Electrochemistry (Third Stage)

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Syllabus of Electrochemistry

1. Introduction about electrochemistry science.
2. Faraday's Laws.
3. Applications of Faraday's Laws.
4. Electrical conductance , Resistance, specific resistance, specific conductance, molar and equivalent conductance, cell constant, and solvent correction.
5. Conductivity Measurement.
6. Applications of conductance (Debye-Huckel-Onsagar equation, Kohlrausch Law, Ostwald dilution Law, Determine the hydrolysis constant for salt, and Conductometric titration.
7. Debye- Huckel theory.
8. Migration of ions towards the electrodes.
9. Hittorf's method, and transport number of ions.
10. Electrochemical cell and electrolytic cell.
11. Electromotive force (EMF).
12. Type of electrodes.

References

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Electrochemistry

Electrochemistry science is

1- The science which studies transformation of chemical energy into electrical energy and vice versa.

2- The science which deals with the consequence of the transfer of electric charges from one place to another

3- The study of the relationship between chemical and electrical change. Electrochemical science has a multitude of applications, ranging from solar technology to biomedical innovations.

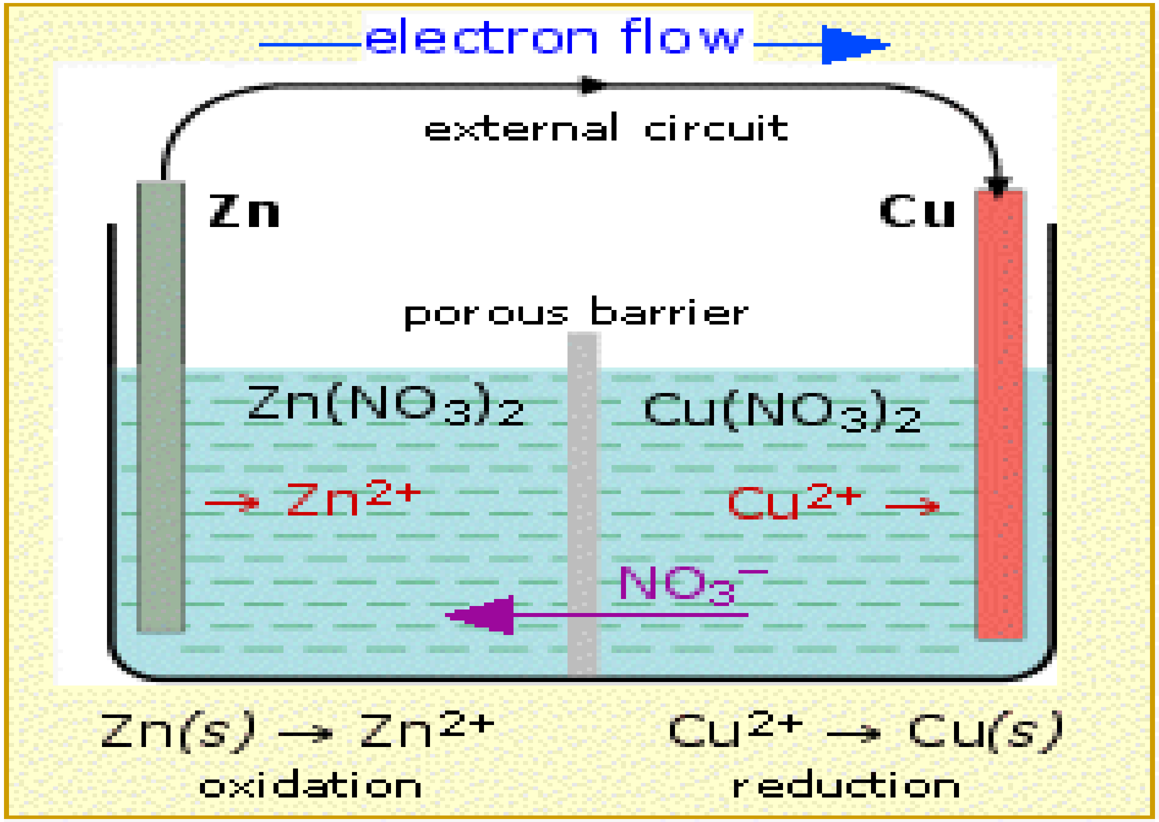
International system

Physical Quantity	Name of Unit	Unit Symbol	Unit Expressed In terms of Base Units
Force	Newton	N	$m.Kg.s^{-2}$
Energy	Joule	J	$N.m$ or $m^2.Kg.s^{-2}$
Power	Watt	W	$J.s^{-1}$
Quantity of electricity	Coulomb	C	$A.s$
Electromotive force	Volt	v	$J.A^{-1}.s^{-1}$
Electro resistance	Ohm	Ω	$V.A^{-1}$ or $m^2.Kg.s^{-3}.A^{-2}$
Electric conductance	Siemens	S	Ω^{-1}
Electrical capacitor	Farad	F	$A.v^{-1}.s$ or $m^{-2}.Kg^{-1}.s^4.A^2$
Current density	Current	i	$A.cm^{-2}$
Current	Amper	I	A

Faraday's Laws

Any electrochemical reaction involves passage a current through the electrode solution interface.

The current is carried by electrons, therefore, at the electrode/ solution interface electrons are transferred from the electrode to the solution ions (at the cathode) or conversely, from the ions to the electrodes (at the anode)



$$Cu^{+2} + 2e \xrightarrow{\text{reduce}} Cu^{\bullet} \downarrow$$ **(Reduction Process) (cathode)**

$$Zn^{\bullet} \xrightarrow{\text{oxide}} Zn^{+2} + 2e$$ **(Oxidation Process) (anode)**

Reduction Processes

The processes which involve the transfer of electron from the electrode to the solution

Oxidation Processes

The processes which involve the transfer of electron from the solution to the electrode

Faraday's First Law

The amount of substance which reacted at the electrodes is directly proportional to the quantity of electricity which has passed through the solution.

$Q \alpha W$

$Q = It$

$W \alpha It$

$W = E_e It$

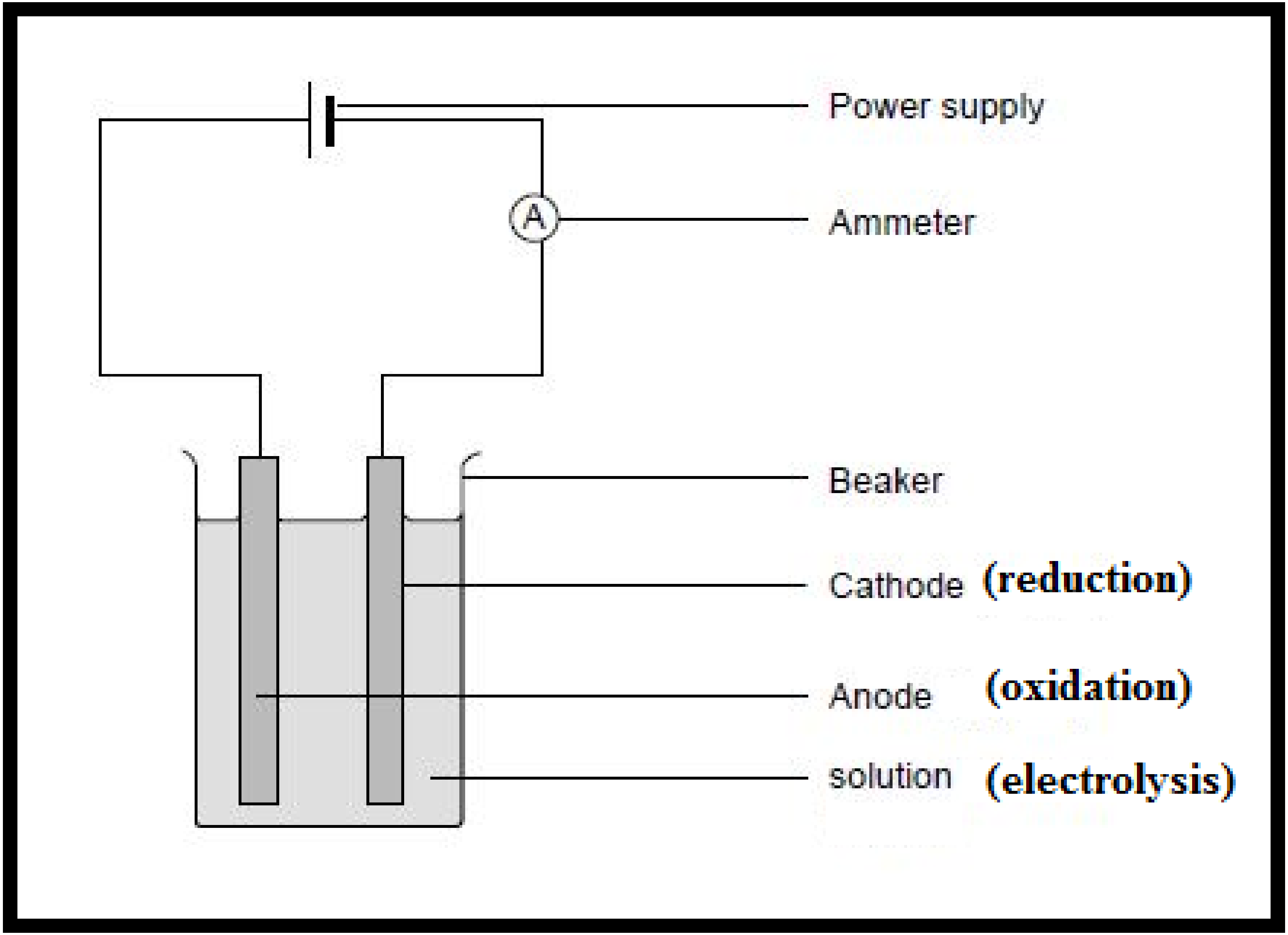
where W is weight of chemical change at an electrode (g)

Q is the amount of electricity (C)

I is the intensity of current (Ampere)

t is the time (s)

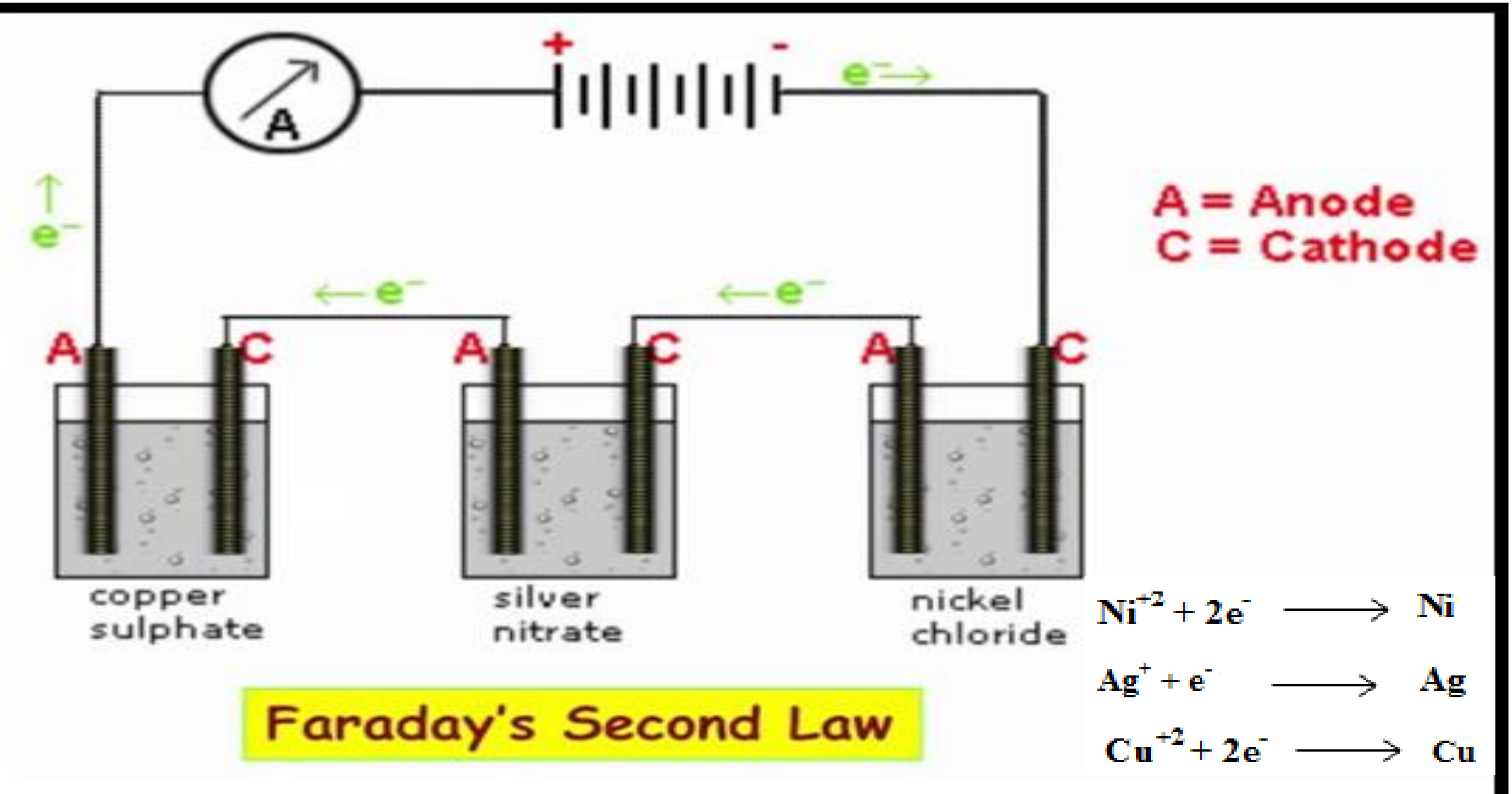
E_e is electrochemical equivalent



Power supply
A
Ammeter
Beaker
Cathode (reduction)
Anode (oxidation)
solution (electrolysis)

Faraday's Second Law

When the same quantity of electricity is passed through different electrolytes, the mass of various substances which reacted or deposited at the electrodes is directly proportional to the chemical equivalent or equivalent weight of these substance.



$Ni^{+2} + 2e^- \longrightarrow Ni$

$Ag^{+} + e^- \longrightarrow Ag$

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

W α e

Chemical Equivalent (e) = Atomic Weight / valence

$$e = \frac{M}{z}$$

Q/ Calculate the chemical equivalent of Cu^{+2}, Ag^{+1}, H^{+}. If you know the atomics weights of the cations respectively are 63.6, 107.9, and 1.008

Link between first and second lows of Faraday's

as

$W \alpha Q$……….(From Faraday's first Low) ….. (1)

$W \alpha e$ …….(From Faraday's second Low)…..(2)

Therefore

$W \alpha Qe$ ………………………………… ….(3)

as $Q = It$

therefore

$W \alpha Ite$ ……………………………………(4)

as $e = \frac{\mu}{z}$ ……………………………………(5)

after change the α to the constant

$W = \bar{K} It \frac{\mu}{z}$ ………………………………………… (6)

$\bar{K} = \frac{1}{F} = \frac{1}{96487}$

$Q = C = A.s$

So

$W = \frac{It\mu}{FZ}$ ………………………………………………(7)

$W = \frac{Q\mu}{FZ}$ ….. ………………………………………(8)

Note/

$$\bar{e} = \frac{e}{F}$$

$\bar{e}$ = electrical chemical equivalent

Q1/ How many coulombs are required for the following reduction

1- 1 mole of Al^{+3} to Al
2- 1 mole of Cu^{+2} to Cu

Q2/ How many coulombs are required to 50gm of Al from molten Al_2O_3? If you know the Atomic Weight of Al = 27.

Q3/ $Ni(NO_3)_2$ solution is electrolyzed between pt electrodes using a current of 5.0 Ampere for 30 minutes. What is the Weight of Ni will be produced at the cathode? If you know the atomic Weight of Ni =58.69.

Q4/ The current passage was 15A through silver nitrate solution for 10 sec that required to precipitate 9.9gm silver. What is the current efficiency? If you know the atomic Weight of Ag= 108.

Q5/ The current passage was 0.1A through CuSO4 solution for 10 min at 25C°, if used pt electrode as cathode. If you know the atomic Weight of Cu= 63.5.

- **Calculate copper weight at cathode?**
- **Calculate Oxygen volume is evolved at anode at 740 mmHg**?

Applacations of Faraday's Laws

Coulometer is an instrument of chemical analysis that determines the amount of a substance released in electrolysis by measurement of the quantity of electricity used.

There are three types of coulometers:-

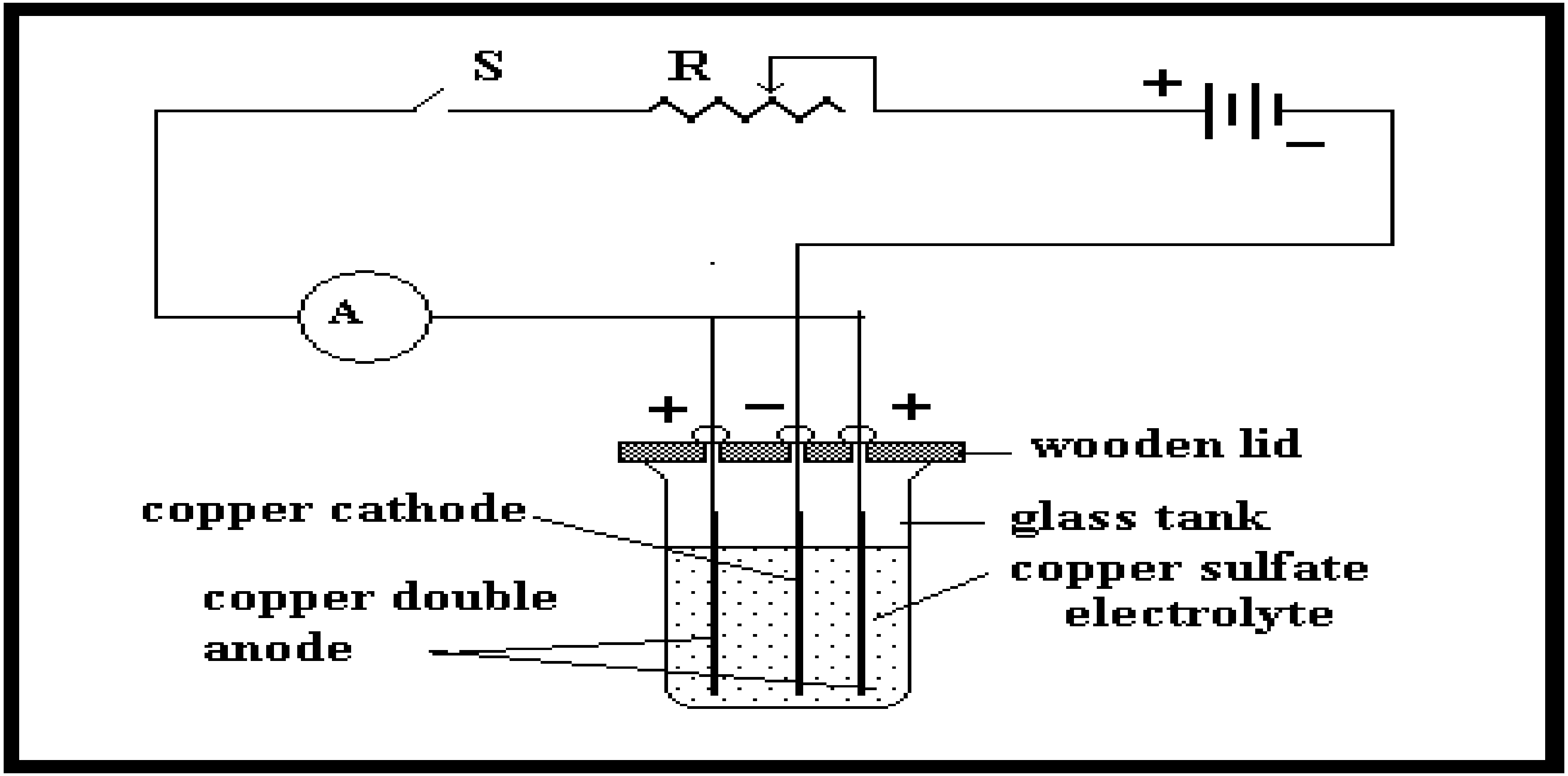
1-Weight coulometer

The quantity of electricity is determined by the amount of metal deposited cathodically silver and copper coulometer.
The copper coulometer is essentially on glass vessels electrolytic copper plates attached to its opposite walls.
The cathode is placed between these plates and the aqueous solution consists of:

$CuSO_4.5H_2O$ (125-150)gm, H_2SO_4 (50 gm) as factor assist, and ethanol (50gm) in order to prevent oxidation of the copper deposited at the cathode.

The current density at the cathode should be within (20 to 200) A/cm². After the electrolysis has been completed, the cathode is quickly washed with distilled water and then ethanol to avoid oxidation of cathode electrode. Then, it's dried and weighted.

The accuracy of copper coulometer is (0.1- 0.05%)



The purpose of using two electrodes of an anode in order to increase the efficiency

2- Titration Coulometer

The quantity of electricity is determined by titration of the substance formed in the solution during electrolysis.

3- Volume coulometer

The quantity of electricity is determined by the volume of gas that evolved during (from anodic) electrolysis.

$H_2O \leftrightarrow H^+$ **(at cathode) +** OH^- **(at anode)** $\rightarrow O_2\uparrow$ **(at anode)**

Electrical conductance

The measurement of the conductivity in solution is carried out in vessels provided with electrodes that surface area (A) and distance (l) between two electrodes must be known.

In general, electrolytes, that conductivity is well known are used to calibrate the cell.

The equation below which gives the resistance

$$R \, \alpha \, \frac{l}{A}$$

$$R = \rho \, \frac{l}{A} \quad \text{..............................}(1)$$

$$\rho = R \, x \, \frac{A}{l} \quad \text{..............................} \; (2)$$

Where

R is the resistance (Ω, ohm)

ρ is the specific resistance (Ω.cm)

A is the electrode's area (cm^2)

l is the distance between two electrods (cm)

$$G = \frac{1}{R} \qquad \text{.................................}(3)$$

G is the conductance (Ω^{-1}or S or mho)

$$L = \frac{1}{\rho} \qquad \text{.................................}(4)$$

L = Specific conductance(conductivity)

(Ω^{-1}. cm^{-1}) or (S. cm^{-1})or(mho. cm^{-1})

$$L = \frac{1}{\rho} = \frac{1}{R} \times \frac{l}{A} \qquad \text{.......................}(5)$$

So

$$L = G \times \frac{l}{A} \quad \text{……………………..(6)}$$

$$R = \frac{E}{I} \text{ (from ohm law) …………..(7)}$$

Where **E** = potential

I = Current

After Instead of equation 7 in equation 5

$$L = \frac{I}{E} \times \frac{l}{A} \rightarrow L = \frac{I}{A} \times \frac{l}{E} \quad \text{………(8)}$$

$$L = \frac{I/A}{E/l}$$

As

$$i = \frac{I}{A} \quad \text{and} \quad E_i = \frac{E}{l}$$

So

$$L = \frac{i}{E_i} \text{…………………………(9)}$$

where i is the current density

E_i is the potential energy.

Cell constant

L= G. $\frac{l}{A}$ …………(1)

K = $\frac{l}{A}$ (K= cell constant)

So

L = G.K …………(2)

Equivalent Conductance and Molar Conductance

$\lambda = \dfrac{1000\,L}{C}$ (Equivalent conductance) ($S.cm^2.eq^{-1}$) ……….(3)

$\lambda = \dfrac{1000\,L}{N}$ where N = normality

$\lambda = \dfrac{1000L}{C}$ (Molar conductance) ($S.cm^2.mole^{-1}$) ……… (4)

Equivalent conductance = (Molar conductance)/n

n = (M.Wt)/(Eq.Wt)

Q/ Why use KCl solution when the measured conductivity?

KCl solution has physical properties are

1. It is easily dissolve
2. It is stable at high temperature
3. It has high molecular weight
4. It is non-hygroscopic

Q/ The specific resistance (ρ) of metal is 2.8×10^{-8} Ω.cm. calculate the voltage a cross metal wire if length is 1m and diameter 2mm, the current pass its wire is 1.25A.

Solvent Correction

Solution = Solute + Solvent

$KCl + H_2O \rightarrow K^+ + Cl^-$

R Solution = R Solute + R Solvent

G Solution = G Solute + G Solvent

$$\frac{1}{\text{R Solution}} = \frac{1}{\text{R Solute}} + \frac{1}{\text{R Solvent}}$$

$$\frac{1}{\text{R Solute}} = \frac{1}{\text{R Solution}} - \frac{1}{\text{R Solvent}}$$ (Correction equation)

The equation is used when the diluted solution, weak solution, and contamination solution.

$$CH3COOH + H_2O \rightarrow CH_3COO^- + H_3O^+$$
$$2H_2O \leftrightarrow OH^- + H_3O^+$$
$$HCl + H_2O \rightarrow H_3O^+ + Cl^-$$

Note/

Correction process is carried out for solvent when the question has G or L also when mentioned distilled water.

Conductivity Measurement

Conductance is the reciprocal of resistance. Hence, the Conductance can be obtained by the measurement of the resistance and latter can be found by Wheatstone bridge method shown in Figure 1.

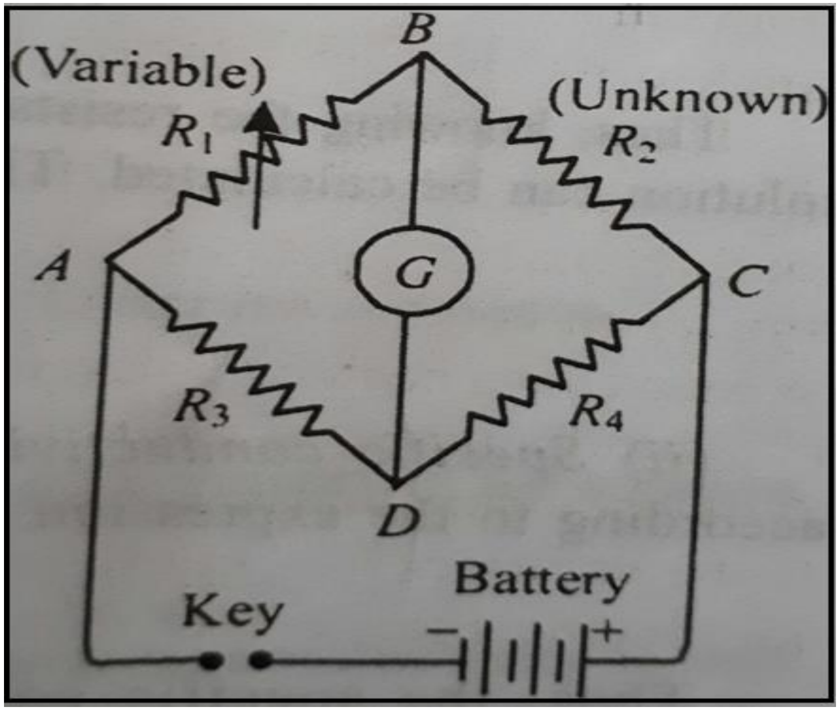


Figure1: Principle of Wheatsatone bridge method

It consists of four resistances R_1, R_2, R_3, R_4 arranged in a manner as shown in figure 1. R_1 is the variable resistance and R_2 is the unknown resistance. When null point is obtained, i.e, there is no deflection in the galvanometer G, we have

$$R_1/ R_2 = R_3/R_4$$

Knowing the values of R_1, R_3 and R_4, R_2 can be calculated.

In finding the resistance of the solution of an electrolyte, a special type of cell has to use such that the solution is present between the two electrolytes. The cell thus used is called conductivity cell. It is made up of Pyrex glass and two platinum electrodes at a fixed distance apart as shown in Figure 2.

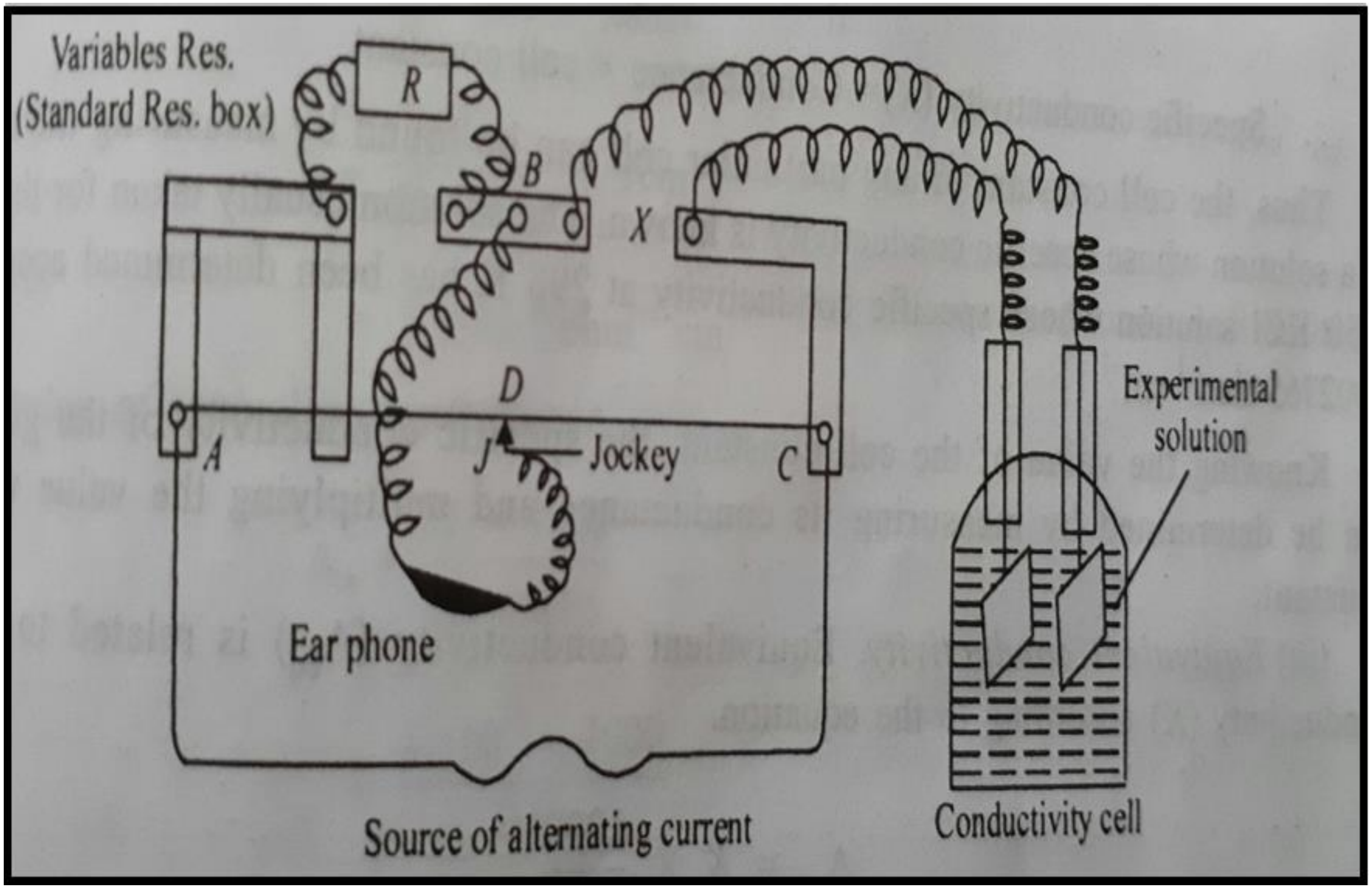


Figure 2: Apparatus for the measurement of electrolytic conductance

Various designs of conductivity cells are available. If direct current is used, it causes electrolysis of the solution and these results in the change in the resistance of the solution. These effects are called polarization effects.

To overcome this problem, an alternating current of frequency 50-200 cycles per second is used. Also we have to use a head phone instead of a galvanometer to detect the null point.

The complete assembly for the measurement of the electrolytic conductance is shown in figure 2.

A suitable value of the resistance R is introduced from the standard resistance box such that when the sliding contact, i.e, the jockey J is moved along the stretched wire, the sound in the earphone is reduced to minimum at a point somewhere in the middle of the wire AC, say at the point D. then, if X is resistance of the electrolyte solution, by Wheatstone bridge principle,

So

$$\frac{Resistance\ R}{Resistance\ X} = \frac{Resistance\ of\ wire\ AD}{Resistance\ of\ \ wire\ CD} = \frac{Length\ AD}{Length\ CD}$$

$$Resistance\ X = Resistance\ R\ .\frac{Length\ CD}{Length\ AD}$$

Q1/what is the purpose of using alternating current instead of direct current?

sol/ using alternating current in order to avoid the polarization effects which causes electrolysis of the solution and these results will change the resistance of the solution.

Q2/ The resistance of a conductivity cell when filled with 0.02M KCl solution is 164 ohm at 298K. However, when filled with 0.05M $AgNO_3$ solution, its resistance is found it be 78.5 ohm. If the specific conductivity of 0.02M KCl is 2.768 x10^{-3} ohm^{-1}.cm^{-}1. Calculate:

A- The specific conductivity (L) of 0.05M $AgNO_3$

B- The molar conductivity of $AgNO_3$ Solution

Q3/ Calculate resistance for 0.01N KCl solution if that equivalent conductance (λ) is equal 141.3 $cm^2.ohm^{-1}.eq^{-1}$, the cell constant is 1.48cm^{-1}, conductivity of distilled water is 10^{-6} $ohm^{-1}.cm^{-1}$.

Q4/ There resistance of conductivity cell, when filled with 0.1N KCl solution, is 24.36 ohm. However, when filled with 0.1M CH_3COOH solution, its resistance it's found 1.1658 ohm. If specific conductivity of 0.1N KCl is 0.01285 $ohm^{-1}.cm^{-1}$ and the conductivity of distilled water is $7.5x10^{-6}$ $ohm^{-1}.cm^{-1}$. How can you calculate the equivalent conductance for CH_3COOH.

variation of conductivity with a concentration

Based on

Debye-Huckel-Onsagar equation that manages the change of conductance of a strong electrolyte with concentration

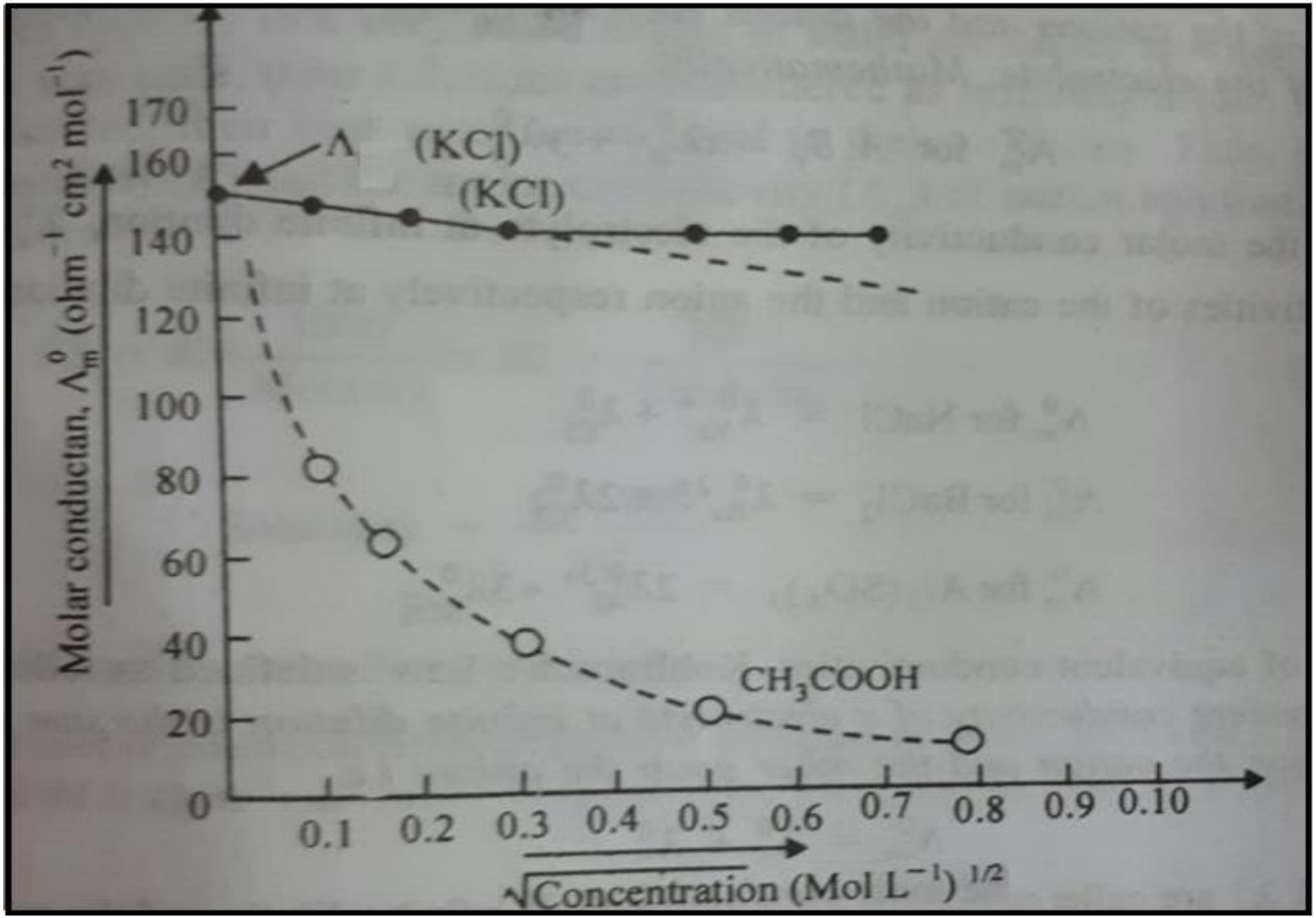
$$\lambda = \lambda_o - k\sqrt{C}$$

where, λ = molar conductance of the solution at the concentration C.

λ_o = molar conductance at infinite dilution.

C = Concentration of the solution. k is constant for a Particular solvent at a particular temperature

The solution Based on Debye-Huckel-Onsagar equation. A plot of λ against $\sqrt{C}$ is a straight line as shown in Figure below. In a strong electrolyte as KCl, there is not much variation in conductance with dilution. This is because of the fact that a strong electrolyte is 100% ionized even in a concentrated solution. In a concentrated solution, there are interionic attractions which decrease the mobility of the ions. With dilution, these attractive forces are weakened resulting in greater mobility of the ions. Thus, there is slight increase in the conductance of the solution of a strong electrolyte on dilution. The plot becomes linear at low concentration can be extrapolated to y-axis.



Variation of molar conductivity with concentration of strong electrolyte (KCl) and weak electrolyte (CH_3COOH) with concentration

Based on Kohlrausch Law

$$\lambda_{o} = \lambda_{o}^{+} + \lambda_{o}^{-}$$

λ_{o} is molar conductivity of the electrolyte at infinite dilution.

λ_{o}^{+} , λ_{o}^{-} are the conductivities of the cation and the anion respectively at infinite dilution.

2-Application of Kohlrausch Law

A- Calculation of molar conductivity at infinitedilution (λ) for weak electrolyte.

Ex/ CH_3COOH

$\lambda°(CH_3COOH) = \lambda^{o}_{\mathrm{CH_3COO^-}} + \lambda^{o}_{H^+}$

This equation can be arrived at by knowing the molar conductivity at infinite dilution for the strong electrolytes KCl, CH_3COOK, and HCl. As per Kohlrausch's Law,

$\lambda°(KCl) = \lambda^{o}_{\mathrm{K^+}} + \lambda^{o}_{Cl^-}$

$\lambda°(CH_3COOK) = \lambda^{o}_{\mathrm{CH_3COO^-}} + \lambda^{o}_{K^+}$

$\lambda°(HCl) = \lambda^{o}_{\mathrm{H^+}} + \lambda^{o}_{Cl^-}$

Hence, we have

$\lambda^{o}_{\mathrm{CH_3COO^-}} + \lambda^{o}_{H^+} = (\lambda^{o}_{\mathrm{CH_3COO^-}} + \lambda^{o}_{K^+}) + (\lambda^{o}_{\mathrm{H^+}} + \lambda^{o}_{Cl^-}) - (\lambda^{o}_{\mathrm{K^+}} + \lambda^{o}_{Cl^-})$

$\lambda°(CH_3COOH) = \lambda°(CH_3COOK) + \lambda°(HCl) - \lambda°(KCl)$

B-Calculate of the degree of dissociation for weak electrolyte At infinity dilution.

then we have

Degree of dissociation, (α) = $\frac{\lambda^{C}}{\lambda^{O}}$

The value of λ^{O} **for weak electrolytes can be calculated using Kohlrausch Law.**

C-Calculation of solubility of a sparingly soluble salt

Such as AgCl, $BaSO_4$, $PbSO_4$ etc., which dissolve to a very small extent in water, are called sparingly soluble salt. As they dissolve very little, their solutions are considered as infinity dilute. Further as their solutions are saturated, their concentration is equal to their solubility. Thus, by determining the specific conductivity (L) and the molar conductivity (λ^{O}) of such solution, we can obtain solubility as follows:

$$\lambda^{O} = \frac{1000\,L}{Molarity} = \frac{1000L}{Solubility(S)}$$

$$Solubility = \frac{1000\,L}{\lambda^{O}}$$

Q1/ If the molar conductivities at infinity dilution of NaCl, HCl, and CH_3COONa are 126.4, 426.1, and 91.0 $ohm^{-1}.cm^2. mol^{-1}$. What will be that of acetic acid?

Q2/ At 291 K, the molar conductivity, at infinity dilution of NH_4Cl, NaOH, and NaCl are 129.8, 217.4, and 108.9 ohm^{-1} cm^2 $mole^{-1}$ respectively. if the molar conductivity of a normal solution of NH_4OH is 9.33 ohm^{-1} cm^2 $mole^{-1}$, what is the percentage dissociation of NH_4OH at this dilution.

Q3/ From the following molar conductivity at infinity dilution:

λ^{o} for $Ba(OH)_2$ = 457.6 ohm^{-1} cm^2 mol^{-1}
λ^{o} for $BaCl_2$ = 240.6 ohm^{-1} cm^2 mol^{-1}
λ^{o} for NH_4Cl = 129.8 ohm^{-1} cm^2 mol^{-1}
Calculate λ^{o} for NH_4OH.

3-Application of Ostwald dilution Law

Calculation of dissociation constant of weak electrolytes

	AB	$\leftrightarrow$	A^+	+	B^-
Initial concentration	C		0		0
Concentration at equilibrium	$C(1-\alpha)$		$C\alpha$		$C\alpha$

$$K_d = \frac{[A]^+[B]^-}{AB} = \frac{C\alpha \, . \, C\alpha}{C(1-\alpha)}$$

$$K_d = \frac{C\alpha^2}{1-\alpha}$$

If the degree of dissociation α is very small, as in the case of weak electrolytes at ordinary concentration, α can be neglected in comparison to 1 in the denominator of expression.

$$K_d = C\alpha^2 \text{ or } \quad \alpha^2 = \frac{K_d}{C}$$

$$\alpha = \sqrt{\frac{K_d}{C}}$$

α = degree of dissociation, C = Concentration (mole/L),

K_d = dissociation constant

Q4/ A base has a dissociation constant equal to 1.8×10^{-5} at 298 K. Calculate its degree of dissociation at a concentration of 0.1 N at the same temperature.

Q5/ A solution of ammonia gives the following values of equivalent conductivity at different dilution:

V (L)	8	16	32
λ ohm^{-1} cm^{2} eq^{-1}	3.02	4.45	6.32

If equivalent conductivity in infinite dilution of NH_4OH is 237 ohm^{-1} cm^{2} eq^{-1}, show that the above given data establish the truth of Ostwald's dilution law.

Q6/ Calculate the hydrogen ion concentration of a solution of formic acid containing 0.092 g of acid per liter. The dissociation constant at 25C° is 2.14×10^{-4}.

Q7/ The specific conductance of AgCl solution at 25 C° is 3.41×10^{-6} $ohm^{-1} cm^{-1}$ while the specific conductance of water 1.6×10^{-6} ohm^{-1} cm^{-1}. Calculate the solubility of AgCl in the water. If you know the equivalence conductivity of salt in infinity dilution is 134.3 ohm^{-1} cm^2 eq^{-1}

Q7/ The specific conductance of AgCl solution at 25 C^{o} is 3.41 x 10^{-6} ohm^{-1}cm^{-1} while the specific conductance of water 1.6 x 10^{-6} ohm^{-1} cm^{-1}. Calculate the solubility of AgCl in the water. If you know the equivalence conductivity of salt in infinity dilution is 134.3 ohm^{-1} cm^{2} eq^{-1}

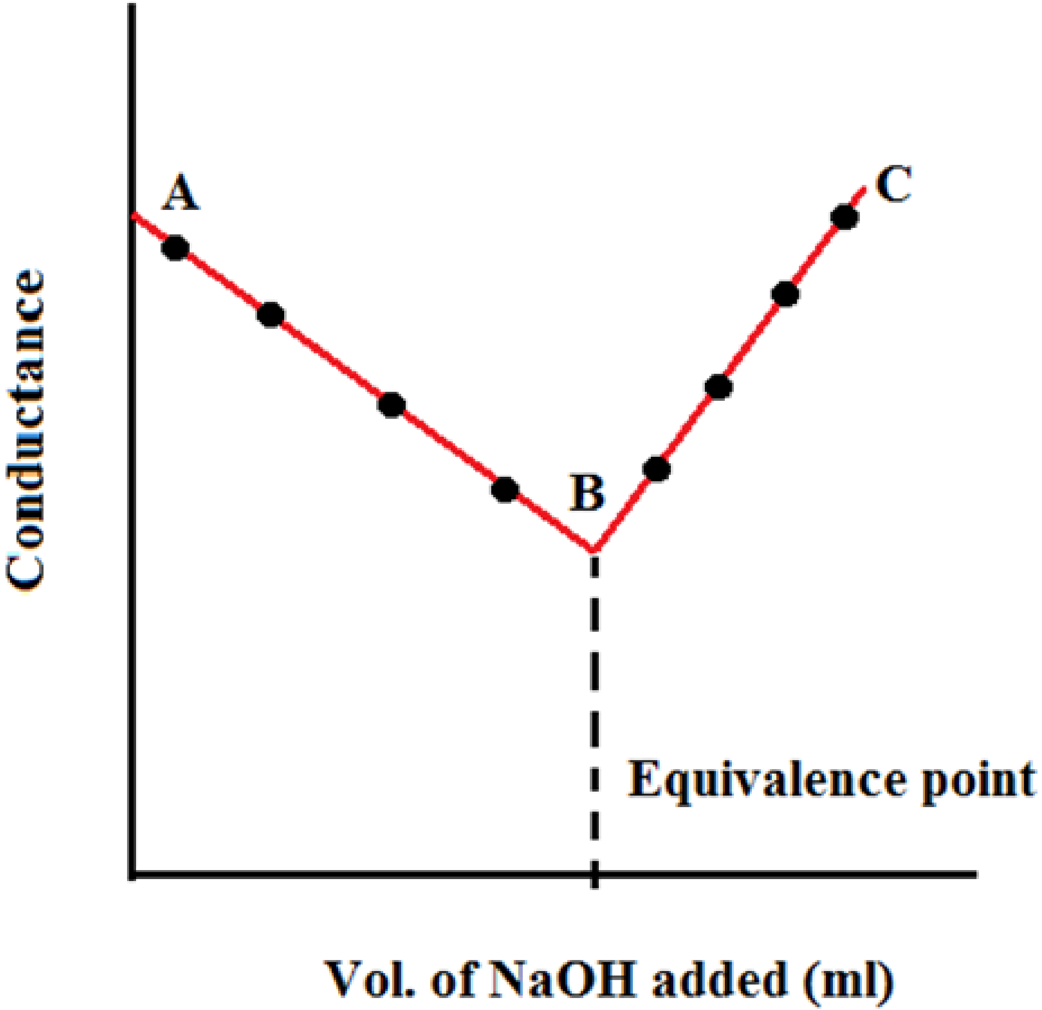
Conductometric titration

A. Conductometric titration of strong acid with strong base

Suppose a solution of HCl is to be titrated against NaOH solution. For this purpose, the acid solution is taken in a beaker and the NaOH solution in the burette. The conductance of the acid solution is noted initially as well as after successive additions of small amount of NaOH solution. Evidently, the conductance of the acid solution in the beginning is very high because it contains highly mobile H^+ ions ($HCl \rightarrow H^+ + Cl^-$). As NaOH solution is added to the HCl solution, the H^+ ions are replaced by the slow moving Na^+ ions and hence the conductance of the solution after all the H^+ ions are replaced by Na^+ ions decreases.

$$H^+ + Cl^- + Na^+ + OH^- \rightarrow Na^+ + Cl^- + H_2O$$

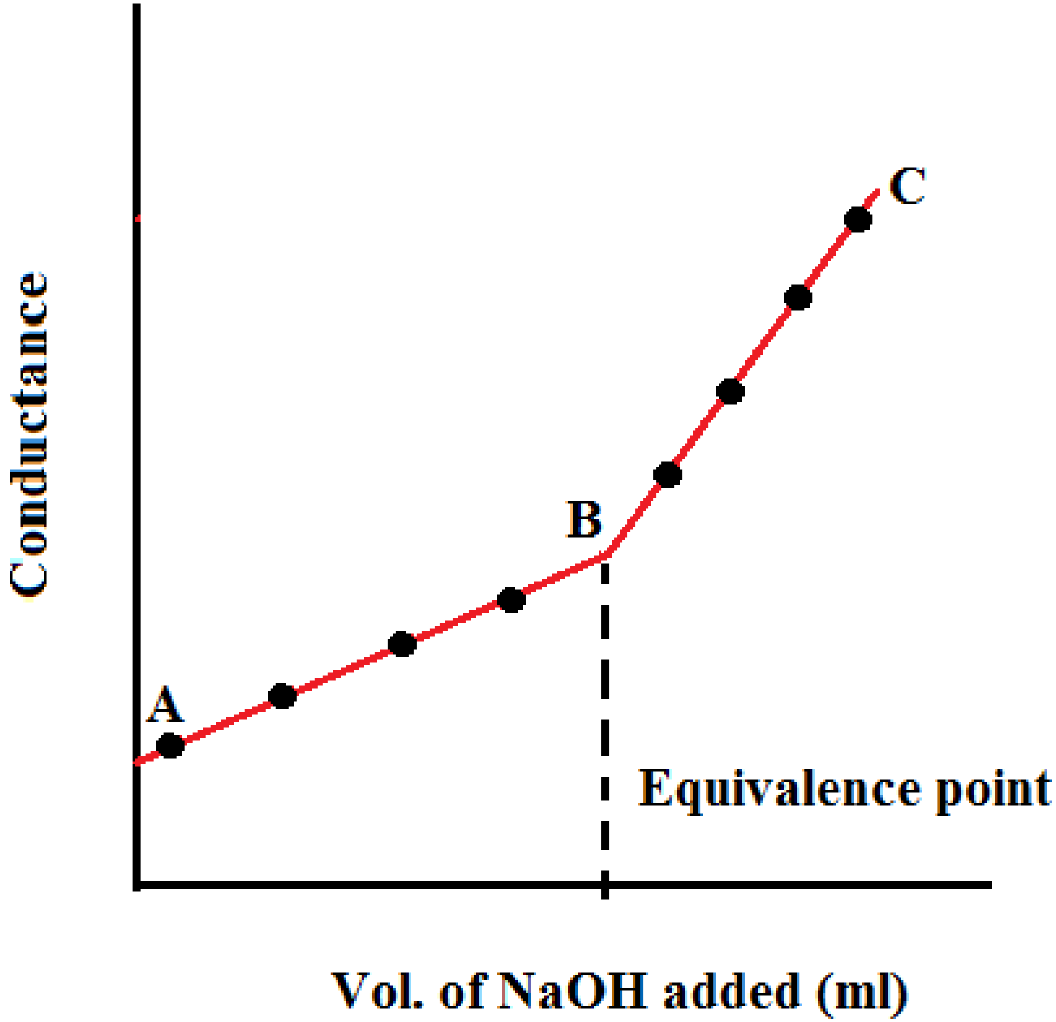
After the end point, further addition of NaOH solution brings in fast moving OH^- ions and hence the conductance of the solution again starts increasing. If conductance values are plotted against the volume of the alkali added, a curve of type ABC is obtained as shown fig below. Point of intersection (point B) corresponds to the end point.



Strong acid with strong base

B. Conductometric titration weak acid with strong base

Suppose a weak acid like acetic acid is titrated against a strong base like NaOH. The conductance of the acid initially is very low because of low ionization of the acid. However as NaOH solution is added more and more to the acid solution, the salt produced (CH_3COONa). CH_3COONa is highly ionized and hence the conductance keeps on increasing along the line AB as shown in figure below. When the whole of acetic acid has been neutralized, further addition of NaOH solution causes the conductance to increase sharply along the line BC because the NaOH added introduces the fast moving OH^- ions. Intersection of the two lines AB and BC, at the point B gives the equivalent point.



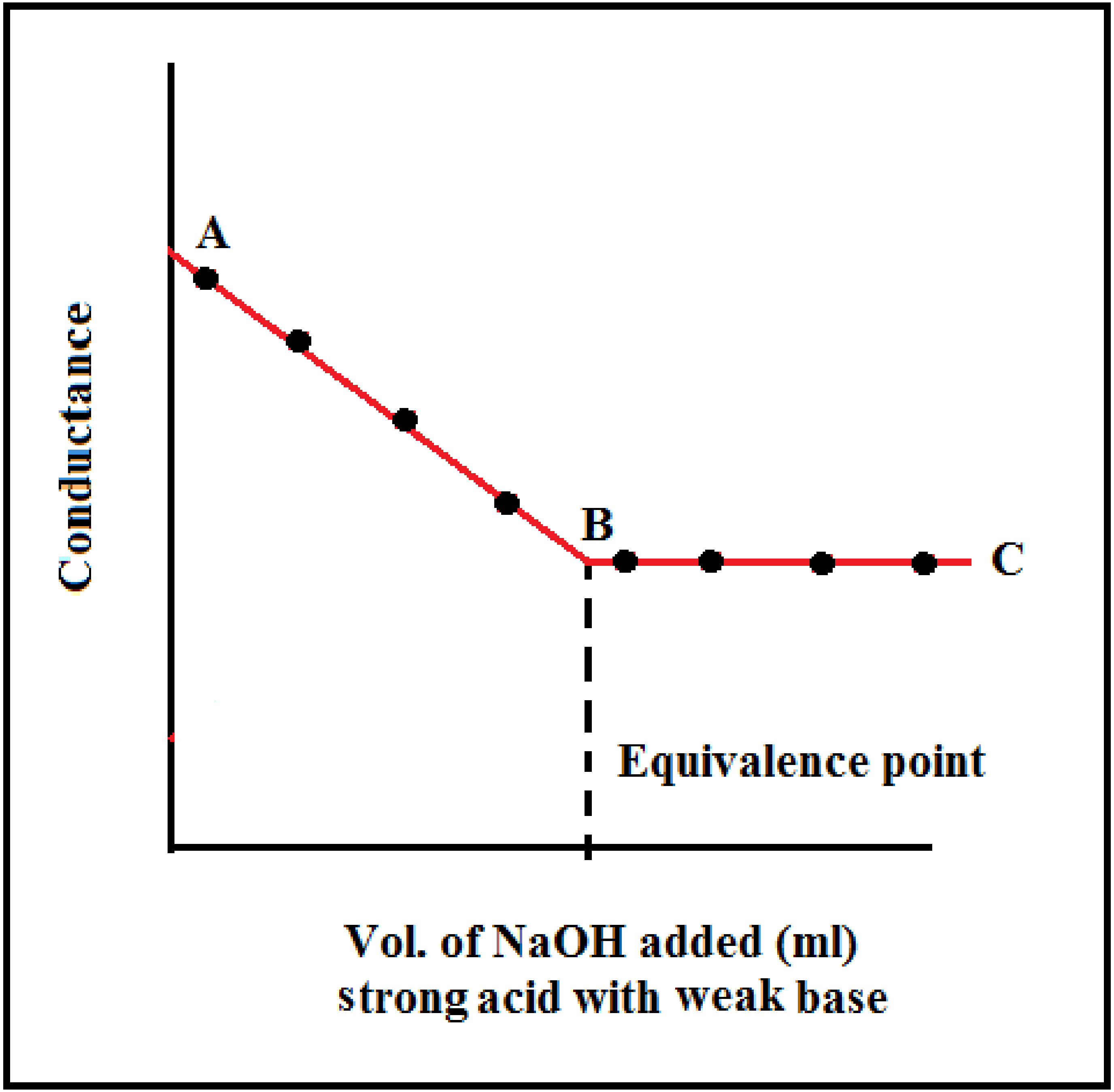
weak acid with strong base

C. Conductometric titration strong acid with weak base

Titration strong acid with a weak base let us consider the titration of HCl against NH_4OH solution. The conductance of HCl solution is initially high because of the presence of the fast moving H^+ ions. As NH_4OH solution is added, the fast moving H^+ ions are replaced by the slower NH_4^+ ions and hence the conductance falls along the line AB.

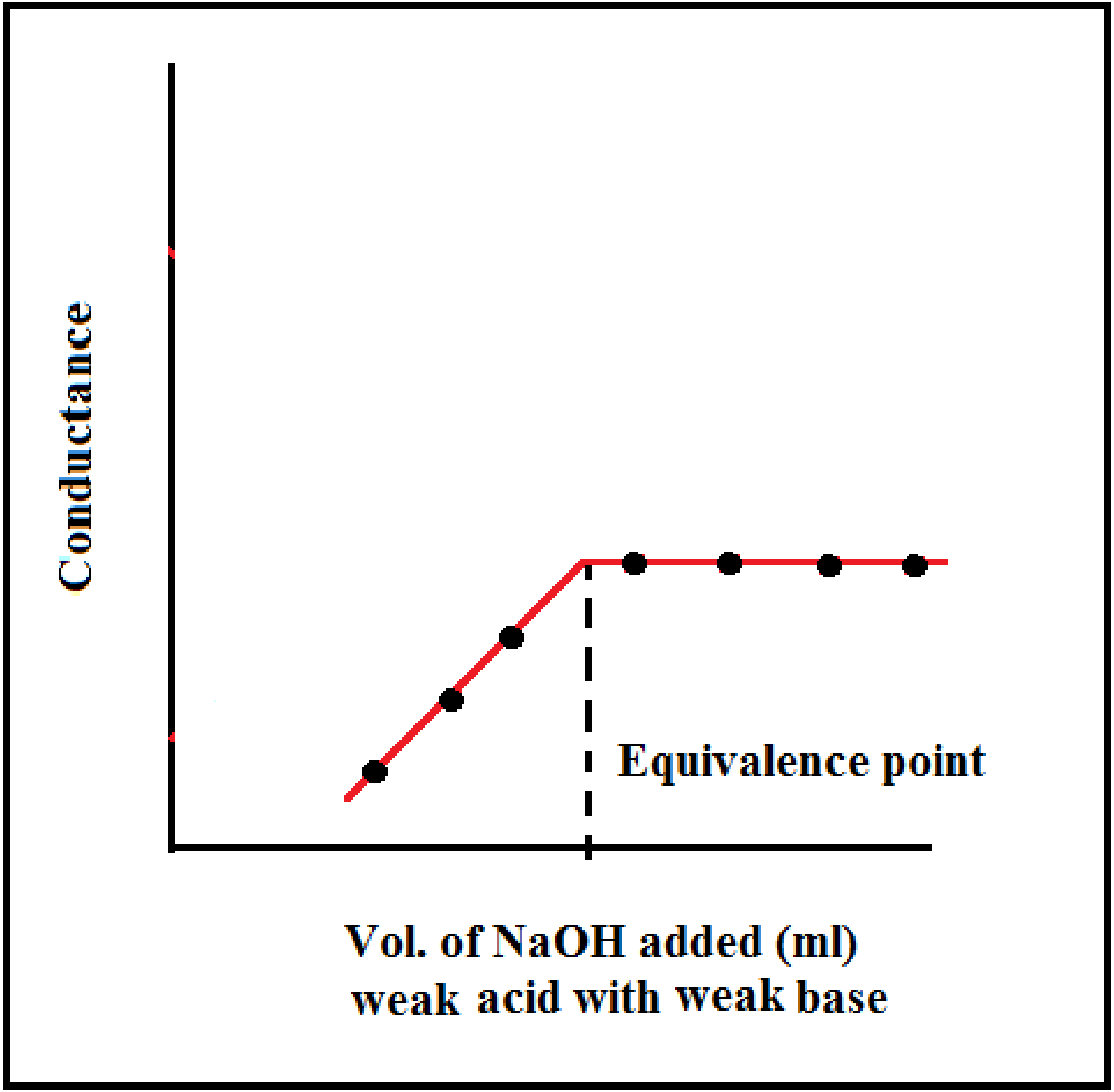
$H^+ + Cl^- + NH_4OH \rightarrow NH_4^+ + Cl^- + H_2O$

When the end point is passed, further addition of NH_4OH does not cause much change in the conductance because NH_4OH is a weakly ionized substance. The line BC is thus almost horizontal (figure below).


A
B
C
Conductance
Equivalence point
Vol. of NaOH added (ml)
strong acid with weak base

D. Conductometric titration weak acid with weak base

Conductometric titration are particularly valuable as we do not get sharp end points with indicators. Consider the titration of acetic acid with ammonium hydroxide. Initially, the conductance of the solution is low due to poor dissociation of acetic acid. As the base is added to it, the conductance starts picking up due to the formation of ionizable ammonium acetate. After the neutralization point, conductance remains almost constant, because the free base NH_4OH is a weak electrolyte. This is illustrated in the figure below.


Conductance
Equivalence point
Vol. of NaOH added (ml)
weak acid with weak base

Advantages of conductometric titration

1. These titrations can be used for colored solution where ordinary indicators fail.

2. As the end point in these titrations is the intersection of two lines, no extra care is needed near the end point.

3. These can be used for the titration of mixture of weak and strong acids. These can be used for the titration of even very dilute solutions.

Ionic Mobility

Ionic Mobility (U): It is the distance travelled by the ion per second under the potential gradient of 1 volt/cm.

Potential Gradient (P.G) or (E): It is the potential applied between two electrodes present at a distance of 1 centimeter.

If the distance between two electrodes is (x)

So

P.G or (E) = P.D/ x

Where

P.G or (E) = Potential Gradient (V/cm)

P.D = Potential Difference (V)

x = distance between two electrodes (cm)

U = Velocity of ion/ E ($V^{-1}cm^{2}\ sec^{-1}$)

Ionic Mobility depends on

1- The charge and size of ion
2- Electric field
3-The number of molecular of solvent.

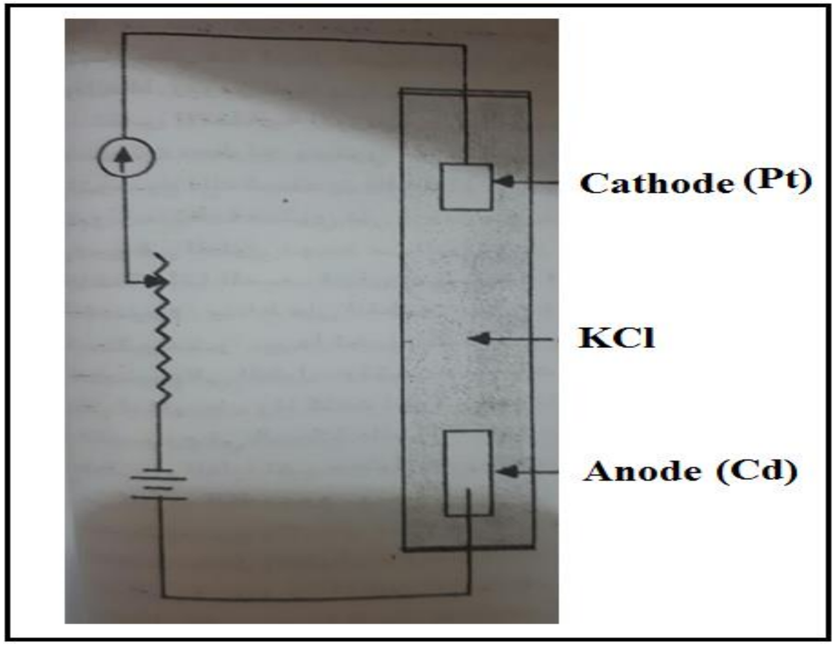
The velocities of ion changed with electric field.

Ionic velocities at field strength of E are known as absolute ionic velocities.

So

Velocity of ion = $\frac{X}{t}$

The ionic mobility is practically measured by boundary method through measured the velocity of moving a boundary between two solutions, one of which contains a certain concentration of ions as shown in figure below



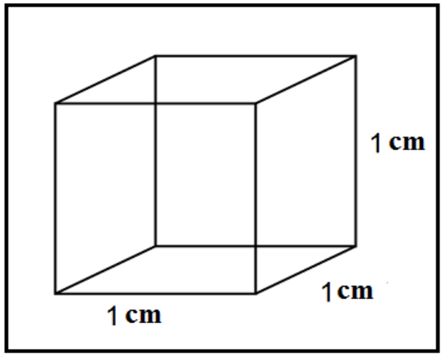
Moving boundary method

The ionic mobility is

$U = \frac{X}{tE}$ (v^{-1} cm^{2} s^{-1})

as

the resistance of the solution in cubic is



$E = iR$

as

$R = \frac{1}{L}$

$i = \frac{I}{A}$

So

$E = \frac{I}{A} \cdot \frac{1}{L}$

$$U = \frac{X}{tE}$$

So

$$U = \frac{X}{t\left(\frac{I}{A.L}\right)}$$

$$U = \left(\frac{X.A}{tI}\right).L$$

Where ($\frac{X}{t}$) is the velocity, ($\frac{X.A}{t}$) is unit of volume in unit of time, and ($\frac{X.A}{tI}$) is unit of volume in unit of time and current.

If we replace the value of ($\frac{X.A}{tI}$) by volume (v) the equation becomes

U = vL

Where v = is the volume of solution for ampere in time and current unit.

Relationship between ionic mobility and limiting ionic conductance

According to ohm's low, the relationship between the current and the applied voltage is given by

$$R = \frac{E}{I}$$

$$I = \frac{E}{R} = \frac{E}{1/L}$$

as

$$E = 1 \text{ volt/cm}$$

$$\therefore I = \frac{1}{1/L} = L$$

$$\therefore I = L$$

For the solution contain (cation and anion) for 1-1 electrolyte

Strong electrolyte

$C = C^+ = C^-$

$U = U^+ = U^-$

Where

U^+ = mobility of cation

U^- = mobility of anion

$C^+ U^+$ =equivalent of cation which transfer to cathode

$C^- U^-$ = equivalent of anion which transfer to anode

Then

The total current is

$I = L = F\,[C^{+} U^{+} + C^{-} U^{-}]$

$L = CF\,[U^{+} + U^{-}]$

as

$\lambda = \frac{L}{C} = CF\,[U^{+} + U^{-}]$

as

$\lambda = \lambda_{+} + \lambda_{-}$

$\lambda_{+} = FU^{+}$

$\lambda_{-} = FU^{-}$

where

λ_{+} and λ_{-} are limiting ionic conductance for cation and anion respectively.

Q1/ A potential of 9 volts is applied between two electrodes placed 0.15 cm apart. A dilute solution of ammonium chloride is placed between the electrodes and NH_4^+ ions is found to cover a distance of 1.6×10^{-2} cm in 1 hour. What is the ionic mobility of the NH_4^+ ion?

Q2/ Calculate the specific conductance for 0.1 mole of 1L of sodium chloride solution in 25 C^o if you know: Ionic mobility of Na+, Cl^- in this solution are $42.6 \times 10^{-5}\ V^{-1} cm^2\ sec^{-1}$ and $68 \times 10^{-5}\ V^{-1} cm^2\ sec^{-1}$ respectively.

Q3/ Boundary method was carried to determine ionic mobility using a 0.1 N of potassium chloride solution. The applied potential and current was passed led to move a barrier to 4.64 cm through 67 minutes. If you know the current was 5.21 mA and a tube's area was 0.230 cm^2. The specific conductance of the potassium chloride solution at 25 ° C is 0.0129 $ohm^{-1}cm^{-1}$. Calculate ionic mobility of potassium ion.

Q4/ what is the distance that ammonium ion was moved by one hour in a dilute solution of an ammonium salt at 25 C^o. the distance between two electrodes was 9.8 cm and the applied potential was 5.6 volt. If you know the conductivity of infinity dilution of ammonium ion is73.4 $ohm^{-1}\ cm^2\ mole^{-1}$

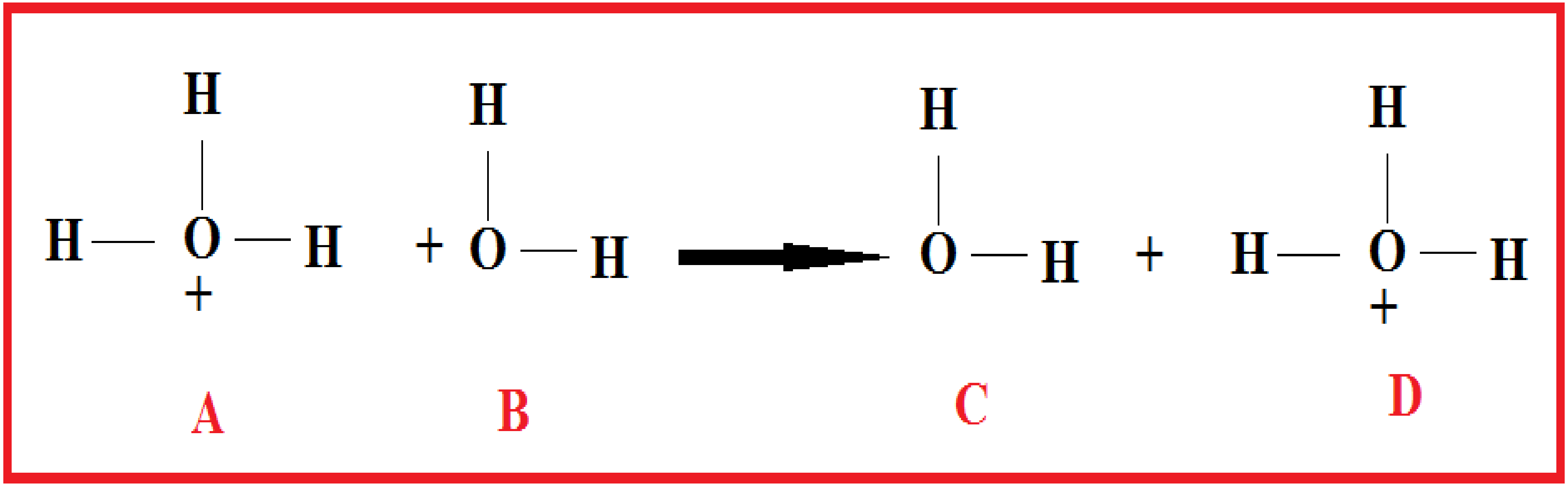
Mobilities of hydrogen and hydroxyl ion

The high mobility of hydrogen ion is observed only in hydroxylic solvents, such as water and alcohols

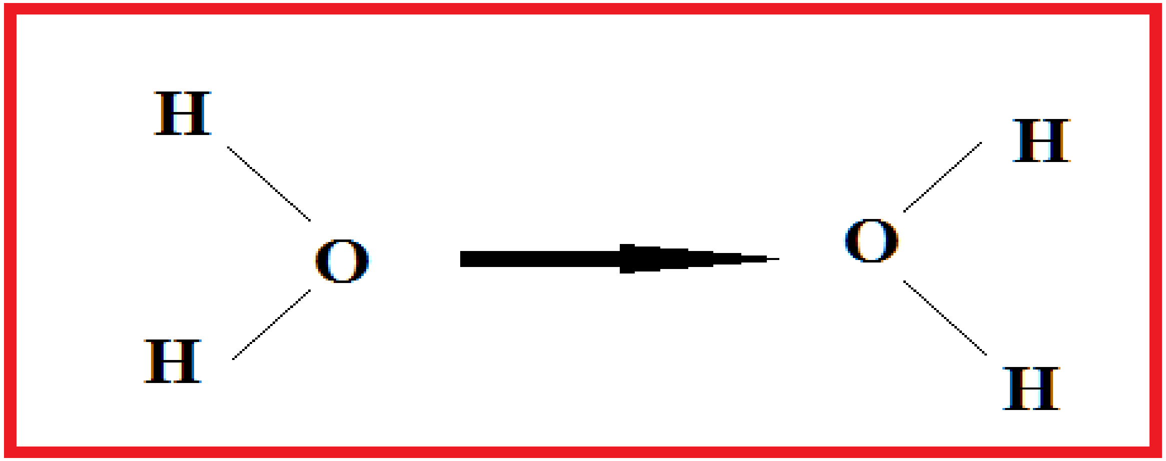
$2H_2O \leftrightarrow H_3O^+ + OH^-$

$R\text{-}OH + H_2O \leftrightarrow RO^+H_2 + OH^-$

In which it is strongly solvated in water, the hydronium ion (H_3O^+), thus, the H_3O^+ ion is able to transfer an proton to neighboring water molecules.

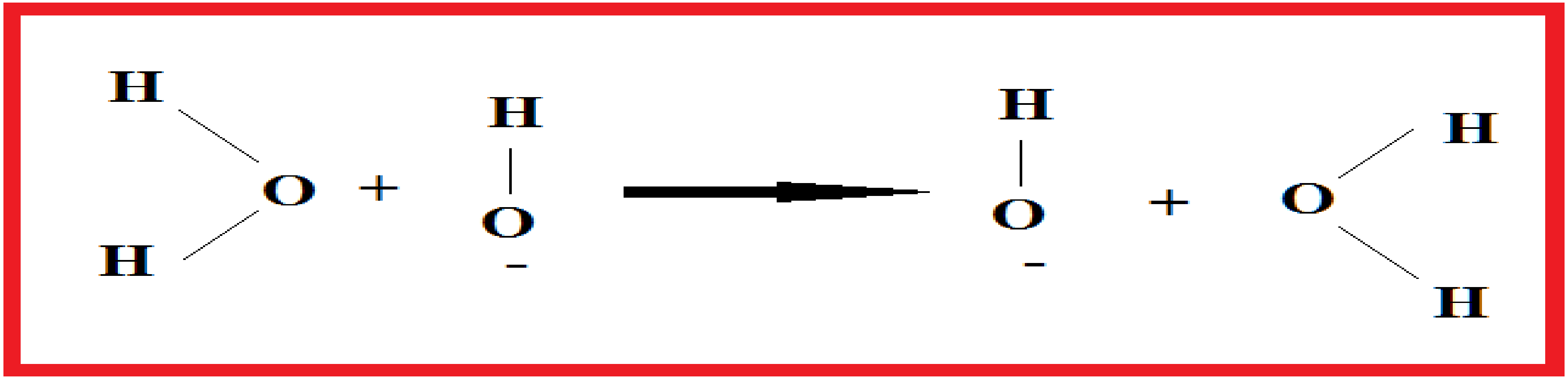


This process may be followed by the rotation of the donor molecules, so that it is again, in an apposition to accept a proton.



This process occurred very fast, this process and high velocity that attached with this process explained the high ionic conductivity of hydrogen ion compared with others ions.

The high mobilities of hydroxyl ion in water, as also believed to be caused by a proton transfer between hydroxyl ions and water molecules



Note/ velocity of hydrogen ion is three times of velocity of hydroxyl ion.

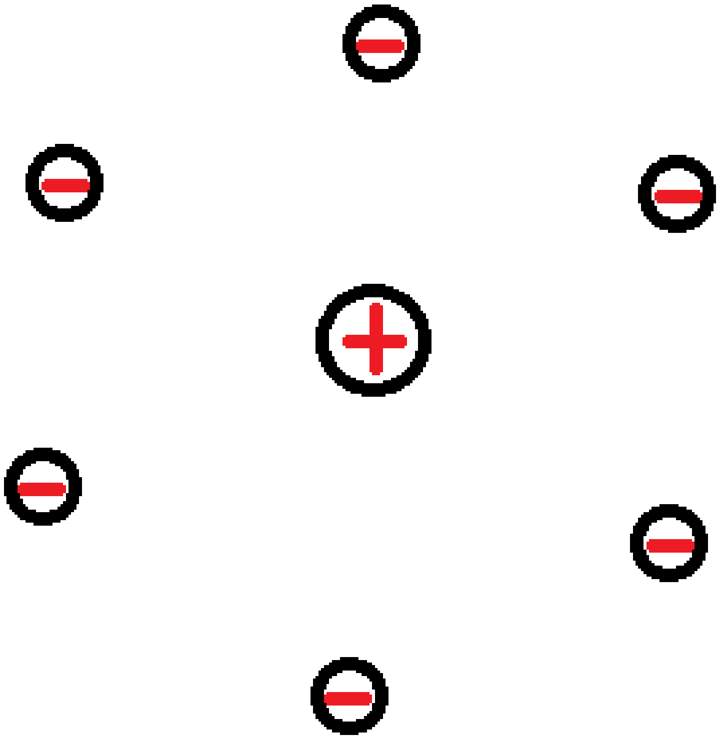
Theory of electrolytic conductance

- **Debye-Huckel theory**

it explains the increase in conductance of strong electrolyte on dilution based upon following two effects:

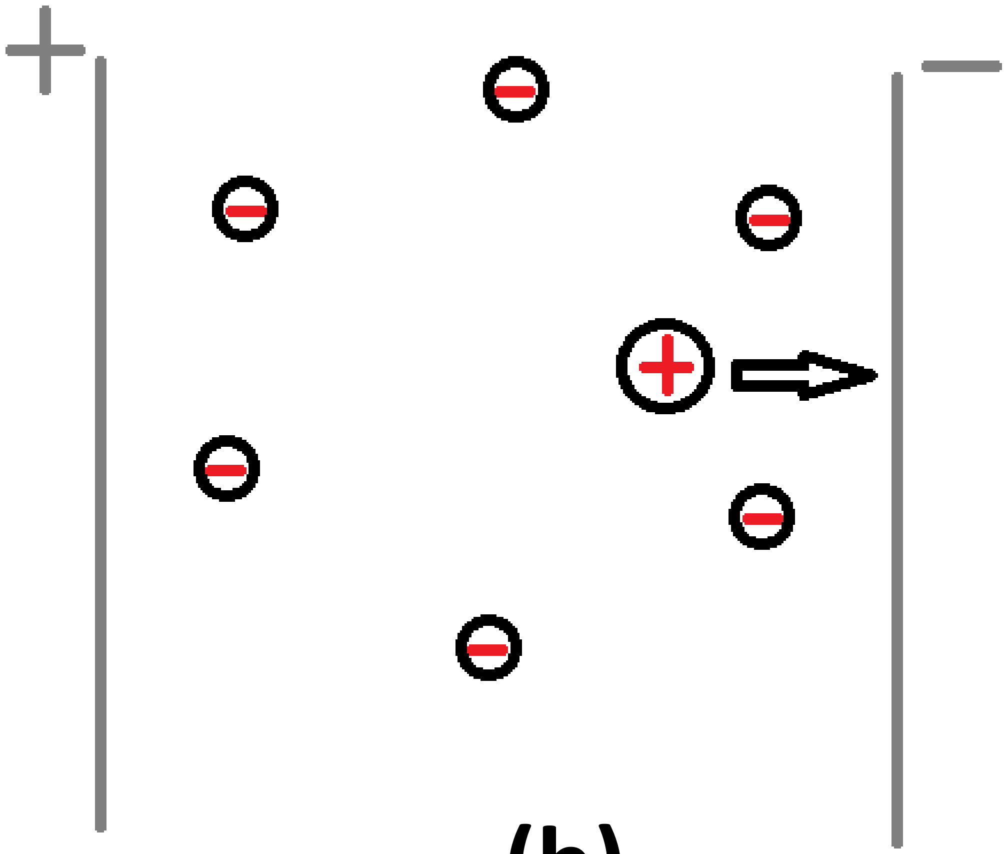
1- Relaxation effect or Asymmetry effect:

In the solution, each ion is surrounded by an ionic atmosphere of opposite charge. So long as no electric field is applied, the ionic atmosphere remains symmetrical around the central ion as shown in figure (a). However, when a current is passed through the solution, the central ion moves towards the oppositely charged electrode. As it is moving out of the ionic atmosphere, it has to rebuild an ionic atmosphere of opposite charged around it and the old ionic atmosphere dies out. However, the destruction of the old ionic atmosphere and the formation of the new ionic atmosphere do not take place at the same time. There is some time lag called time of relaxation between the destruction of the old and the formation of new ionic atmosphere. During this time, the old ionic atmosphere pulls the moving ion backward and hence retards its motion (figure b). Hence this effect is called relaxation effect. Alternatively, it may be argued that as the central ion moves, the symmetry of the ionic atmosphere is lost; more ions of the ionic atmosphere are left behind than are present in the front (figure b). The excess ions of the ionic atmosphere present behind the moving ion drag the ion backward and retard its motion. Thus, the effect arises because of the asymmetry of the ionic atmosphere of the moving ion and hence is also called asymmetry effect.



(a)

Symmetrical ionic atmosphere around a positive ion

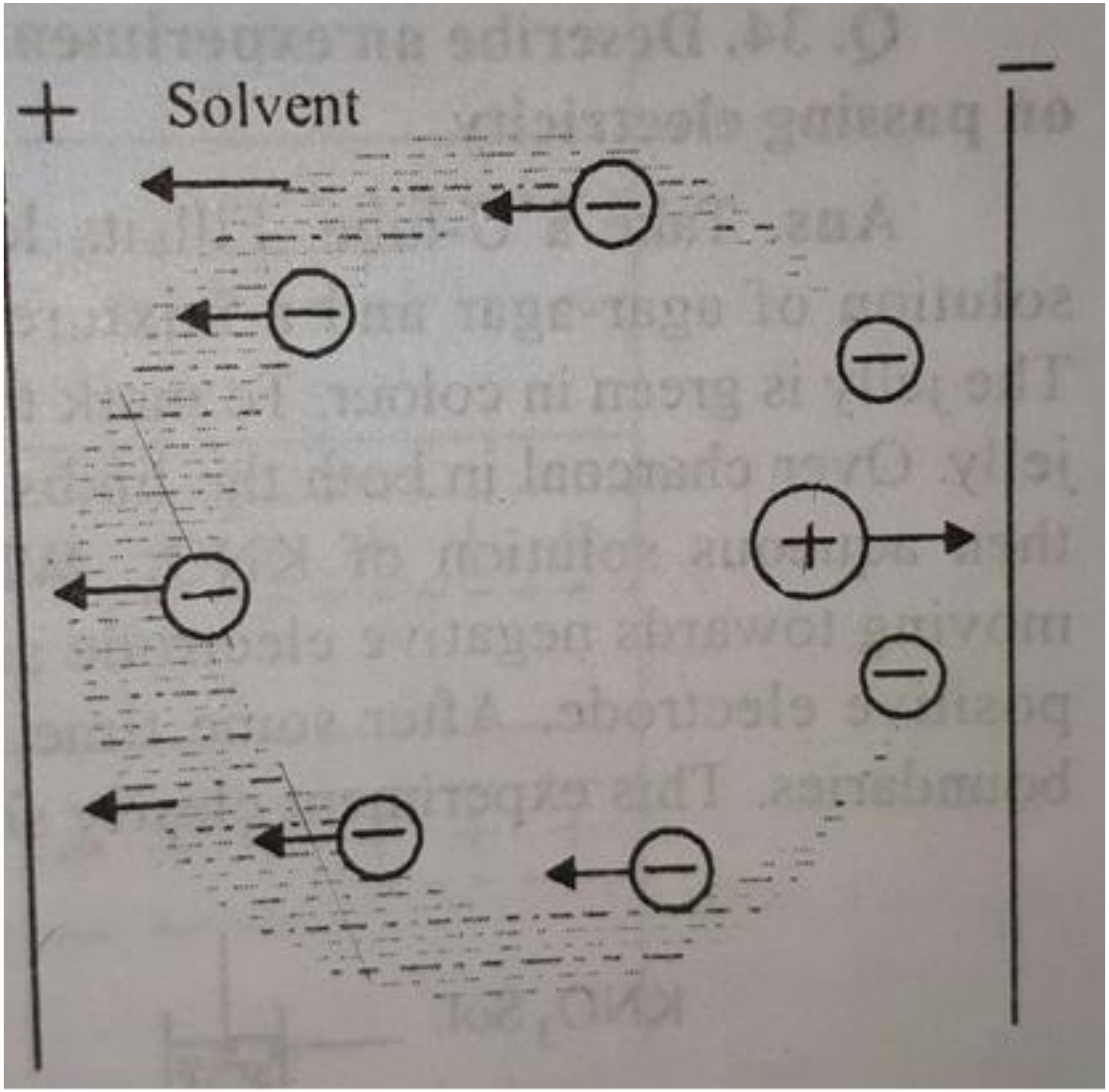


(b)

Ionic atmosphere becoming asymmetric when central ion move

2- Electrophoretic effect:

When Electromotive force (EMF) is applied, the central ion moves in one direction and the oppositely charged ionic atmosphere moves in the opposite direction. As this ionic atmosphere moves, the solvent molecules associated with it also move. Thus the flow of the ionic atmosphere and that of the solvent molecules attached to it takes place in a direction opposite to that of the movement of the central ion. In other words, the central ion is moving against the stream. Hence motion of the ions is retarded. This effect is called electrophoretic effect (Figure c).



(c)

Besides the above two effects, the third retarding force is the normal frictional resistance offered by the medium which depends on the viscosity of the medium, its dielectric constant etc.

Based upon the above ideas, Debye and Huckel (1923) derived a mathematical expression for the variation of equivalent conductance with concentration. This equation was further improved by Onsagar and now the equation is known as Debye-Huckel-Onsagar equation or simply Onsagar equation. it is written in the form.

$$\lambda_c = \lambda_o - \left[\frac{82.4}{\eta (DT)^{1/2}} + \frac{8.20+10^5}{(DT)^{3/2}} \lambda_o \right] \sqrt{C}$$

Where

λ_c= equivalent conductance at concentration C

λ_o = equivalent conductance at infinity dilution

D = Dielectric constant of the medium

η= Viscosity of the medium

T = Temperature of the solution in degrees absolute

C = concentration of the solution in moles/litre

As D and η are constant for a particular solvent, therefore, at constant temperature, the above equation can be written in the form

$$\lambda_c = \lambda_o - (A + B\lambda_o)\sqrt{c}$$

Where A and B are constant for a particular solvent at a particular temperature.

Transport number (τ)

Transport number (τ) which is defined as the fraction of total current carried by the ions of a specified type.

$I_+ = C_+ . Z_+ . V_+ . F. A$ …………………………………1

I_+ = current carried by cation

C_+ = concentration of cation

Z_+ = charge of cation

V_+ = velocity of cation

F = Fariday's number (constant)

A = the area (constant)

While

$I_- = C_- . Z_- . V_- . F. A$ 2

I_-= current carried by anion

$I\ total = I_+ + I_-$ 3

$$\tau_+ = \frac{I_+}{I\ total} = \frac{c_+.Z_+.V_+\ .F.A}{c_+.Z_+.V_+\ .F.A + c_-\ Z_-.V_-\ .F.A}$$ 4

$$\tau_- = \frac{I_-}{I\ total} = \frac{c_-.Z_-.V_-\ .F.A}{c_+.Z_+.V_+\ .F.A + c_-\ Z_-.V_-\ .F.A}$$ 4

Where

τ_+ and τ_- are fraction of the current carried by the cation and inion respectively.

as

F and A are constant

So

$$\tau_{+} = \frac{c_{+}.Z_{+}.V_{+}}{c_{+}.Z_{+}.V_{+} + c_{+}\,Z_{-}.V_{-}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 5$$

As

C and V are considered constant for symmetric electrolytes

C+ = C- = C

$Z_{+} = Z_{-} = Z$

$$\tau_+ = \frac{V_+}{V_+ + V_-} \quad \text{..6}$$

As

$V = U.E$ 7

$V_+ = U_+ E$ 7

$V_- = U_- E$ 7

When compensation in an equation 6

$$\tau_+ = \frac{u_+ E}{u_+ E + u_- E} \quad \text{..8}$$

as E is still constant , therefore, E deleted from the equation.

$$\tau_+ = \frac{u_+}{u_+ + u_-} \quad \text{.. 9}$$

as

$$u = \frac{\lambda}{FZ}$$

so

$$\tau_+ = \frac{\frac{\lambda_+}{F\,Z_+}}{\frac{\lambda_+}{F\,Z_+} + \frac{\lambda_-}{F\,Z_-}} \quad \text{...10}$$

As

F and Z are constant

$$\tau_+ = \frac{\lambda_+}{\lambda_+ + \lambda_-} \quad \text{...11}$$

As

$\Lambda_o = \lambda_+ + \lambda_-$

So

$$\tau_+ = \frac{\lambda_+}{\Lambda_o} \quad \text{..} \mathbf{12}$$

Note/

$$\tau_+ + \tau_- = 1$$

Q1/ the transport number of silver ion is 0.466 and that of nitrate ion is 0.533 at 18 C^o, the molar conductivity at infinity dilution is 115.8 ohm^{-1} cm^2 mole^{-1} at the same temperature.

Calculate:-

a- The ionic conductance of silver and nitrate ions

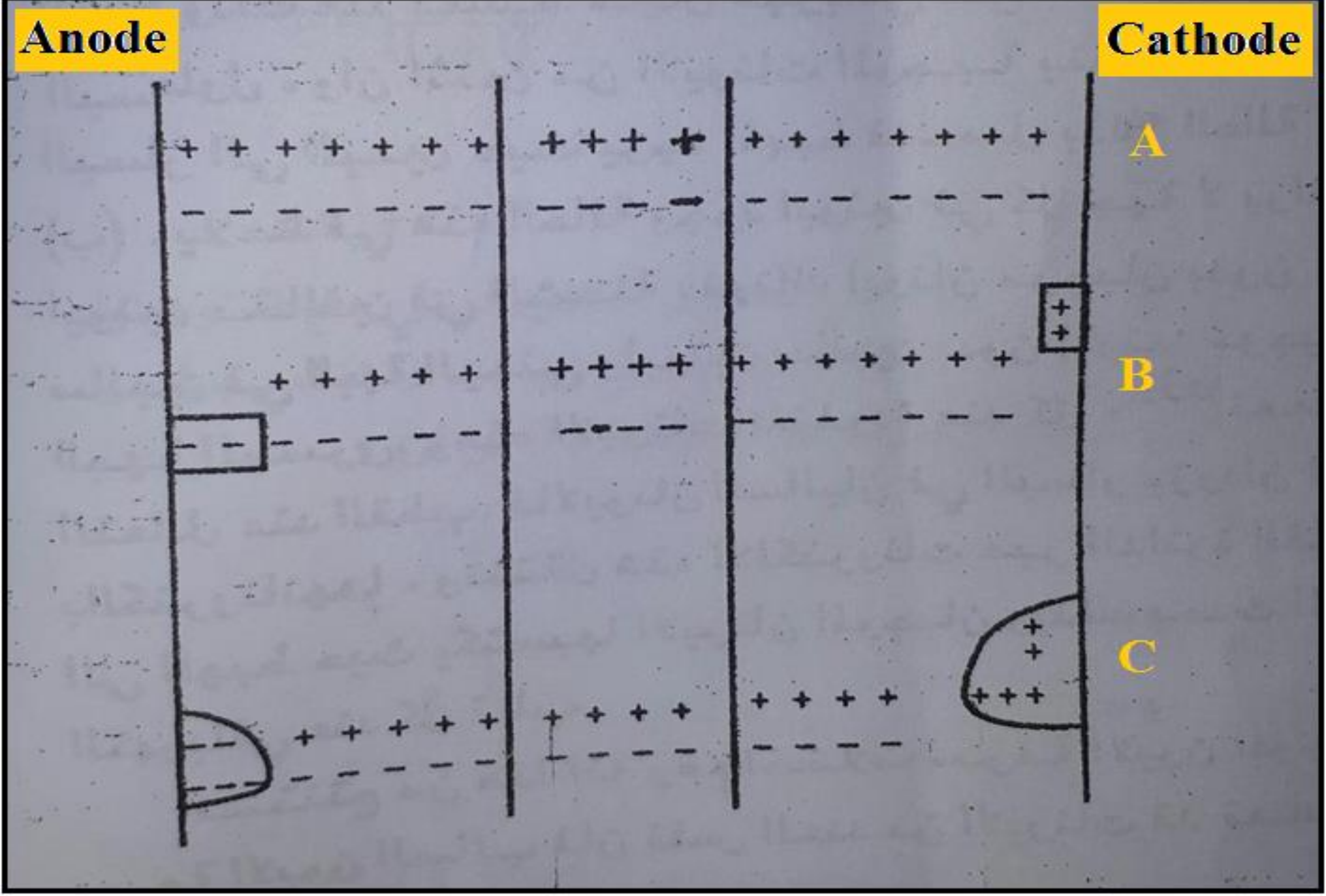
b- The ionic mobilities of the two ions

Experimental of Determination of Transport number

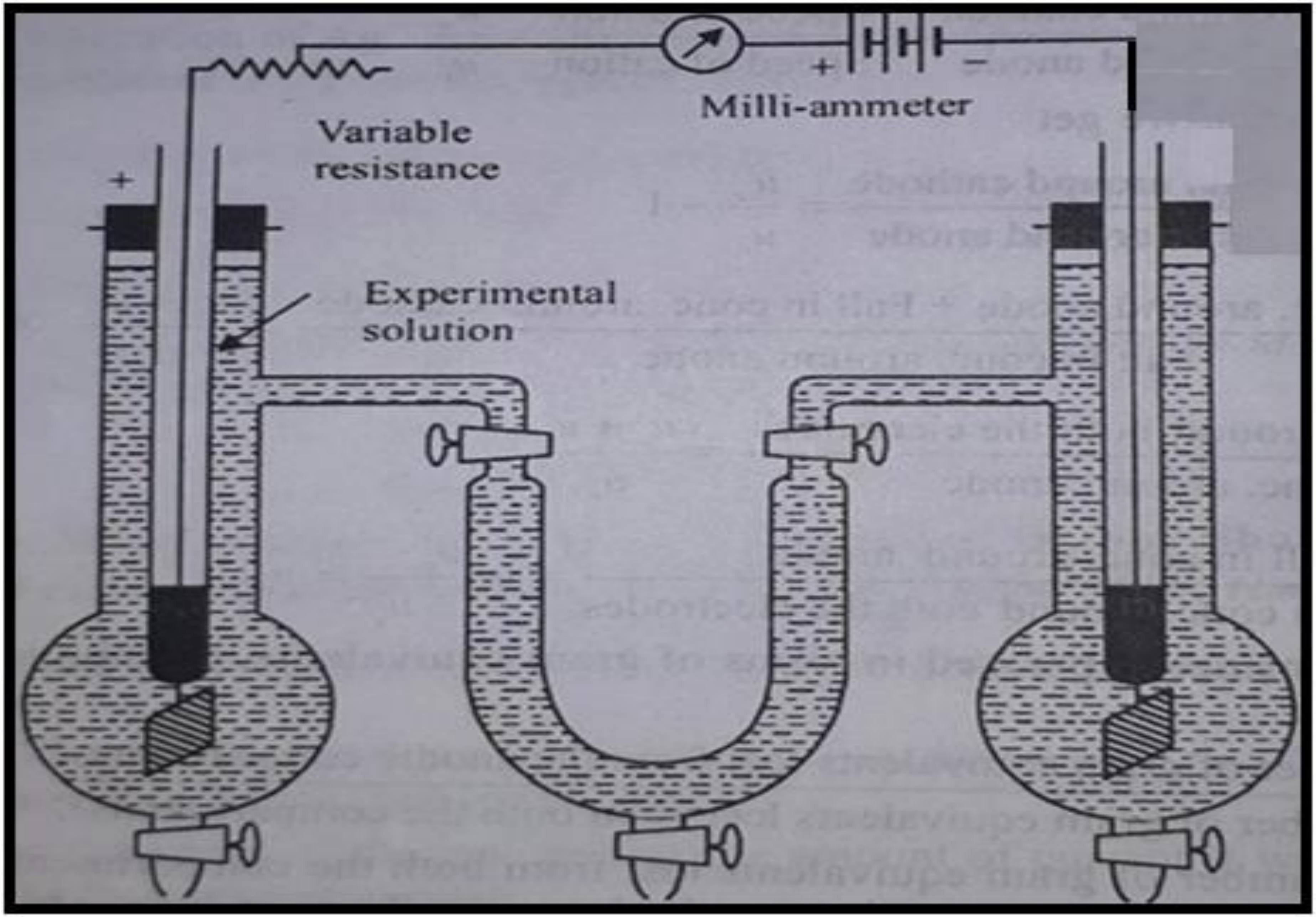
(Hittrof Method)

This method is based on the measurement of changes in the solution concentration near the electrodes. As direct current passes through the solution, the anions are transported to the anode, and the cations, to the cathode. Suppose equivalents of anions are transported from the cathode during the electrolysis. As result the electrolyte near the cathode, called catholyte contains excess equivalents of cations.

They should discharge on the cathode so that the solution remains electrically neutral. In this case, the decrease in the amount of the salt in the catholyte in similar way, the decrease in the amount of the salt near the anode will be equivalents of cations which have moved away from the anode. The charge of equivalent of ions is equal to the faraday constant.



migration of ions



Apparatus for the determination of transport number by Hittorf 's method.

$$\tau_{-} = \frac{\textit{decrease in equ. of anion in cathode region}}{\textit{quantite of electrical } (\mathbf{F})}$$

$$\tau_{+} = \frac{\textit{decrease in equ. of cation in anode region}}{\textit{quantite of electrical } (\mathbf{F})}$$

Q1/ During the electrolysis of KCl solution between pt electrodes 0.0137 gm of the chloride was lost from anodic compartment and 0.0857 gm of silver was deposited in silver coulometer connect in series with cell. Determine the transport number of K^+ and Cl^- ions. If you know the atomic weight of Ag and Cl are 107.9 and 35.5 respectively.

Q2/During the electrolysis of a solution of $AgNO_3$ between pt electrodes, its found that 10.058 gm of solution contain 0.0847 gm of $AgNO_3$ before electrolysis and found of 27.04 gm of solution in anodic region contain 0.2818 gm of AgNO3 after electrolysis, and 0.0194 gm of the Cu coulometer connected in series with cell. Determine the transport number of two ions.

Q3/ At 25 C° the lowest specific conductance that can be obtained with the most carefully distilled water is 58x 10^{-7} ohm^{-1} m^{-1} and this conductance must be attributed to the equilibrium concentration of at H^+ and OH^-.

Calculate of the equilibrium constant (Kw) for water dissociation reaction. If you know $\Lambda_o = 0.05478$.

Ionic Strength

$$I = 1/2 \pounds C_i Z_i^2$$

Q1/ Calculate the ionic strength of 0.1M NaCl?

Q2/ Calculate the ionic strength of 0.1M $CaCl_2$?

Q3/ Calculate the ionic strength of 0.1gm from NaCl dissolve in quarter liter of water?

Activity Coefficients

$$\text{Log } F_+ = -AZ_+^2\sqrt{I}$$

F_+ = Activity Coefficients of cation.

A = Constant = 0.509

I= ionic strength

Z = Charge

$$\text{Log } F_- = -AZ_-^2\sqrt{I}$$

$F_{+-} = F_+ . F_-$

F_{+-} = mean activity

a = F . C

a = Activity

NOTE/ Log F_{+-} uses when the concentration dilution (less than 0.1 N)

Q4/ Calculate the F_{+-} for ionic strength is equal 0.01 of $CaCl_2$.

$$\text{Log } F_{+} = -AZ_{+}^{2}\sqrt{I}$$

$$\text{Log } F_{+} = -509\,(2)^{2}\sqrt{0.01}$$

$$\text{Log } F_{+} = -0.2036$$

$$F_{+} = 0.\,626$$

$$\text{Log } F_{-} = -AZ_{-}^{2}\sqrt{I}$$

$$\text{Log } F_{-} = -509\,(-1)^{2}\sqrt{0.01}$$

$$\text{Log } F_{+} = -0.0509$$

$$F_{-} = 0.\,824$$

$$CaCl_2 \longrightarrow Ca^{+2} + 2Cl$$

$$F_{+-} = F_+ . F_-$$

$$F_{+-} = F_+ . F^2_-$$

$$F_{+-} = 0.626 . (0.824)^2$$

$$F_{+-} = 0.497$$

Q5/ Calculate the activity coefficients and activity for 0.02M $BaCl_2$ solution if the ionic strength is 0.01?

$$BaCl_2 \longrightarrow Ba^{+2} + 2Cl$$

$$\text{Log } F_+ = -AZ_+^2\sqrt{I}$$

$$\text{Log } F_+ = -0.509(2)^2\sqrt{0.01}$$

$$F_+ = 0.626$$

$$\text{Log } F_- = -AZ_-^2\sqrt{I}$$

$$\text{Log } F_- = -509(-1)^2\sqrt{0.01}$$

$$F_- = 0.89$$

$$F_{+-} = F_+ \,.\, F_-$$

$$F_{+-} = F_+ \,.\, F_-^2$$

$$F_{+-} = 0.626 \,.\, (0.89)^2$$

$$F_{+-} = 0.497$$

Ba^{+2}

Cl^{-1}

$$a \quad = F \,.\, C$$

$$a \quad = (F \,.\, C)_{+} \,.\, [(F^{2}) : (2C)]-$$

$$a \quad = (0.497.\ 0.0008)$$

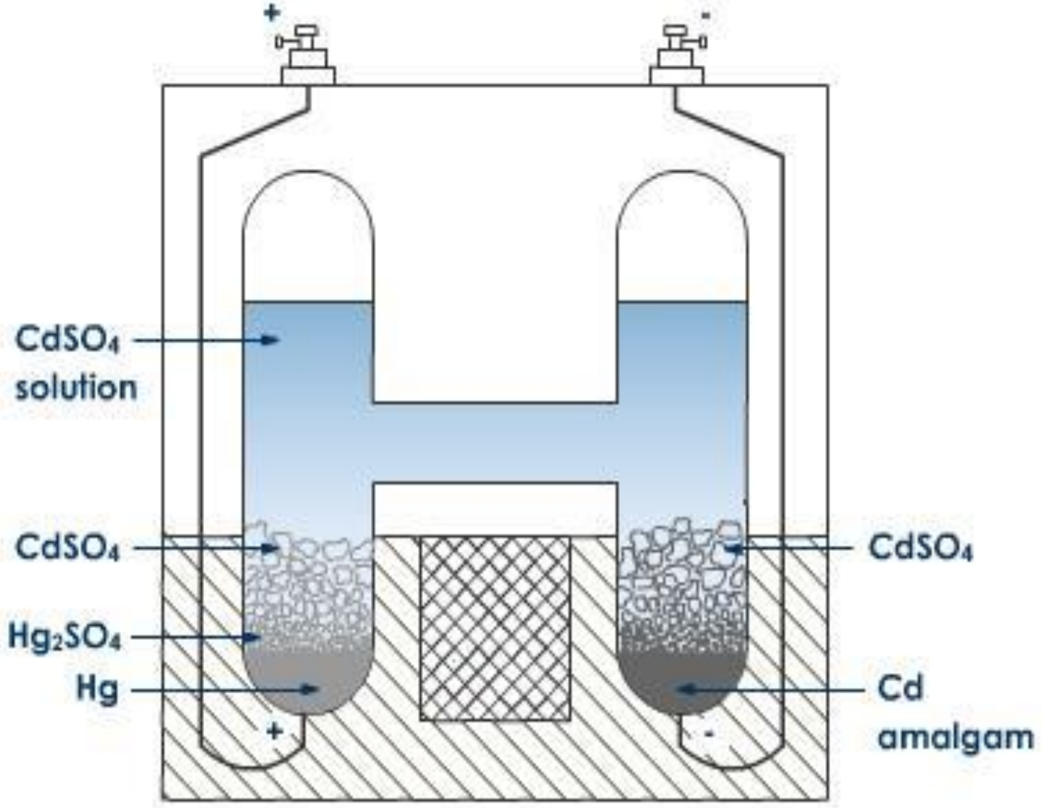
$$a \quad = (0.0003976$$

Electromotive Force (emf) of Electrochemical Cell

The electromotive force (emf) of the cell is defining as the limiting value of the electrical potential difference ΔE as the current the goes to zero.

In experimental, it is possible to measure E under conditions in which the current drawn from the cell is as small as to be negligible. The most widely used standard is the **Weston cell**, which is written:-

$Cd(Hg)\ |\ CdSO_{4(aq)},\ Hg_2SO_4\ |\ Hg.$



Weston cell

$$Cd(Hg) + HgSO_4 + H_2O \rightarrow CdSO_4.8/3\ H_2O + 2Hg$$

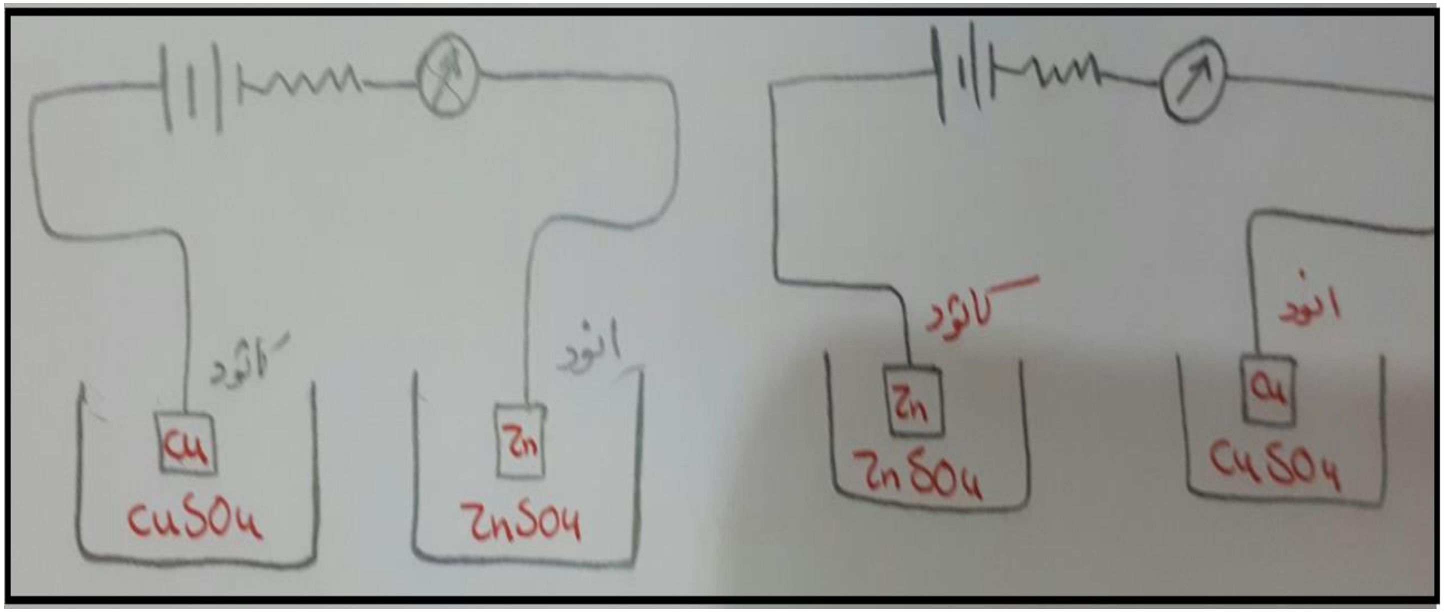
emf is volt at 0C° is given by E

$E = E_{R\ (cathode)} - E_{L\ (anode)}$

E is Potential of cell

NOTE/ If E of cell = + (that means connect of cell is correct.

Q/ Which one from the connection of cells is correct?



if you know

$E\ Cu^{+2}/\ Cu = 0.334$ volt

$E\ Zn^{+2}/Zn = -0.76$ volt

Sol/

$E = E_R - E_L$

$E = E_{cu} – E_{Zn}$

$E = 0.33 – (-0.76)$

$E = 1.1$ volt $\rightarrow \Delta G = -$

$Zn^o/Zn^{+2}//\ Cu^{+2}/Cu^o$

$E = E_{Zn} – E_{Cu}$

$E = -0.76 – 0.334$

$E = -1.1$ volt $\rightarrow \Delta G = +$

Note/

$$\Delta G = -nFE$$

n= number of reduction or oxidation electrons

F= Faradays number

E= Potential of cell

Note/

To get a final positive cell potential, the more negative half-reaction must act as the anode.

Q/ Which one from Fe and V act as the anode?

$E\ Fe^{+2}/Fe = -0.44$ volt

$E\ V^{+2}/V = -1.19$ volt

Sol/

$Fe^{2+} + 2e^{-} \rightarrow Fe$ $E = -0.44$ volt

$V^{2+} + 2e^{-} \rightarrow V$ $E = -1.19$ volt

$Fe^{2+} + V \rightarrow Fe + V^{2+}$ $E_{cell} = -0.44 - (-1.19) = +0.75\ V$

So the more negative half-reaction (V) must act as the anode.

Q/ Which one from Ag and Sn act as the a cathode?

E Ag^{+}/ Ag = -0.80 volt

E Sn^{+2}/Sn = -0.14volt

Sol/

$Sn^{2+} + 2e^{-} \rightarrow Sn$ E = -0.14 volt

$2Ag^{+} + 2e^{-} \rightarrow Ag$ E = -+0.80 volt

$2Ag^{+} + Sn \rightarrow 2Ag + Sn^{2+}$ E_{cell} = -0.80 - (-1.14) = +0.94 V

So the more negative half-reaction (Sn) must act as the anode and Ag acts the cathode.

Dr. Asmaa Kadim Ayal