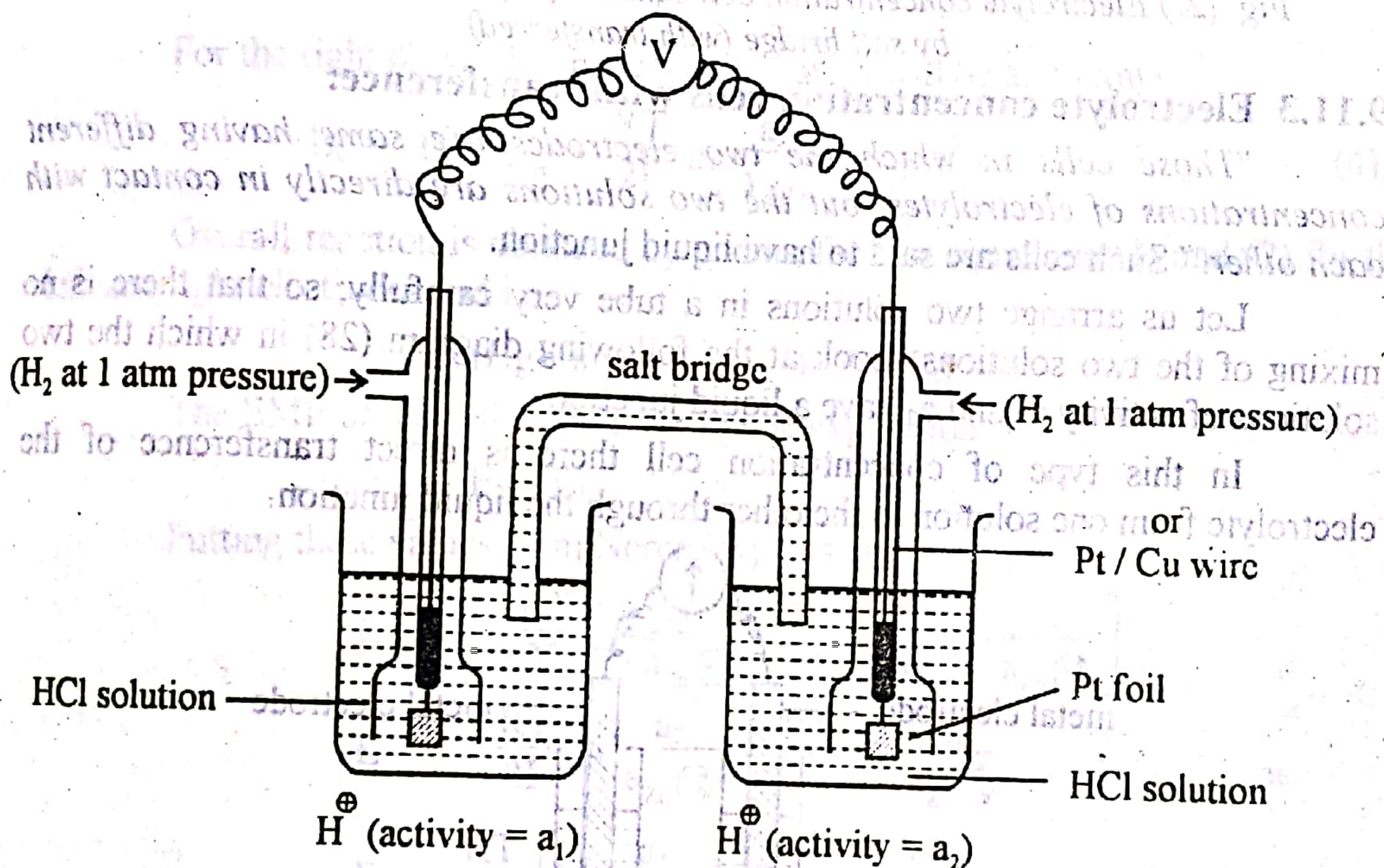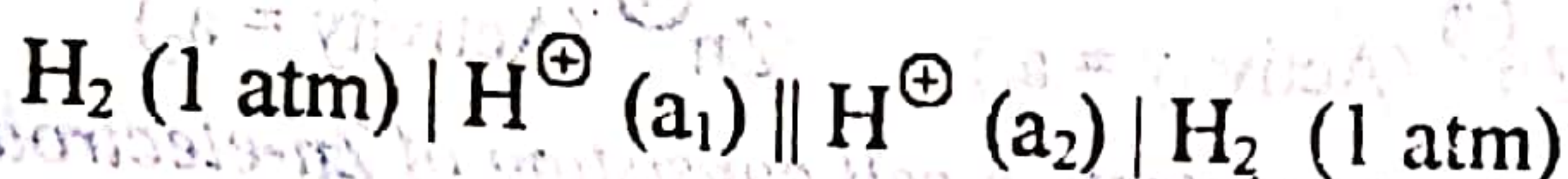
Fig. (26) Electrolyte concentration cells consisting of hydrogen electrode connected by a salt bridge (without transference)

2. Zinc-electrode:

When zinc rod is dipped in zinc ion, then it is a zinc electrode. If we have two beakers with different concentrations of zinc ions and zinc rodes are dipped in each at same temperature, then it gives a electrolyte concentration cell Fig. (27). Salt bridge is used for the connection of two beakers. The cell can be written as,

$$Zn \,/\, Zn^{+2} (a_1) \,\|\, Zn^{+2} (a_2) \,|\, Zn.$$
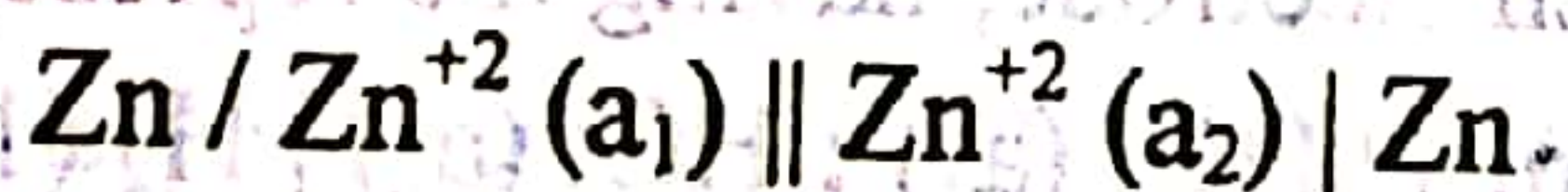
'a_1' and 'a_2' are the activities of zinc ion in the two beakers. Following diagram (27) makes the idea clear. This cell is a concentration cell without transference.
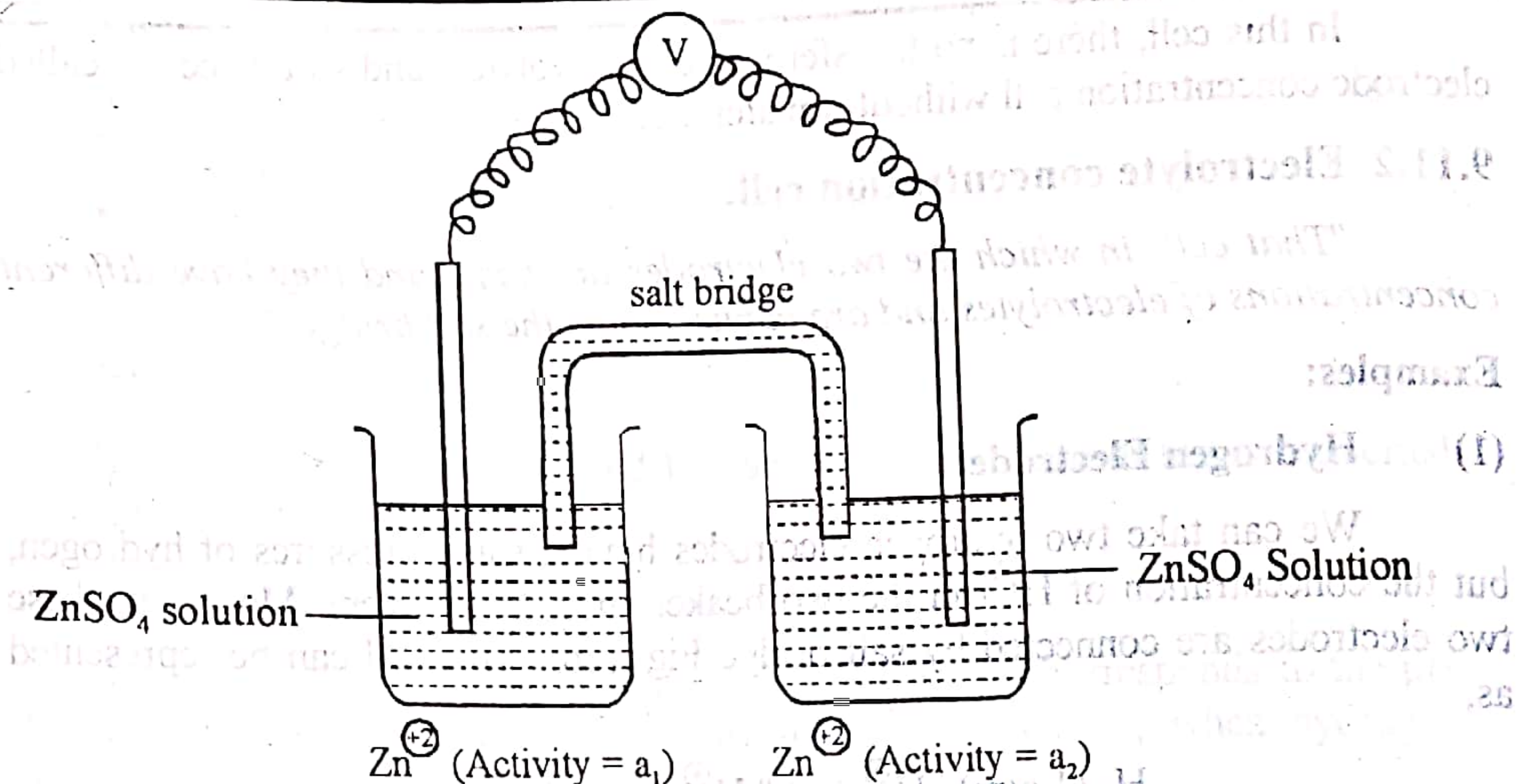
Fig. (27) *Electrolyte concentration cell consisting of Zn-electrode connected by salt bridge (with transferred)*

9.11.3 Electrolyte concentration cells with transference:

"Those cells in which the two electrodes are same having different concentrations of electrolytes, but the two solutions are directly in contact with each other." Such cells are said to have liquid junction.

Let us arrange two solutions in a tube very carefully, so that there is no mixing of the two solutions. Look at the following diagram (28) in which the two solutions of activity a_1 and a_2 have a liquid junction.

In this type of concentration cell there is direct transference of the electrolyte from one solution to the other through the liquid junction.
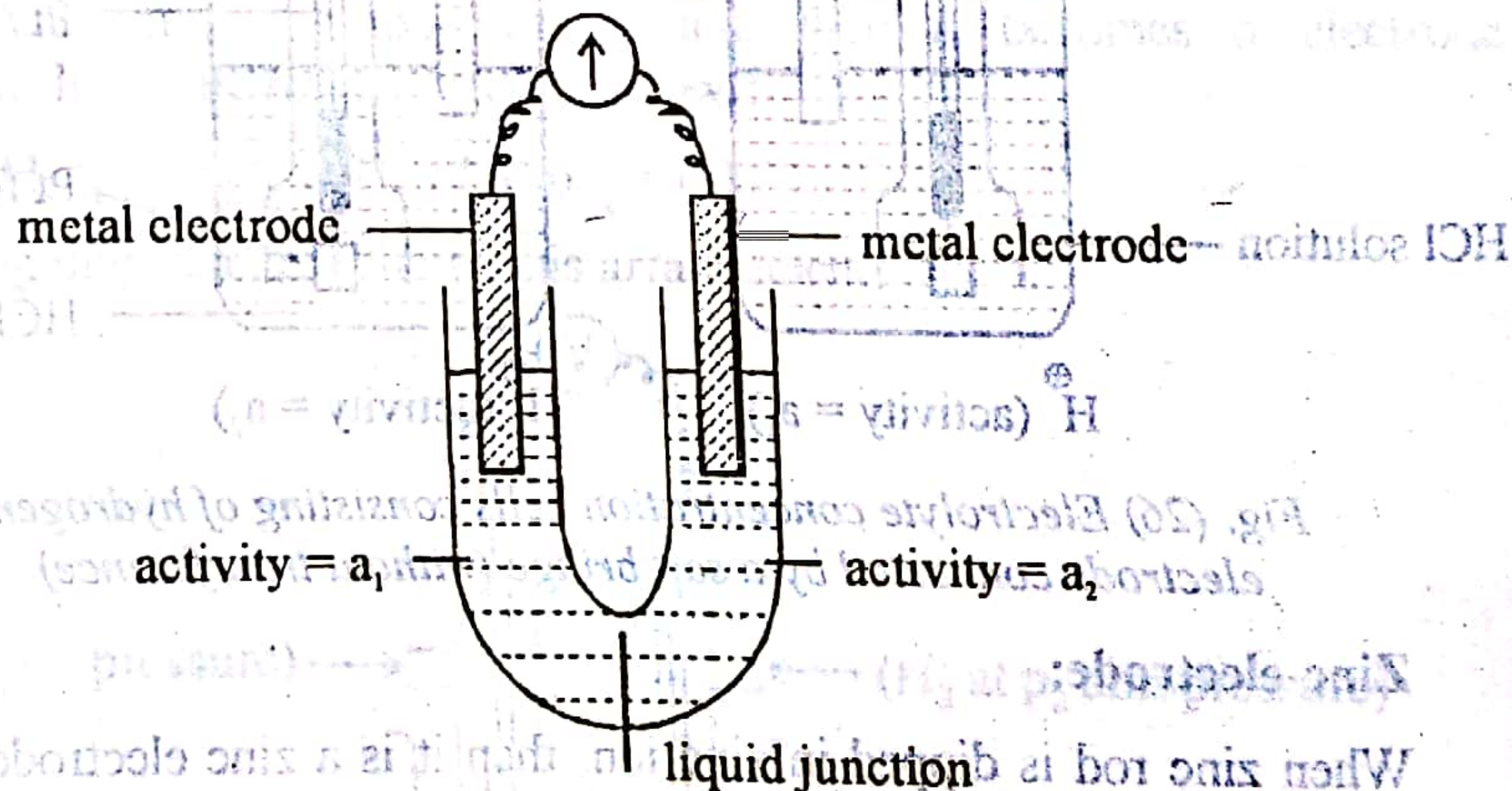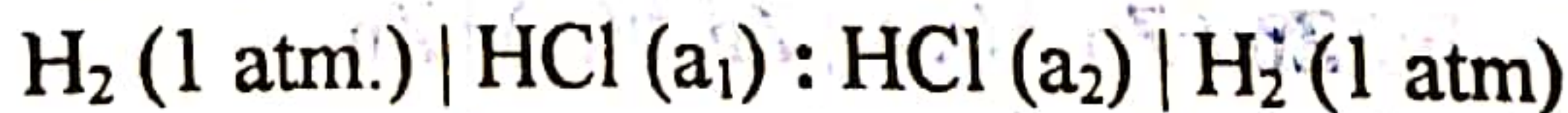

Fig. (28) *Electrolyte concentration with a liquid junction.*

We can take two electrodes as:

   (i)   Hydrogen electrode, having the representation

$$H_2 \,(1 \text{ atm.}) \,|\, HCl \,(a_1) : HCl \,(a_2) \,|\, H_2^+ \,(1 \text{ atm})$$

or   (ii) $Zn \,|\, ZnSO_4(a_1) : ZnSO_4 \,(a_2) \,|\, Zn^0$

In the representation of these cells, the double line is replaced by two dots because there is no salt bridge, but there is liquid junction.

## 9.11.4 EMF of electrode concentration cell without transference:

In order to illustrate it, let us take the example of electrode concentration cell consisting of amalgam electrodes. One of the examples in this reference is zinc-amalgam electrode which is represented as follow?

$$Zn(Hg) \ (a_{Zn} = a_1) \ | \ Zn^{+2} \ (a_{Zn+2}) \ | \ (a_{Zn} = a_2) \ Zn \ (Hg)$$
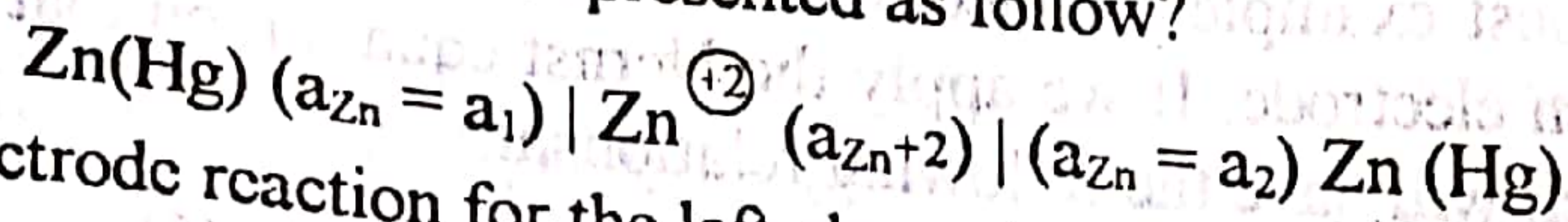
The electrode reaction for the left electrode

$$Zn^0(Hg) \ (a_1) \longrightarrow Zn^{+2} \ (a_{Zn}^{+2}) + 2e^{\ominus} \qquad \dots \dots \ (1)$$
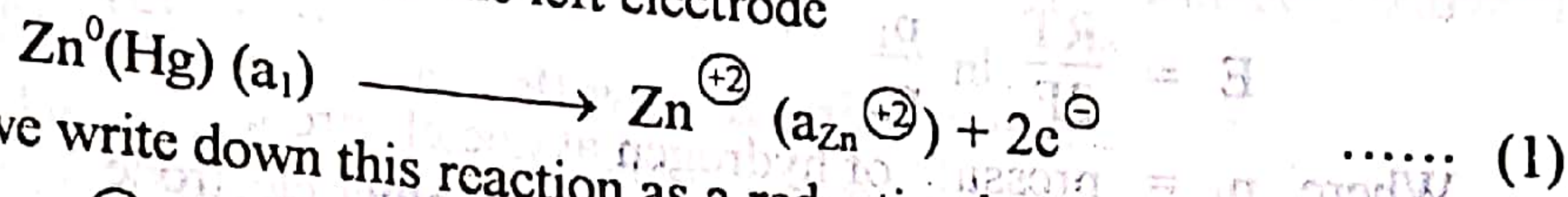
When we write down this reaction as a reduction half reaction, then,

$$Zn^{+2} \ (a_{Zn+2}) + 2e^{\ominus} \longrightarrow Zn(Hg) \ (a_1) \qquad \dots \dots \ (2)$$
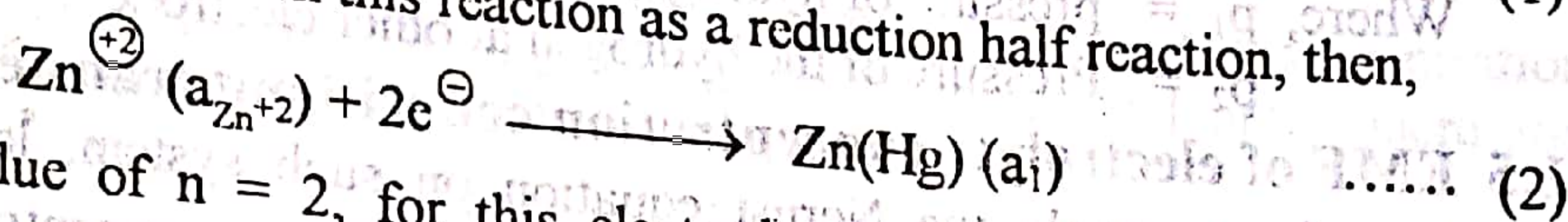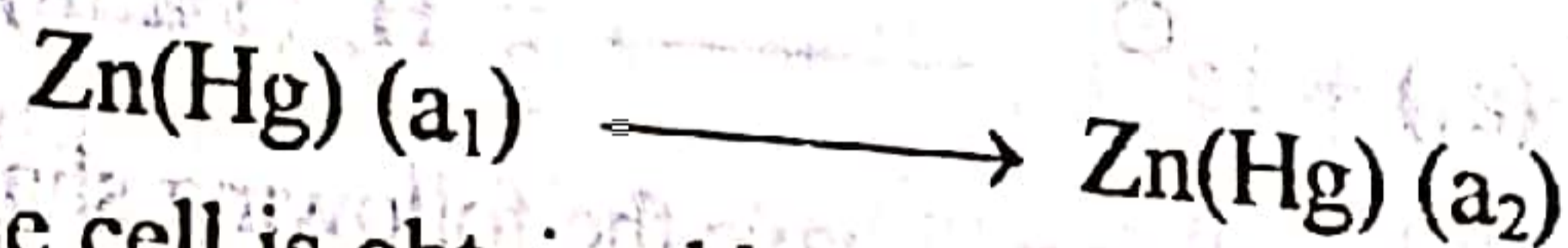
The value of n = 2, for this electrode and the Nernst equation can be written as,

$$E_1 = E^0_{Zn^{+2}/Zn^0} - \frac{RT}{2F} \ln \frac{a_1}{a_{Zn^{+2}}} \qquad \dots \dots \ (3)$$

For the right electrode, the Nernst equation will be as follows

$$E_2 = E^0_{Zn^{+2}/Zn} - \frac{RT}{2F} \ln \frac{a_2}{a_{Zn^{+2}}} \qquad \dots \dots \ (4)$$

Overall reaction is obtained by adding the two equations (1) and (2) for the left and right electrodes and i.e.

$$Zn(Hg) \ (a_1) \longrightarrow Zn(Hg) \ (a_2)$$

The EMF of the cell is obtained by the expression

$$E = E_2 - E_1$$

Putting these values from Nernst expression

$$E = \left[-\frac{RT}{2F} \ln \frac{a_2}{a_{Zn}^{+2}} \right] - \left[-\frac{RT}{2F} \ln \frac{a_1}{a_{Zn}^{+2}} \right]$$

$$E = -\frac{RT}{2F} \ln \frac{a_2}{a_{Zn}^{+2}} + \frac{RT}{2F} \ln \frac{a_1}{a_{Zn}^{+2}}$$

$$E = \frac{RT}{2F} \left(\ln \frac{a_1}{a_{Zn}^{+2}} - \ln \frac{a_2}{a_{Zn}^{+2}} \right)$$

$$E = \frac{RT}{2F} \ln \frac{a_1}{a_2} \qquad \dots \dots \ (3)$$

This equation (3) tells us, that the EMF of the cell originates due to the reason that there happens a transference of zinc from zinc amalgam with its activity a_1 to zinc amalgam, where its activity is a_2. There is no transference of electrolyte, i.e. Zn^{+2} ions. This equation also tells us that the EMF of the cell depends only upon the activity of Zn^{+2} in the solution. It is interesting to note that there is no role of E^0. In this equation keep it in mind that E^0 will not appear in all the concentration cells. It means that for concentration cell, $E^0 = 0$.

We can generalize the equation (3) as follows:

$$E_{cell} = \frac{RT}{nF} \ln \frac{a_1}{a_2} \qquad \cdots\cdots (4)$$

Another best example for electrode concentration cell without transference is that of hydrogen electrode. If we apply the Nernst equation on that situation then the EMF of the cell will have the following relationship

$$E = \frac{RT}{2F} \ln \frac{p_1}{p_2} \qquad \cdots\cdots (5)$$

Where, p_1 = pressure of hydrogen at one electrode

$\qquad p_2$ = Pressure of the hydrogen at other electrode

9.11.5 EMF of electrolyte concentration cell without transference:

In order to apply the Nernst equation on such system, let us take the example of hydrogen concentration cell, having different concentrations of $H^{\oplus}$ ion. Let these concentrations be denoted by a_1 and a_2. Cell is represented as

$$H_2 \,(1\ atm) \,|\, H^{\oplus} \,(a_1) \,\|\, H^{\oplus} \,(a_2) \, H_2 \,(1\ atm)$$
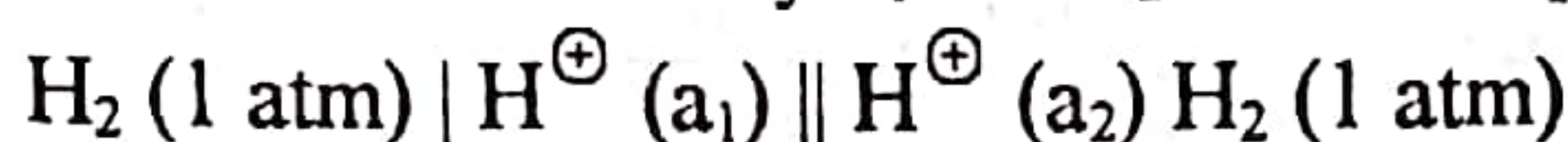
It is a convention that oxidation takes place at the left electrode

$$\frac{1}{2} H_2 \,(1\ atm) \longrightarrow H^{\oplus} \,(a_1) + 1e^{\ominus}$$
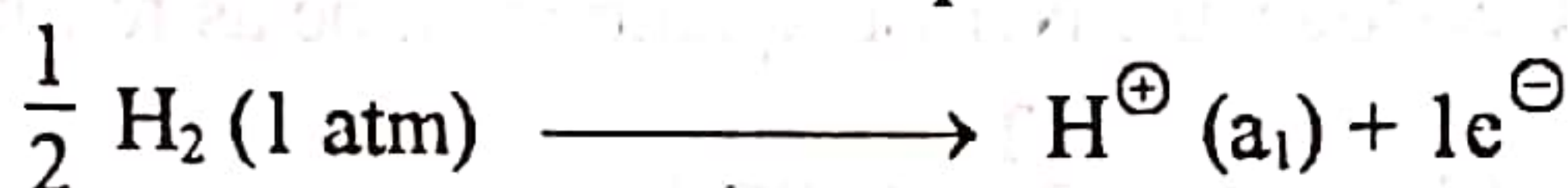
If we want to apply the Nernst equation on this electrode, we should write down its reduction half reaction

$$H^{\oplus} \,(a_1) + 1e^{\ominus} \longrightarrow \frac{1}{2} H_2 \,(1\ atm)$$

$n = 1$, for this step and Nernst equation will have the following shape for this electrode.

$$E_1 = E^0{}_{H^{\oplus}/H_2} - \frac{RT}{F} \ln \frac{(a_{H_2})^{1/2}}{a_1}$$

Since, $a_{H_2} = 1$

So, $\qquad E_1 = E^0{}_{H^{\oplus}/H_2} - \frac{RT}{F} \ln \frac{1}{a_1}$

or $\qquad E_1 = E^0{}_{H^{\oplus}/H_2} + \frac{RT}{F} \ln a_1 \qquad \cdots\cdots (1)$

Since $E^0{}_{H^{\oplus}/H_2} = 0$ $\quad$ So, $\quad E_1 = + \frac{RT}{F} \ln a_2 \qquad \cdots\cdots (2)$

Reduction takes place at the right electrode by convention and so the reaction is written as follows:

$$H^{\oplus} \,(a_2) + 1e^{\ominus} \longrightarrow \frac{1}{2} H_2 \,(1\ atm)$$

$n = 1$, for this reaction and Nernst equation will have the following shape for this electrode

$$E_2 = \frac{RT}{F} \ln a_2 \qquad \cdots\cdots (3)$$

The EMF of the cell is given by, the difference of E_2 and E_1 given in the equation (2) and (3)

$$E = E_2 - E_1$$

Subtracting equation (2) from (3),

$$E = \frac{RT}{F} \ln a_2 - \frac{RT}{F} \ln a_1$$
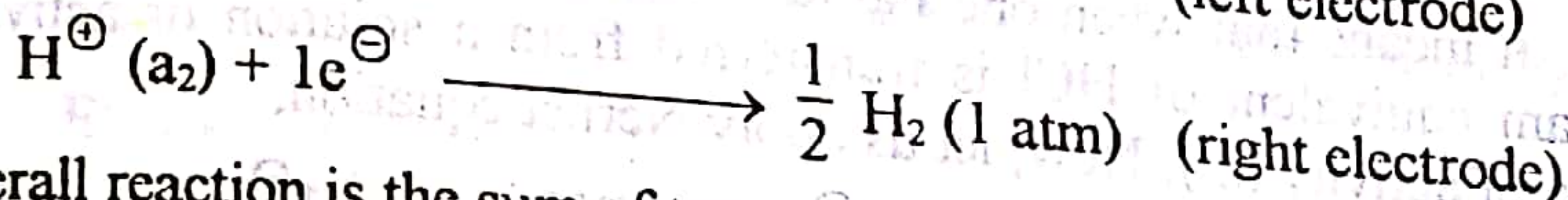
$$E = \frac{RT}{F} \ln \frac{a_2}{a} \qquad \qquad \cdots \cdots (4)$$
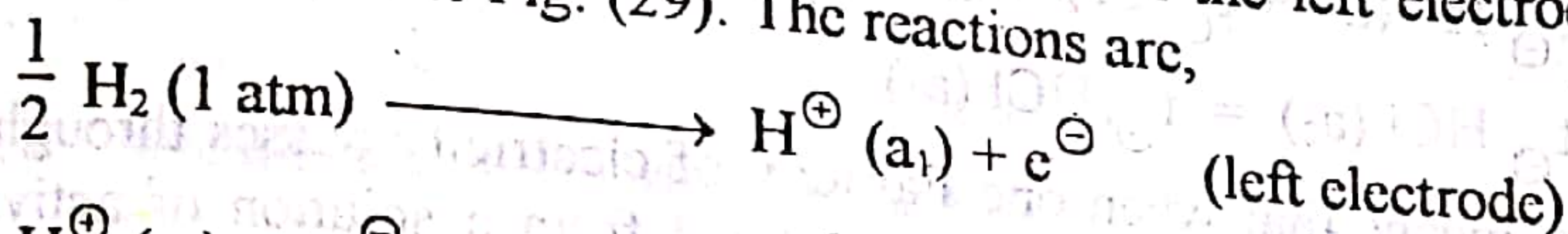
The EMF of the cell depends upon 'a₁' and 'a₂'. EMF will be positive, if $a_2 > a_1$.

### 9.11.6 EMF of a concentration cell with transference:

Let us take the example of hydrogen electrode in which the concentration of HCl solutions are different. The pressure of the hydrogen is 1 atmosphere and the two solutions are contacted Fig. (29) by liquid junction

$$H_1 (1\ atm) \mid HCl\ (a_1) : HCl\ (a_2) \mid H_2\ (1\ atm)$$
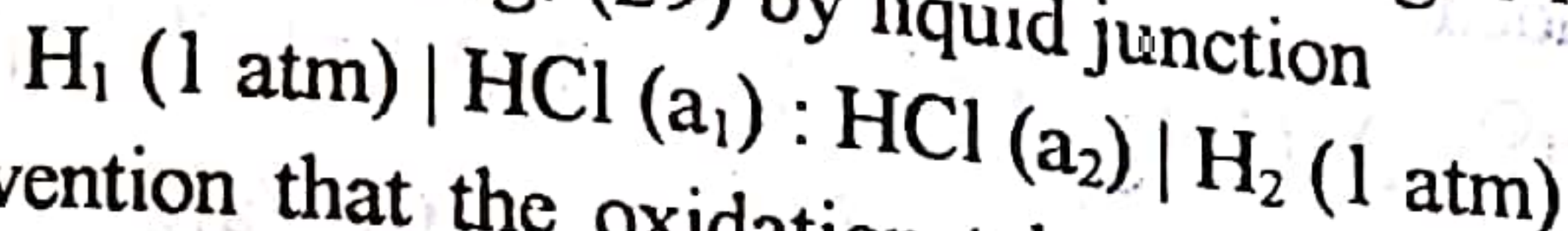
It is a convention that the oxidation takes place on the left electrode and the reduction at the right electrode Fig. (29). The reactions are,

$$\frac{1}{2} H_2\ (1\ atm) \longrightarrow H^{\oplus}\ (a_1) + e^{\ominus} \qquad \text{(left electrode)}$$

$$H^{\oplus}\ (a_2) + 1e^{\ominus} \longrightarrow \frac{1}{2} H_2\ (1\ atm) \quad \text{(right electrode)}$$

The overall reaction is the sum of two reactions

$$H^{\oplus}\ (a_2) \longrightarrow H^{\oplus}\ (a_1) \qquad \qquad \cdots \cdots (1)$$
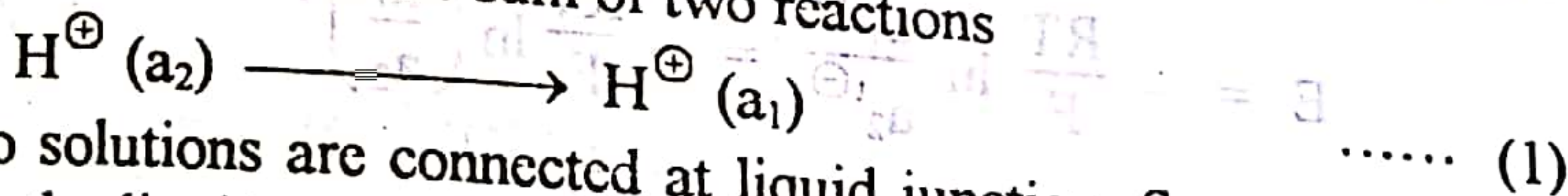
The two solutions are connected at liquid junction. So we want to look at the processes at the liquid junction. Electrons flow in the external circuit from left to the right. $H^{\oplus}$ are produced in the left electrode and $Cl^{\ominus}$ are left in the right electrode, so the inner circuit is completed by the transference of $Cl^{\ominus}$ ions from right to the left. $H^{\oplus}$ ions transfer from left to the right across the liquid junction. Following diagram makes the idea clear. Let the transfer number of $Cl^{\ominus}$ ion is t₋.

When one Faraday of electricity passes through the cell, then t₋ gram equivalent of $Cl^{\ominus}$ ion will be transferred from right to the left.
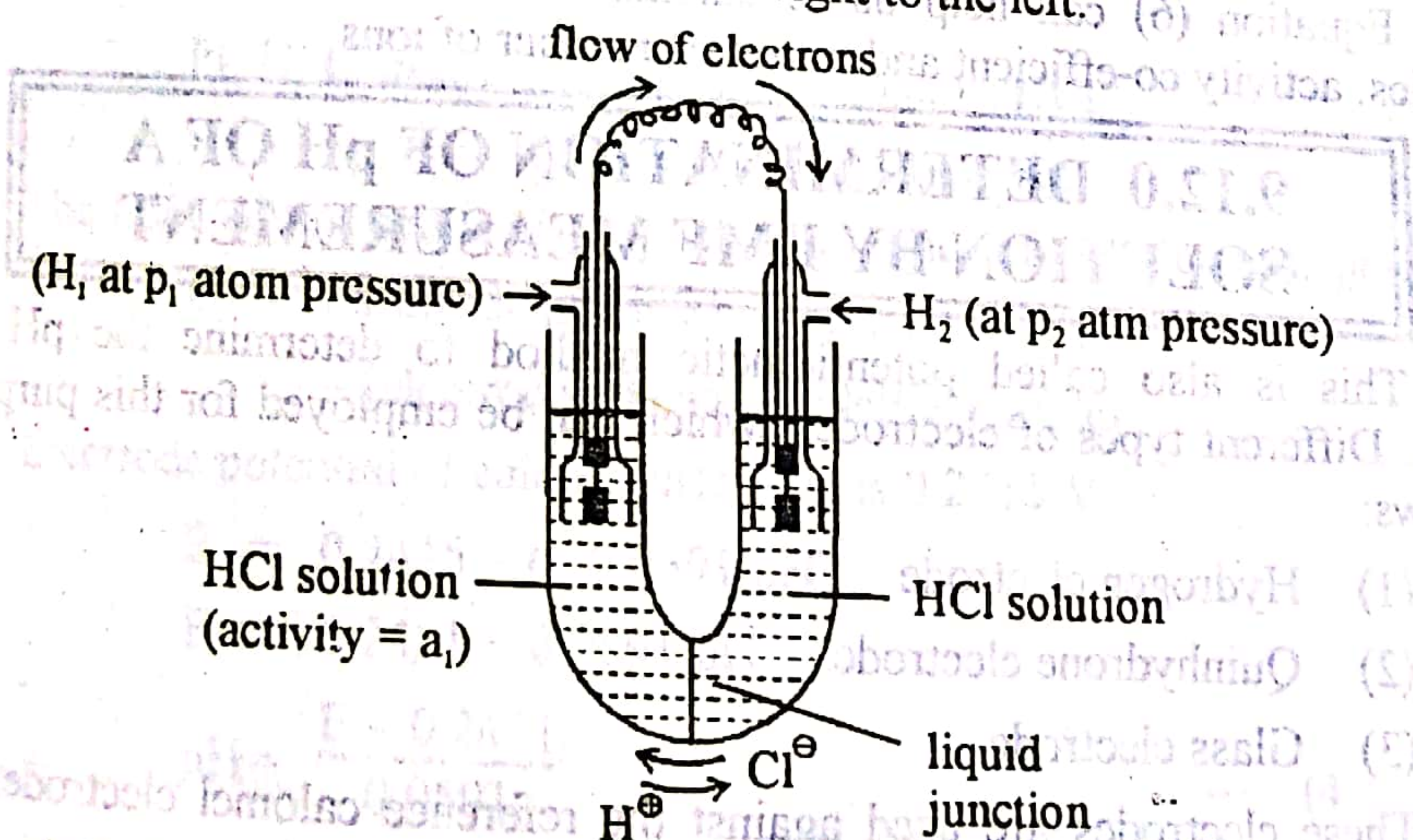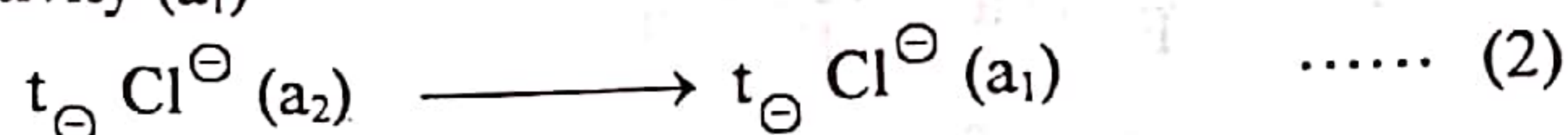

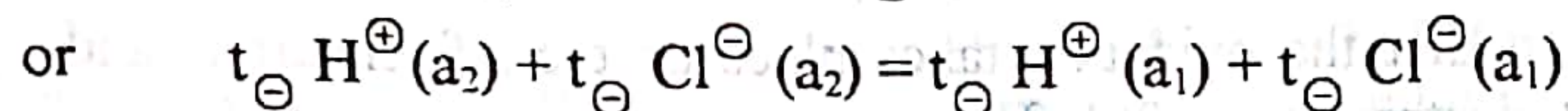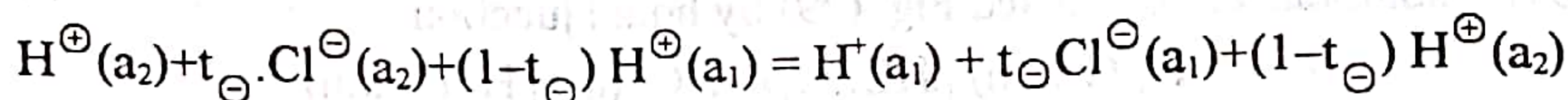**Fig. (29) Concentration cell with transference for hydrogen electrodes.**

In other words, the $Cl^{\ominus}$ ions of activity (a_2), move towards the compartment of activity (a_1)

$$t_{\ominus}\ Cl^{\ominus}\ (a_2) \longrightarrow t_{\ominus}\ Cl^{\ominus}\ (a_1) \quad\quad \cdots\cdots (2)$$

The transport number of $H^{\oplus}$ ion $= (1 - t_{\ominus})$. So, $(1 - t_{\ominus})\ H^{\oplus}$ ions will be transferred from left to right. In other words, $H^{\oplus}$ ions transfer from the solution of activity $'a_1'$ to the solution of activity (a_2).

So, $(1 - t_{\ominus})\ H^{\oplus}\ (a_1) \longrightarrow (1 - t_{\ominus})\ H^{\oplus}\ (a_2) \quad\quad \cdots\cdots (3)$

If we want to calculate the net transfer of the material, then equations (1), (2) and (3) must be added.

$$H^{\oplus}(a_2) + t_{\ominus}.Cl^{\ominus}(a_2) + (1-t_{\ominus})\ H^{\oplus}(a_1) = H^{+}(a_1) + t_{\ominus}Cl^{\ominus}(a_1) + (1-t_{\ominus})\ H^{\oplus}(a_2)$$

or $t_{\ominus}\ H^{\oplus}(a_2) + t_{\ominus}\ Cl^{\ominus}\ (a_2) = t_{\ominus}\ H^{\oplus}\ (a_1) + t_{\ominus}\ Cl^{\ominus}(a_1)$

or $t_{\ominus}\ HCl\ (a_2) = t_{\ominus}\ HCl\ (a_1) \quad\quad\quad\quad \cdots\cdots (4)$

It means that when one Faraday of electricity passes through the cell, then one gram equivalent of HCl is transferred from a solution of activity (a_2) to the solution of activity (a_1). Now, let us apply Nernst equation,

$$E = -\frac{RT}{F}\ \ln \frac{a_1^{t_{\ominus}}}{a_2^{t_{\ominus}}} = -\frac{RT}{F} \ln \left(\frac{a_1}{a_2}\right)^{t_{\ominus}}$$

$$E = t_{\ominus}\ \frac{RT}{F}\ \ln \frac{a_2}{a_1} \quad\quad \cdots\cdots (5)$$

So, in order to get the positive EMF of the cell, a_2 should be greater than a_1. If the activities of the substances are replaced by the molalities and activity co-efficient of the ions, then equation (5) can be written as follows:

$$E = t_{\ominus}\ \frac{RT}{F}\ \ln \frac{m_2\gamma_2}{m_1\gamma_1} \quad\quad \cdots\cdots (6)$$

Equation (6) can help us to calculate EMF of a cell, if we know the molalities, activity co-efficient and transport number of ions.

## 9.12.0 DETERMINATION OF pH OF A SOLUTION BY EMF MEASUREMENT

This is also called potentiometic method to determine the pH of the solution. Different types of electrodes, which can be employed for this purpose are as follows:

(1) Hydrogen electrode

(2) Quinhydrone electrode

(3) Glass electrode

These electrodes are used against the reference calomel electrode. Let us discuss these electrodes one by one.

9.12.1 pH measurement by hydrogen electrode:

Let us write down the electrode reaction of hydrogen electrode in the reduction mode

$$H^{\oplus} + 1e^{\ominus} \longrightarrow \frac{1}{2} H_2 \text{ (1 atm)}$$
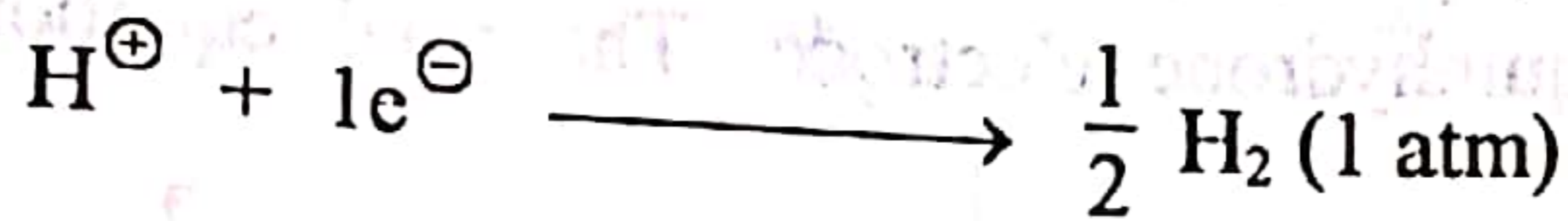
Now, apply the Nernst equation to have the potential of this hydrogen electrode

$$E_{H^{\oplus}/H_2} = E^0_{H^{\oplus}/H_2} + \frac{RT}{F} \ln [H^{\oplus}] \quad \ldots\ldots (1)$$

Let us consider that the cell is working at the temperature of 25C° i.e. 298 K°, $R = 8.3143 \text{ J K}^{-1} \text{mol}^{-1}$ and $F = 96,500$ volts

Hence, equation (1) becomes,

$$E_{H^{\oplus}/H_2} = E^0_{H^{\oplus}/H_2} + 0.0591 \log [H^{\oplus}] \quad \ldots\ldots (2)$$

At these standard conditions, the standard electrode potential of hydrogen is zero. So,

$$E^0_{H^{\oplus}/H_2} = 0$$

Hence,

$$E_{H^{\oplus}/H_2} = 0.0591 \log [H^{\oplus}]$$

Introducing the definition of pH,

$$pH = - \log [H^{\oplus}]$$

$$E_{H^{\oplus}/H_2} = - 0.0591 \text{ pH} \quad \ldots\ldots (3)$$

Now, combine this hydrogen electrode, under these conditions with calomel electrode. The electrochemical series tells us that oxidation takes place at hydrogen electrode and reduction at calomel electrode. So, the cell may be written as follows:

$$\text{Pt. } H_2 \text{ (1 atm.)} | H^{\oplus} \text{ (unknown conc.)} \| KCl$$

$$\text{(saturated)} | Hg_2Cl_{2(s)} | Hg$$
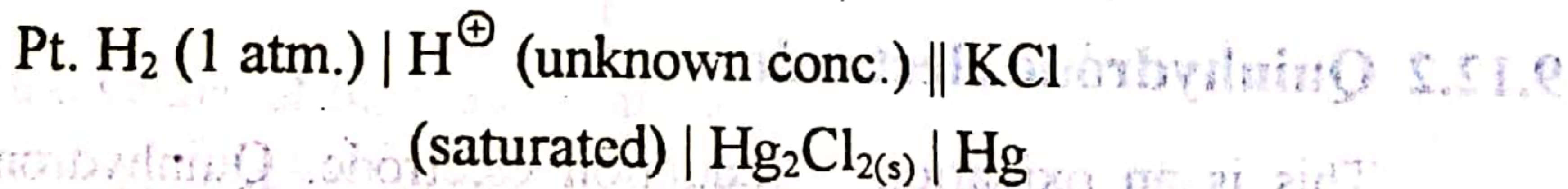
The EMF of this cell is given by the difference of two electrode potentials

$$E = \text{[electrode potential of right electrode]}$$

$$- \text{[electrode potential of left electrode]}$$

Electrode potential of calomel electrode is 0.2415 V

$$E = 0.2415 - (- 0.0591 \text{ pH})$$

$$E = 0.2451 + 0.0591 \text{ pH}$$

$$pH = \frac{E - 0.2451}{0.0591} \quad \ldots\ldots (4)$$

If the we measure the EMF of the cell by a potentiometer (E), then pH of solution can be calculated.

(2)   By using quinhydrone electrode:

On the similar grounds, when a calomel electrode is combined with quinhydrone electrode, then oxidation takes place at the calomel electrode and the reduction at the quinhydrone electrode. The final equation for the pH of the solution is

$$pH = \frac{0.04581 - E}{0.0591}$$

(3)   By using glass electrode:

When glass electrode is connected with calomel electrode, the final equation for the pH of solution is as under

$$pH = \frac{E^0{}_G - E_C + E}{0.0591}$$

where, $E^0{}_G$ =   Standard electrode potential of glass electrode. Its value depends upon the nature of the glass and the pH of the solution which is taken inside the glass bulb.

F_C =   Electrode potential of the calomel electrode whose value depends upon the concentration of the KCl solution used

Glass electrode is more useful as compared to other electrodes due to following reasons:

(i)   It is very easy to use

(ii)   It is not affected by oxidizing and reducing agents

(iii) Even small quantities of solutions can be handled
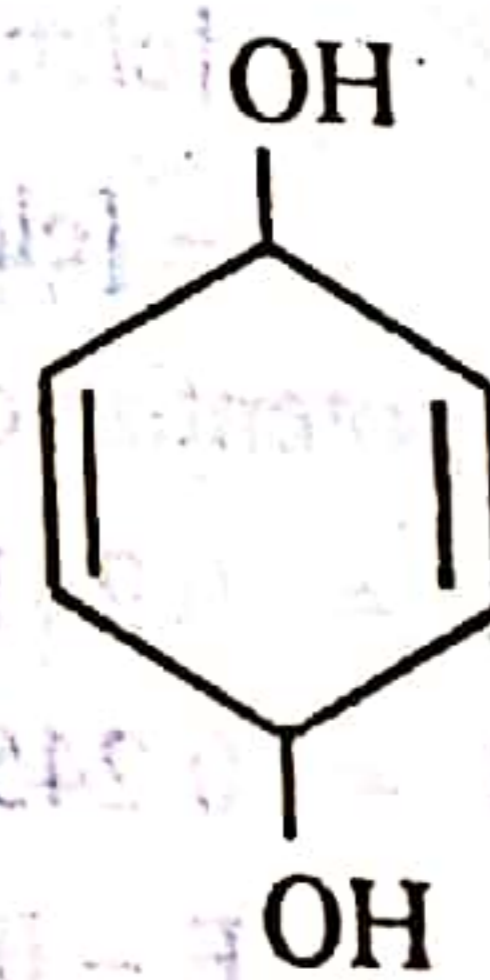
(iv)   It is not poisoned easily.

In these ways, glass electrode is the universal pH electrode.
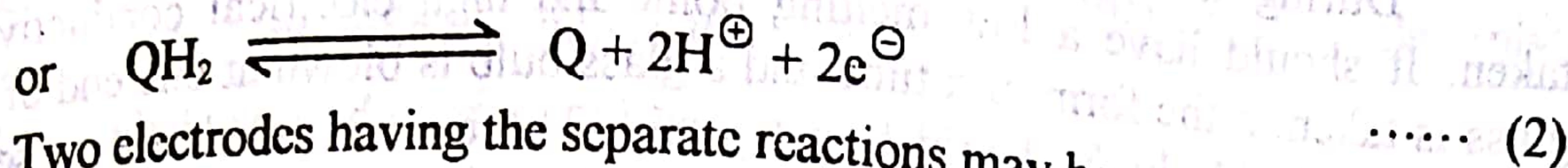
9.12.2 Quinhydrone electrode:
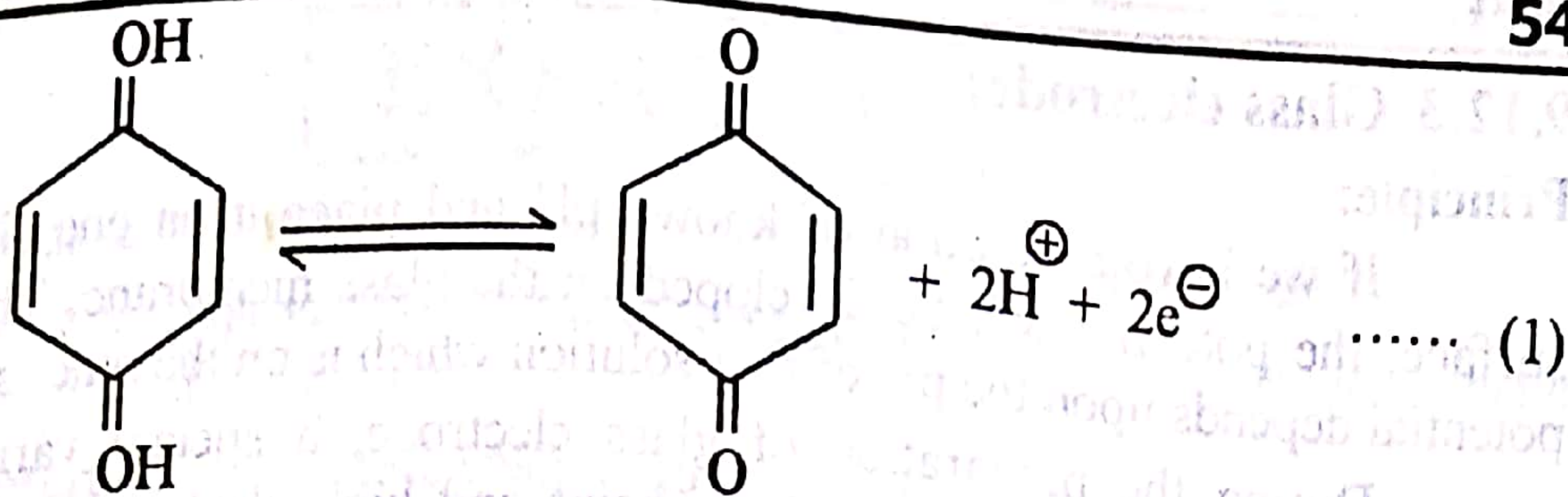
This is an oxidation – reduction electrode. Quinhydrone is a compound which contains equimolar quantities of quinone and hydro-quinone.
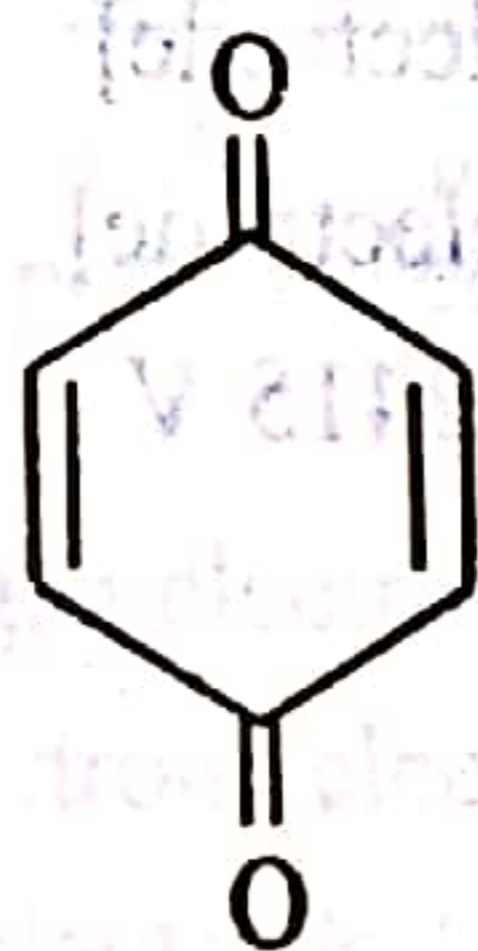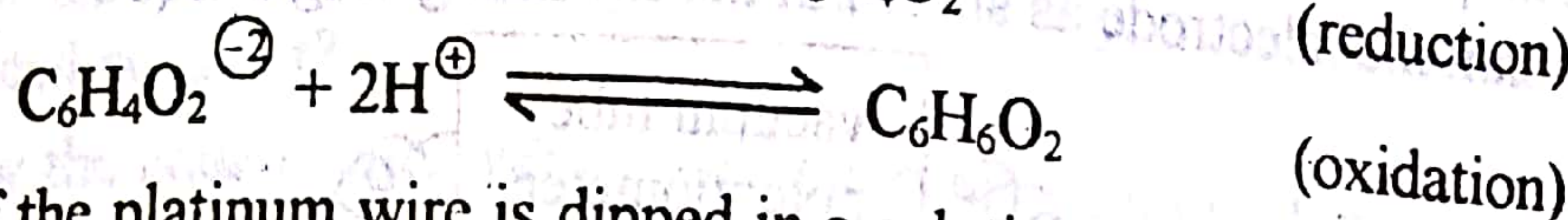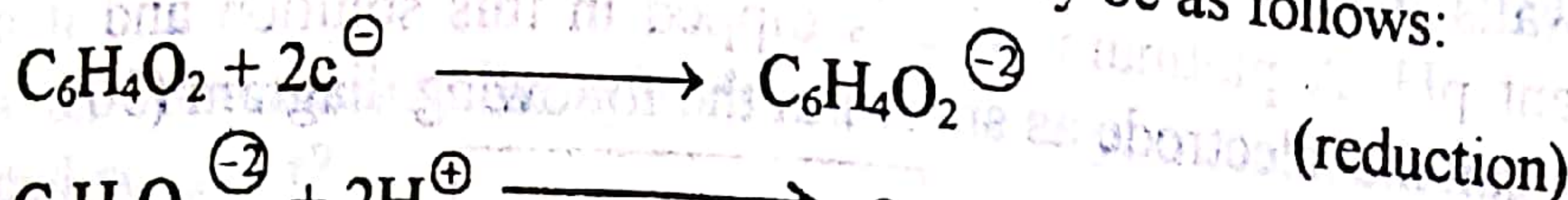

Quinone (Q)   Hydroquinone (QH₂)

The working of this electrode is based upon the reason that quinone is reduced to hydroquinone and hydroquinone is oxidized to quinone.

$$\text{QH}_2 \rightleftharpoons \text{Q} + 2\text{H}^{\oplus} + 2\text{e}^{\ominus} \qquad \ldots\ldots (2)$$

or

Two electrodes having the separate reactions may be as follows:

$$\text{C}_6\text{H}_4\text{O}_2 + 2\text{e}^{\ominus} \longrightarrow \text{C}_6\text{H}_4\text{O}_2^{\ominus 2} \qquad \text{(reduction)}$$

$$\text{C}_6\text{H}_4\text{O}_2^{\ominus 2} + 2\text{H}^{\oplus} \rightleftharpoons \text{C}_6\text{H}_6\text{O}_2 \qquad \text{(oxidation)}$$

Now, if the platinum wire is dipped in a solution, containing $\text{H}^{\oplus}$ ion and a pinch of a hydroquinone which is a mixture of (Q + QH₂), then it acts as a reversible electrode.

Let us write down the reduction reaction of this electrode, so that Nernst equation may be applicable

$$\text{Q} + 2\text{H}^{\oplus} + 2\text{e}^{\ominus} \rightleftharpoons \text{QH}_2 \qquad \ldots\ldots (3)$$
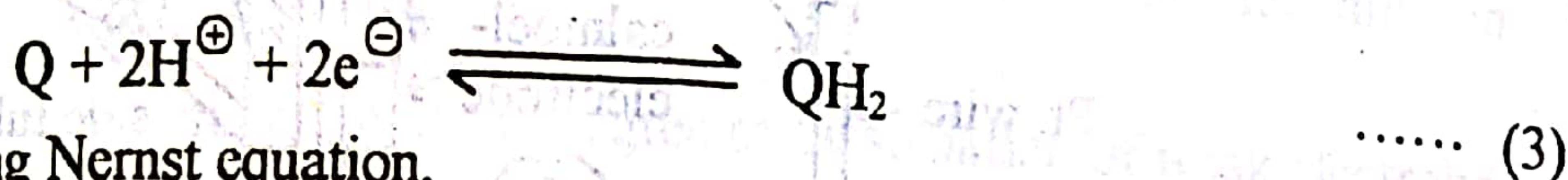
Applying Nernst equation,

$$E_Q = E^0{}_Q - \frac{RT}{nF} \ln \frac{1}{[\text{H}^{\oplus}]} \qquad \ldots\ldots (4)$$

The reason is that the ratio of Q and QH₂, is taken as unity because they have been taken in equal concentrations

$$E_Q = E^0{}_Q + \frac{RT}{F} \ln [\text{H}^{\oplus}]$$

Converting the natural log into common log

$$E_Q = E^0{}_Q + 2.303 \frac{RT}{F} \log [\text{H}^{\oplus}]$$

Putting the values of R, T and F at 25C°

$$E_Q = E^0{}_Q + 0.0591 . \log [\text{H}^{\oplus}]$$

$$E_Q = E^0{}_Q - 0.0591 \, \text{pH} \qquad \ldots\ldots (5)$$

The value of $E^0{}_Q$ is 0.6996 volts. So, equation (5) can be written as,

$$E_Q = 0.6996 - 0.0591 \, \text{pH} \qquad \ldots\ldots (6)$$

If this electrode is connected with calomel electrode, and the electrode potential of calomel electrode is taken as 0.2415 volts, the final equation for pH will be,

$$\text{pH} = \frac{0.4581 - E}{0.0591}$$

Where, E = EMF of the whole cell, when calomel electrode is connected with quinhydrone electrode

9.12.3 Glass electrode:

Principle:

If we have a solution of known pH and place it on one side of the glass surface, the potential will be developed on the glass membrane. The value of this potential depends upon the pH of that solution which is on the other side.

During the preparation of glass electrode, a special variety of glass is taken. It should have a low melting point and high electrical conductivity. This glass is taken in the form of a tube and a glass bulb is blown at one end of the tube. The walls of this bulb should be very thin. The bulb is filled with a solution of constant pH. A platinum wire is dipped in this solution and it may be connected with a calomel electrode as shown in the following diagram (30).
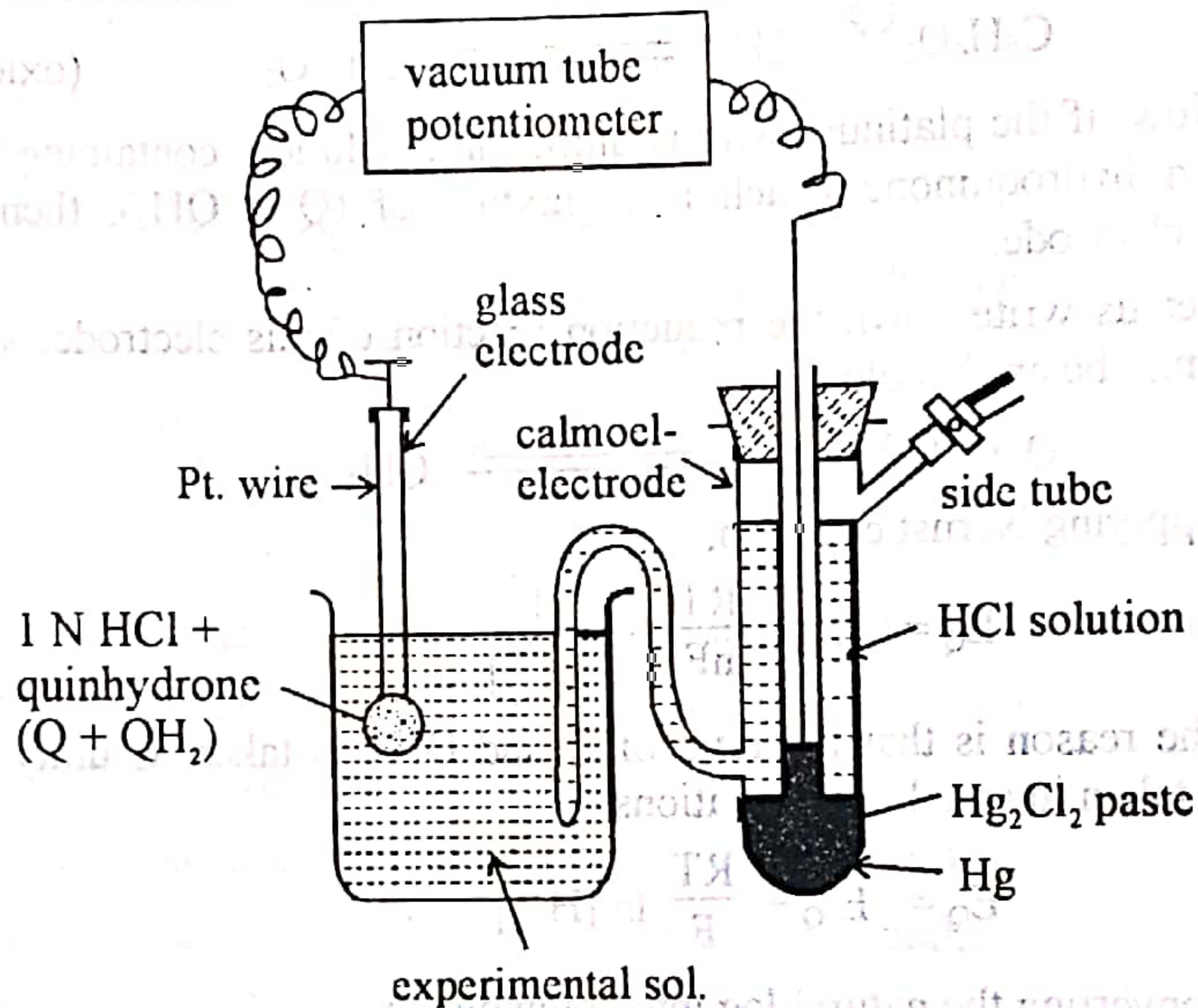

Fig. (30) Combination of a glass electrode with a calomel electrode to measure pH of a solution.

When Nernst equation is applied, then

$$Eg = E^0g + 0.0591 \log [H^{\oplus}]$$
$$Eg = E^0g - 0.0591 \text{ pH} \qquad \cdots \cdots (1)$$

Where,

$E^0g =$ standard electrode potential of glass electrode.

Its value depends upon the nature of the glass and the solution which is taken in the bulb. In order to determine the value of E^0g for a particular glass electrode, the value of Eg is determined for a solution of known pH. When it is connected with calomel electrode, then the pH of the solution which is put in the breaker is calculated by the following equation:

$$pH = \frac{E^0g - E_c + E}{0.0591}$$

In equation (2), E_c is the electrode potential of calomel electrode and E is the EMF of the complete cell.