MIST | Technology for Advancement
Military Institute of Science and Technology

Fundamentals of Chemistry

CHEM 101

Electrochemistry

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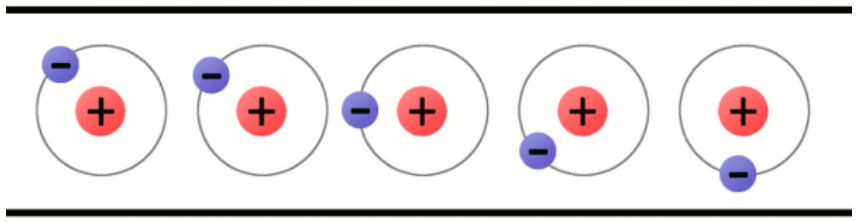
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Electrochemistry

Electrochemistry is the branch of chemistry that deals with the relationship between electrical energy and chemical reactions.

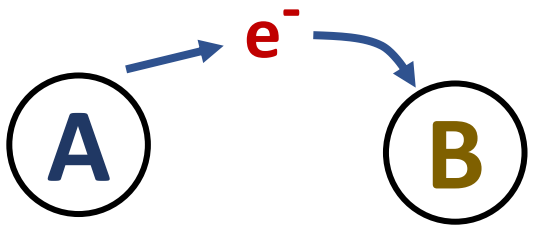
- **Electricity**

Movement of electrons



- **Chemical Reactions**

Electrons move between atoms



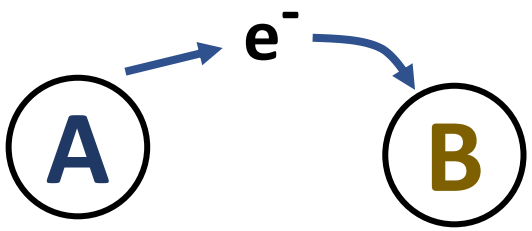
Can create electricity

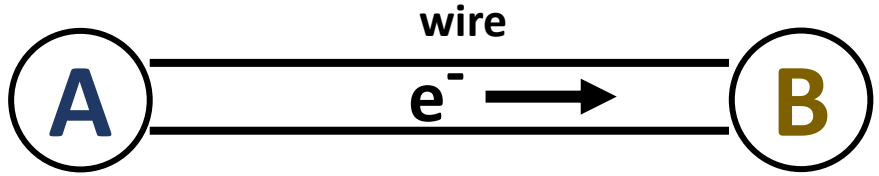
✓ **This branch deals with the study of chemical changes caused by the passage of electric current and the production of electrical energy by chemical reactions**

Electrochemistry

- **Certain chemical reactions can create electricity**

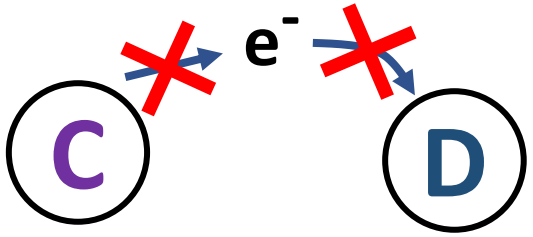
  ✓ Conversion of chemical energy into electrical energy. i.e., the generation of electricity by spontaneous redox reactions.



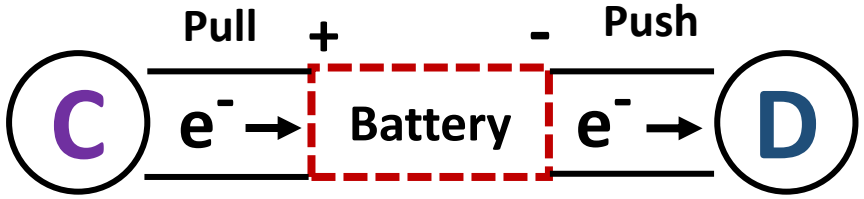


- **Electricity can make certain chemical reactions happen that wouldn't happen otherwise**

  ✓ Production of chemical change by electrical energy with the need of an external source. i.e. the phenomenon of electrolysis



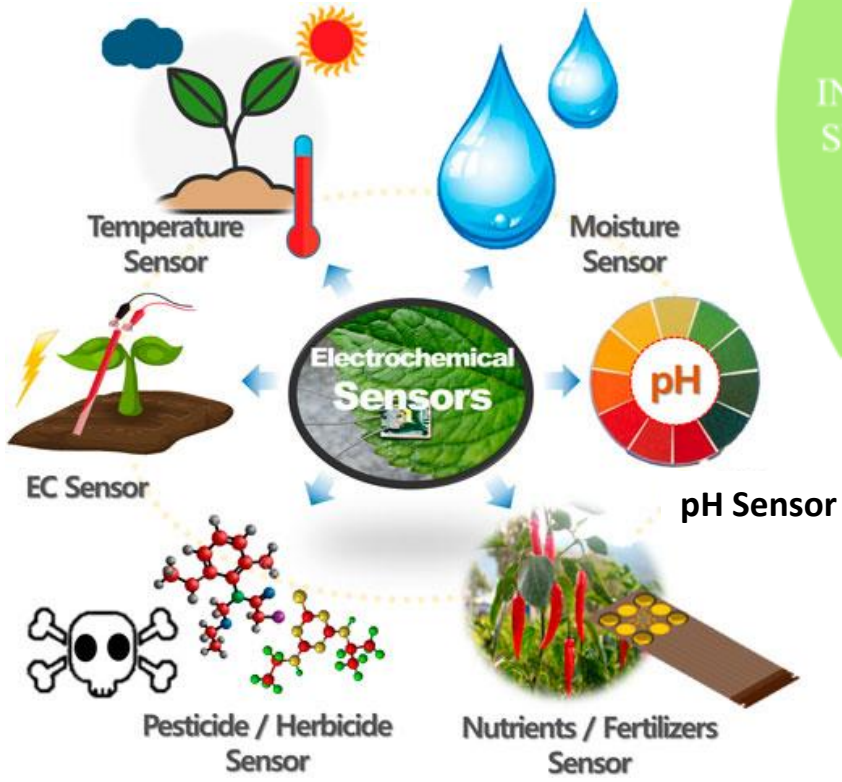
Won't normally happen

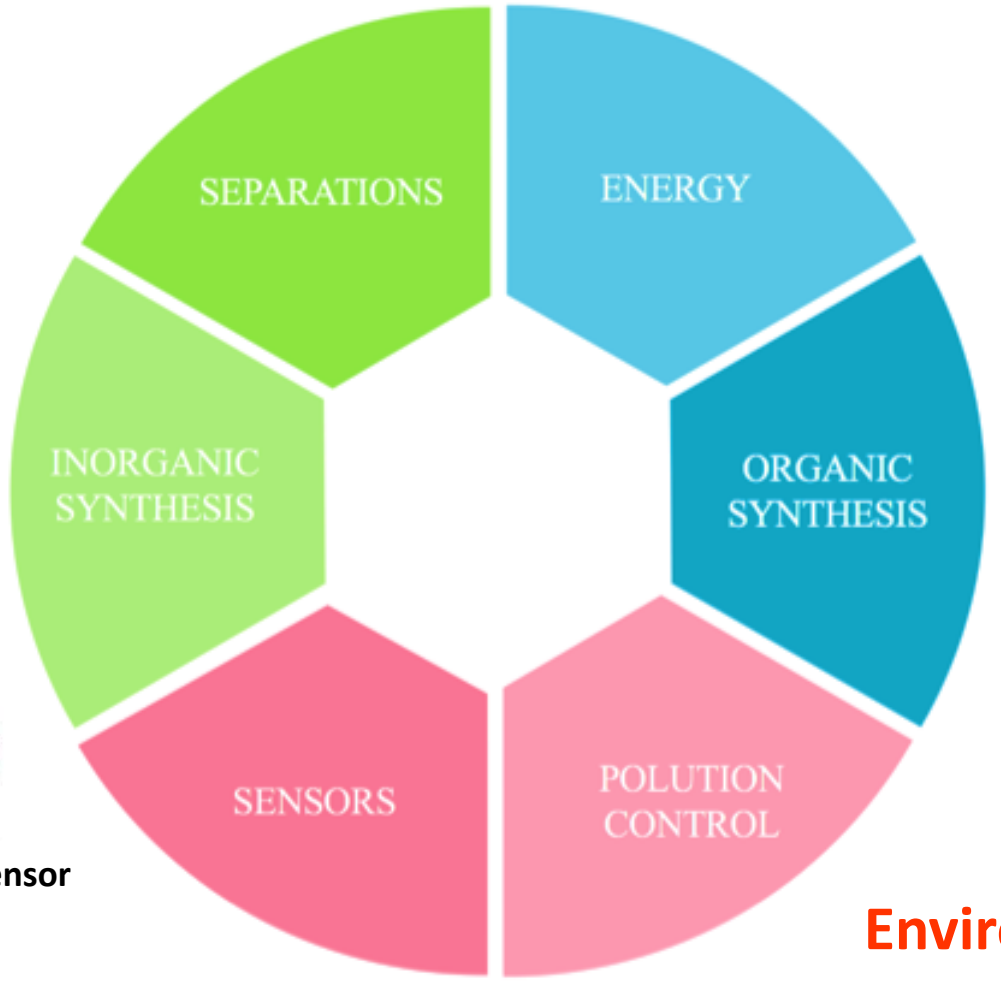


Applications of Electrochemistry

Separations

- Electrodialysis
- Salt Splitting





Energy

- Redox Flow cells
- Fuel Cells
- Batteries

Synthesis

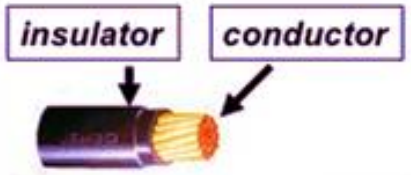
- Inorganic
- Organic
- Pharmaceuticals

Environmental Electro-technology

- Metal recovery
- Water treatment

Conductor –

Any material that allows electric current to pass through it



- copper
- aluminum
- steel



- any metal

Metallic

Insulator –/ Non-Conductor

Any material that does not allow electric current to pass through it

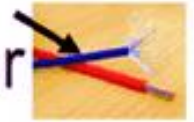
- like the protective coating on wires



- plastic



- cloth



- rubber



- glass



- wood

Electrolytic

- **Aqueous solutions of acid, base and salts**
- **Impure water**

DIFFERENCE BETWEEN METALLIC AND ELECTROLYTIC CONDUCTION :

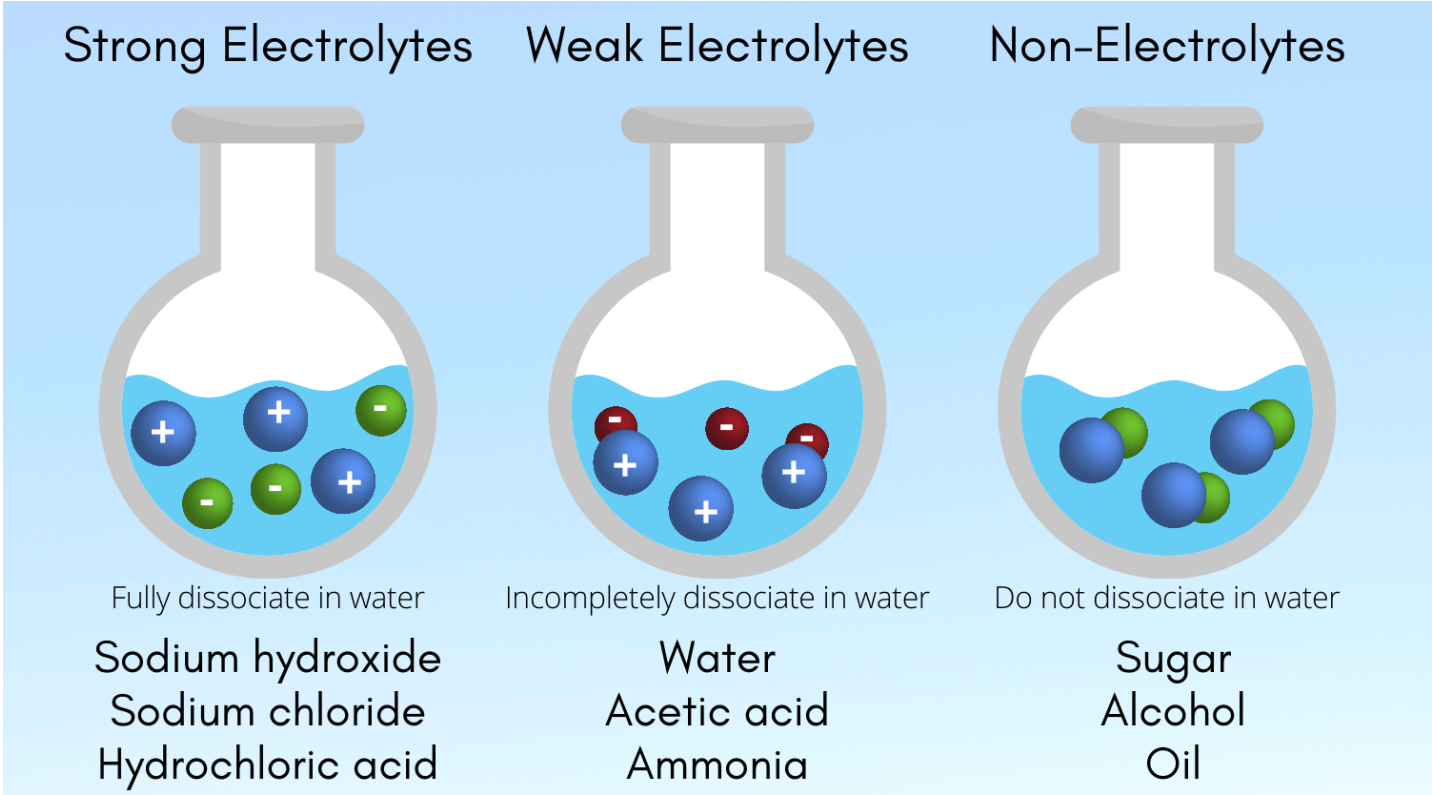
	Metallic conduction	Electrolytic conduction
(i)	Flow of electricity takes place without the decomposition of the substance	Flow of electricity takes place by chemical changes at electrodes.
(ii)	No transfer of matter takes place.	Transfer of matter takes place in the form of ions
(iii)	The resistance to the flow of current increases with the increase in temperature and hence the increase in temperature decreases the conduction.	The resistance to the flow of current decreases with the increase in temperature and hence increase in temperature increases the conduction.

Electrochemistry

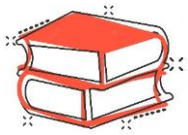
Electrolyte: An electrolyte is a substance that conducts an electric current when dissolved in a solvent, such as water.

- Electrolytes are typically ionic compounds that dissociate into positive and negative ions in solution, allowing the flow of electrical current through the solution.

- Some common examples of electrolytes include sodium, potassium, calcium, magnesium, chloride, and bicarbonate. These electrolytes are found in many fluids in the body, including blood, urine, and sweat.

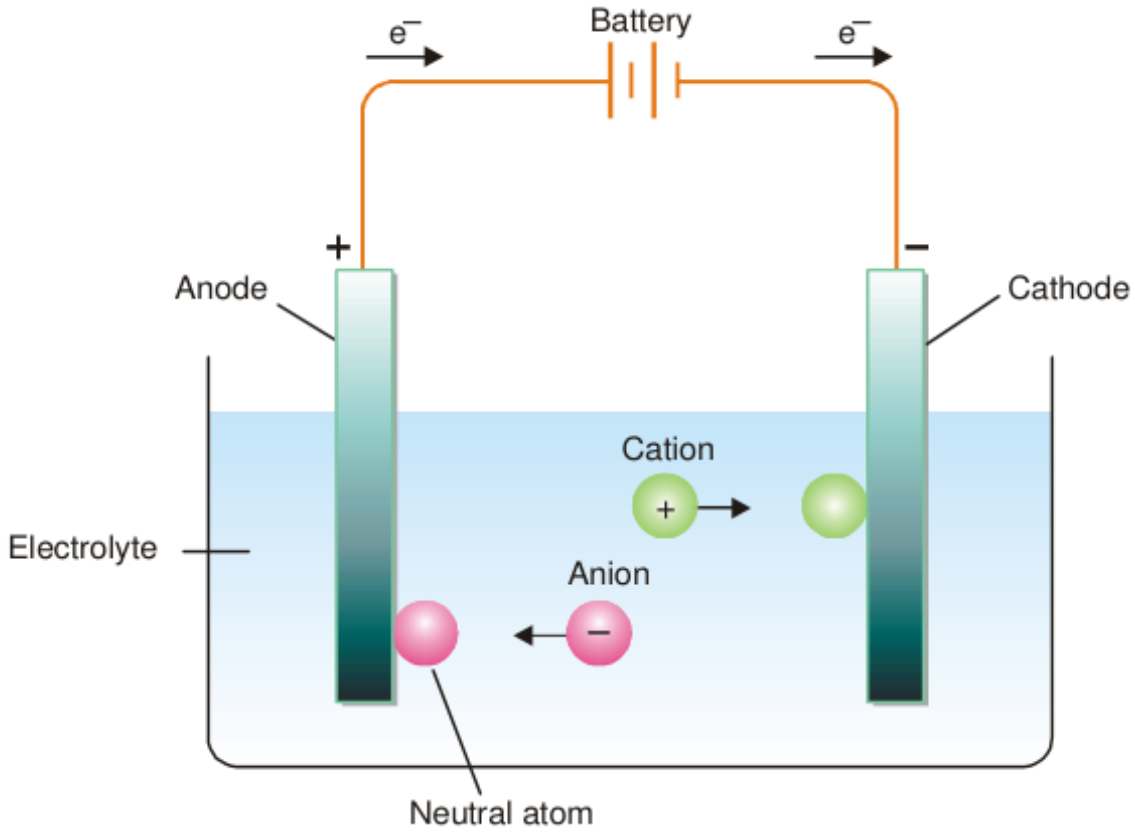


Electrolysis



The phenomenon of decomposition of an electrolyte by passing electric current through its solution is termed Electrolysis.

The process of electrolysis is carried in an apparatus called the Electrolytic cell



APPLICATIONS

- Production of metals
- Electroplating
- Electrolytic refining
- Production of chemicals
- Battery technology
- Water treatment

Mechanism of Electrolysis

- **Direct current is passed through the compound**
- **Electrical energy (From direct current) is changed into chemical energy (the decomposition of the compound).**

In solution, HCl is ionised, $HCl \longrightarrow H^+ + Cl^-$

In the electrolytic cell, Cl^- ions will move toward the anode and H^+ ions will move toward the cathode.

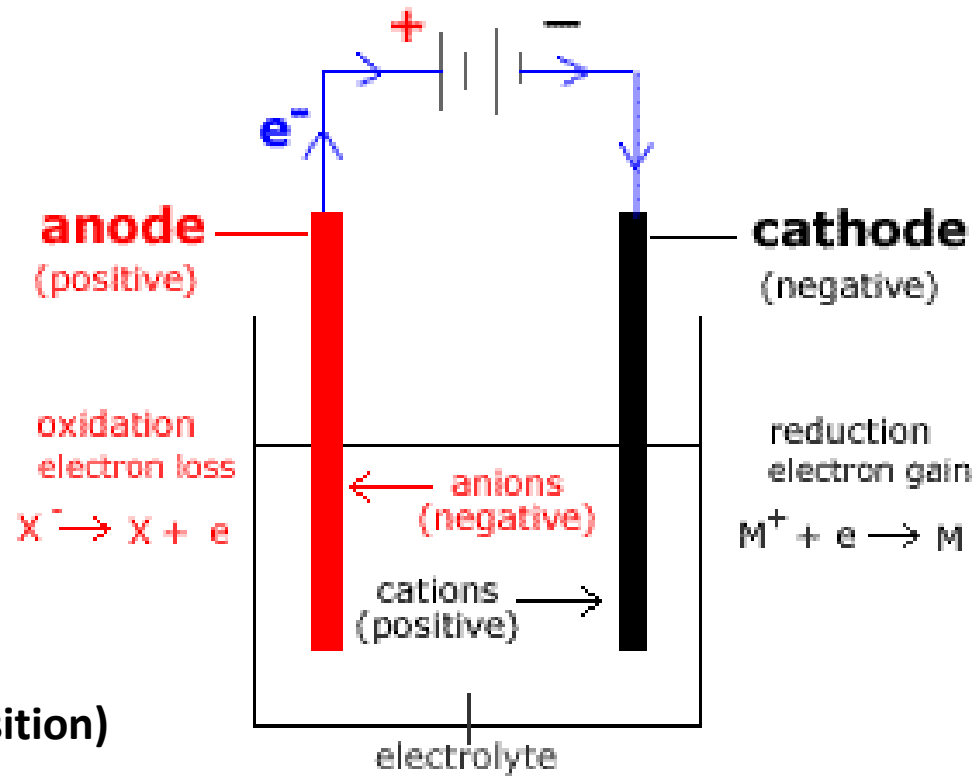
At anode : $Cl^- \longrightarrow Cl + e^-$

Pair of Cl atoms unite to form Cl gas, Cl_2.

At cathode : $H^+ + e^- \longrightarrow H$

Pairs of H atoms then unite to form molecules of H gas, H_2.

The overall reaction is : $2HCl \longrightarrow H_2 + Cl_2$ **(Decomposition)**



Faraday's laws of Electrolysis

- **Faradays First Law (the Law of Electrochemical Equivalence)**

The amount of a given product liberated at an electrode during electrolysis is directly proportional to the quantity of electricity passing through the electrolyte.

The more electricity passes through the system, the greater the amount of substance will be produced.

If w is the mass of substance (in grams) deposited on electrode by passing Q coulombs of electricity,

$$W \propto Q$$

We know, Q = It

The quantity of electricity passed in 1 second by a current of 1 ampere

$$\boxed{W = Z\,I\,t}$$

Here, **Z** is a constant and known as **electrochemical equivalent**.

It is the amount of substance liberated when 1 A current is passed through the electrolyte for 1 sec or when 1 C electricity is passed.

Faraday's laws of Electrolysis

It has been found experimentally that the quantity of electricity required to liberate one gram-equivalent/chemical equivalent of a substance is 96,500 coulombs.
This quantity of electricity is known as Faraday and is denoted by the symbol F.

One mole of substance contains Avogadro's No. of particles.

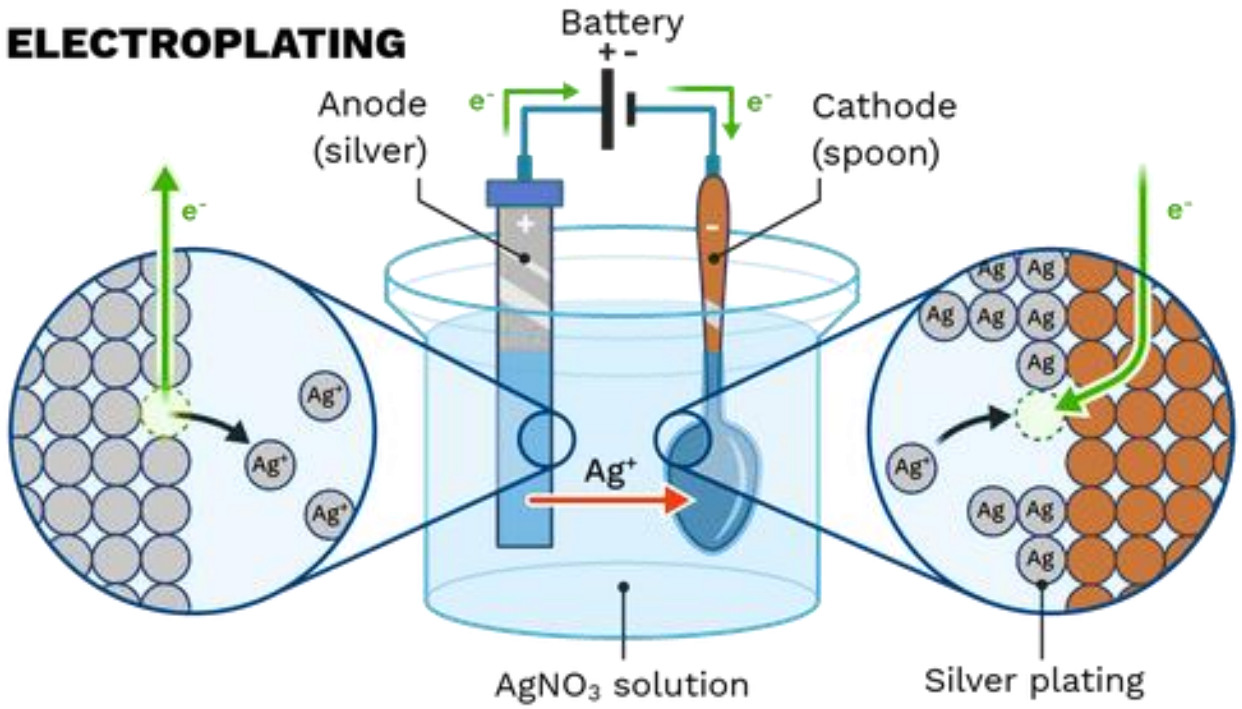
Since one mole of electrons carries a charge of $6.02 \times 10^{23} \times 1.6 \times 10^{-19}$ coulombs (the charge of one electron), one mole of electrons carries a total charge of approximately 96,500 coulombs.

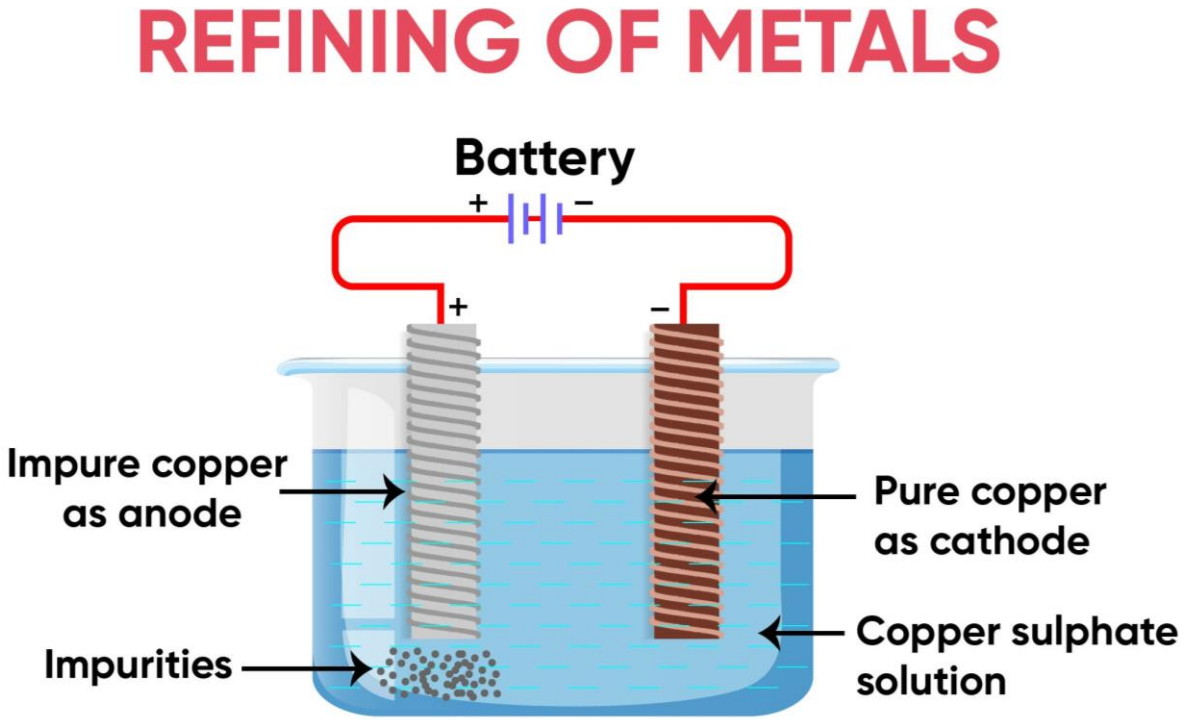
1 Faraday = 96,500 coulombs = 1 Mole electrons

DO Numericals from Bahl and Tuli

Faraday's laws of Electrolysis

Applications of Faradays First Law





At the anode: $Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$

At the cathode: $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$

Faraday's laws of Electrolysis

- **Faradays Second Law**

When the same quantity of electricity passes through solutions of different electrolytes, the amounts of substances liberated at the electrodes are directly proportional to their chemical equivalents or equivalent weight(E).

For acids $E = \dfrac{\text{Molecular weight}}{\text{protocity or basicity of acid}}$

For example, for H_3PO_4, $E = \dfrac{M}{3}$

For H_2SO_4, $E = \dfrac{M}{2}$ (Also for $H_2C_2O_4 \cdot 2H_2O$)

For bases $E = \dfrac{\text{Molecular weight}}{\text{Acidity or number of } OH^- \text{ ions}}$

For example, for $Ca(OH)_2$, $E = \dfrac{M}{2}$

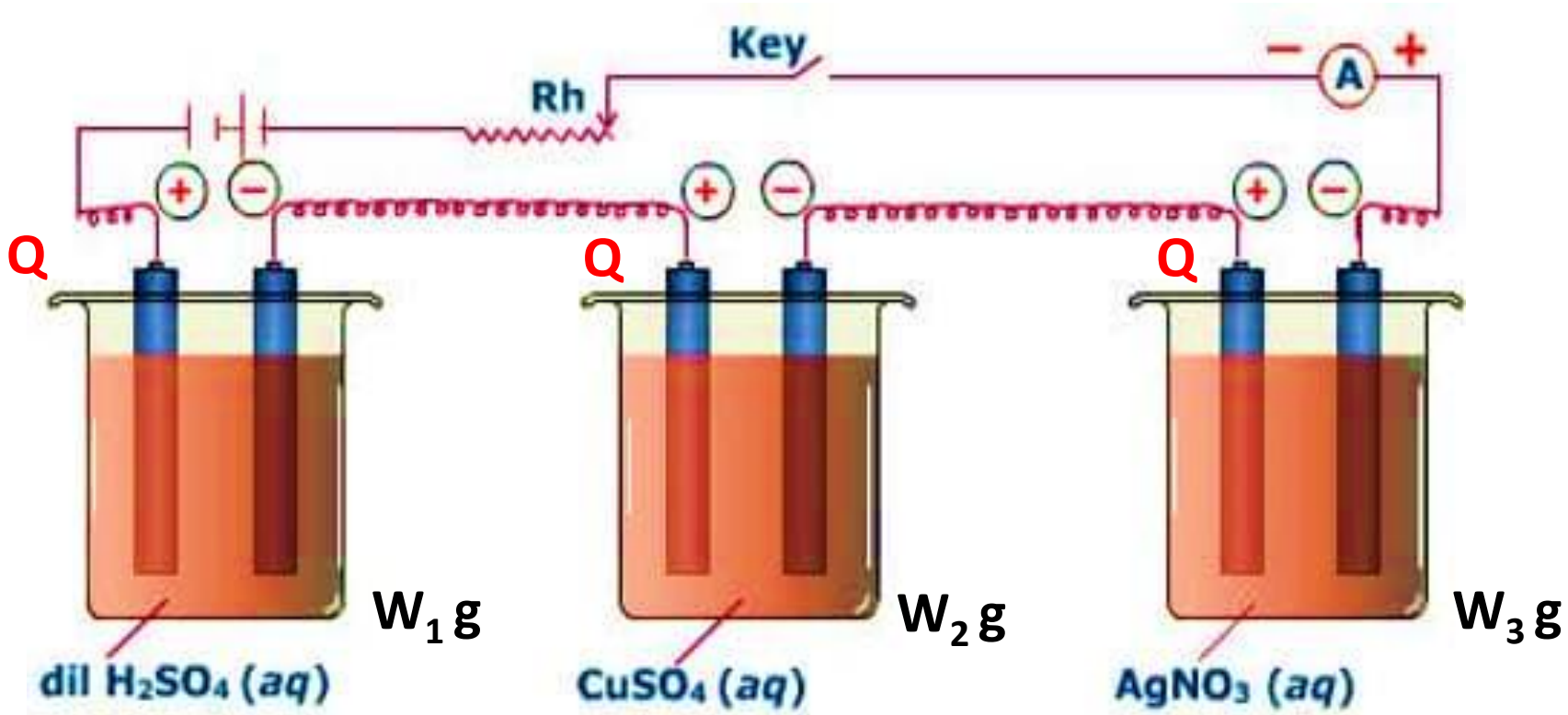
For $Al(OH)_3$, $E = \dfrac{M}{3}$

For ions $E = \dfrac{\text{Molecular weight}}{\text{Charge on ion}}$

For example, for SO_4^{2-}, $E = \dfrac{M}{2}$

For PO_4^{3-}, $E = \dfrac{M}{3}$

Faraday's laws of Electrolysis



$W_1 \propto E_1$

$W_2 \propto E_2$

$W_3 \propto E_3$

$$\frac{W_1}{W_2} = \frac{E_1}{E_2}$$

Combination of Faraday's laws of Electrolysis

Faraday's First Law of electrolysis,

$W \propto Q$, when Z is constant

Faraday's Second Law of electrolysis,

$W \propto E$, when Q is constant

By combining, $W \propto Q \times E$

$$W = \frac{Q \times E}{F}$$

Here, $\frac{1}{F}$ is constant and $F = 96500C$

Faraday's laws of Electrolysis

Relation between Chemical Equivalence and Electrochemical Equivalence

From First Law,

$$W = Z \times Q \text{ , when Z is constant}$$

From Combination law,

$$W = \frac{Q \times E}{F} \quad \text{Here, } \frac{1}{F} \text{ is constant and } F = 96500C$$

Now,

$$Z \times Q = \frac{Q \times E}{F}$$

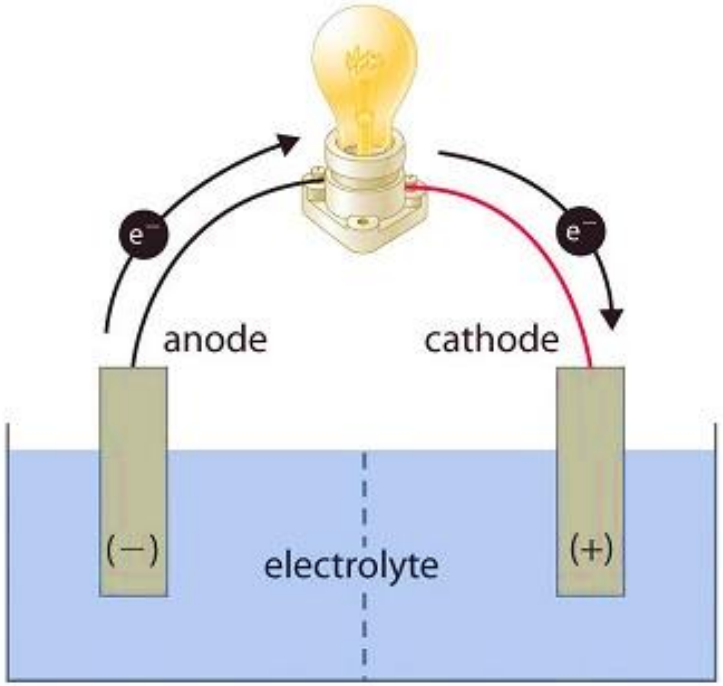
$$Z = \frac{E}{F} \qquad \boxed{E = Z \times F}$$

Chemical Equivalence = Electro-chemical Equivalence × 96500C

Electrochemical Cell

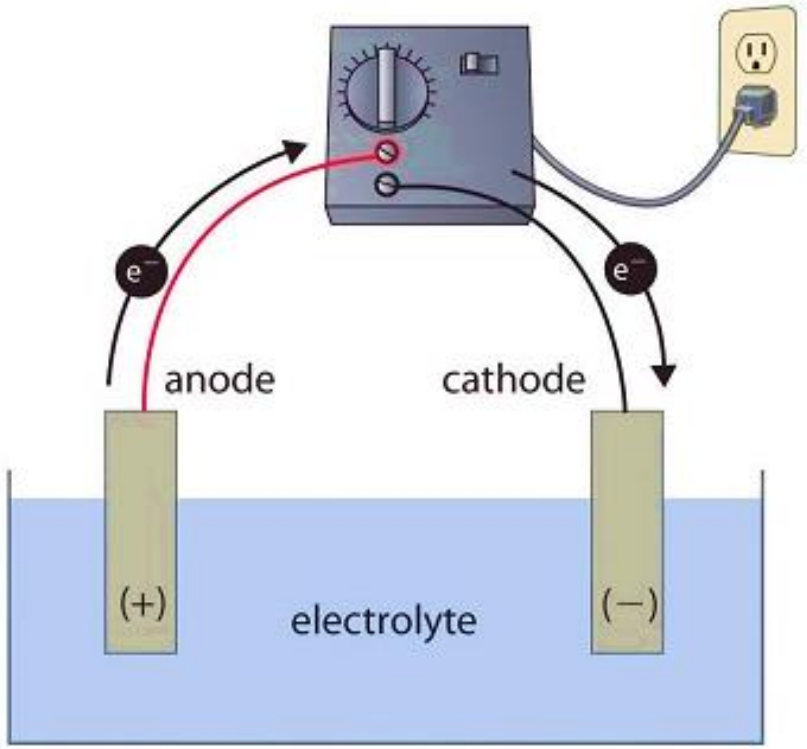
A device for producing an electrical current from a chemical reaction (redox reaction) is called an electrochemical cell.

Types: Galvanic (Voltaic) Cell



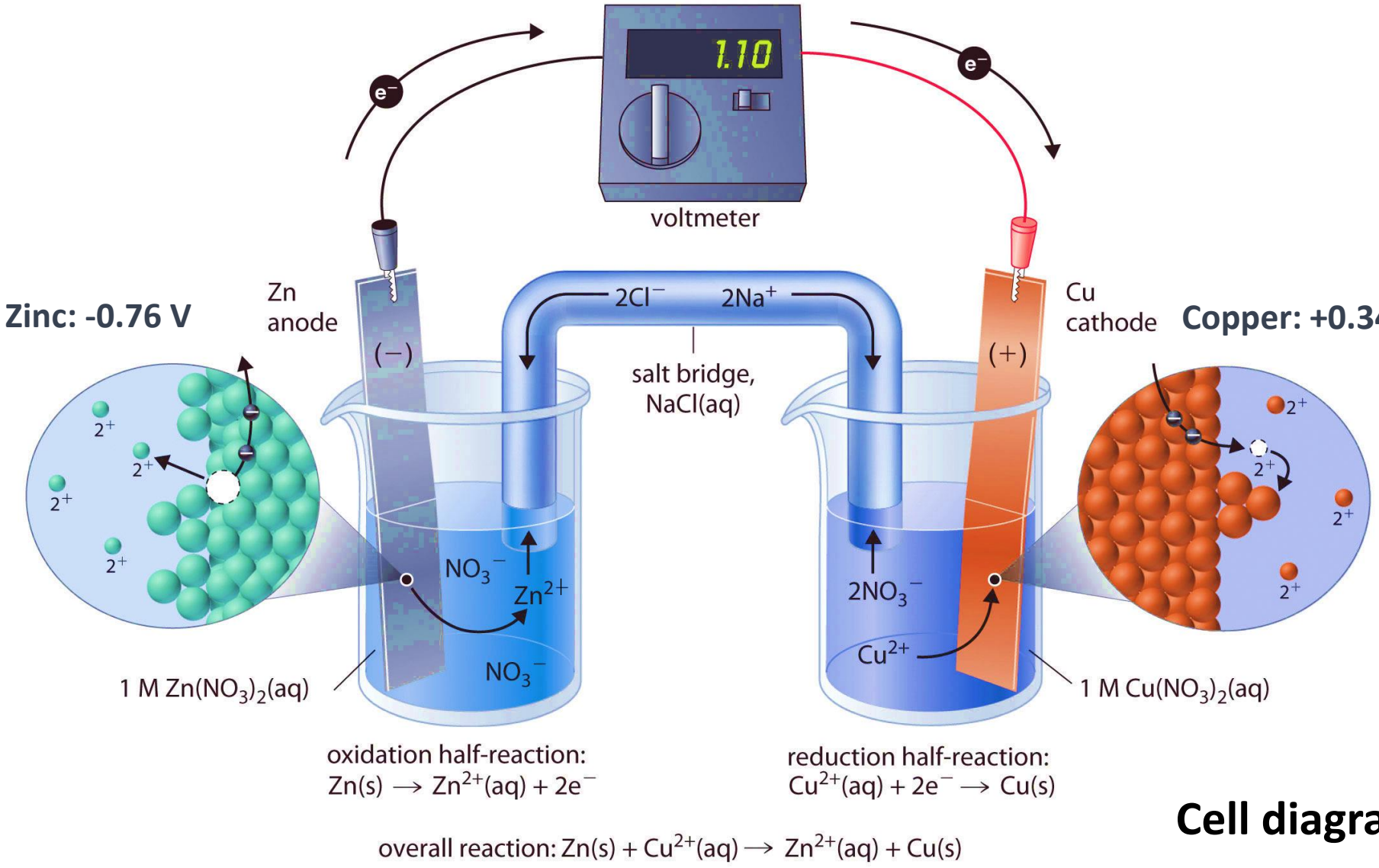
Spontaneous redox reaction produces electricity. Composed of two half-cells.

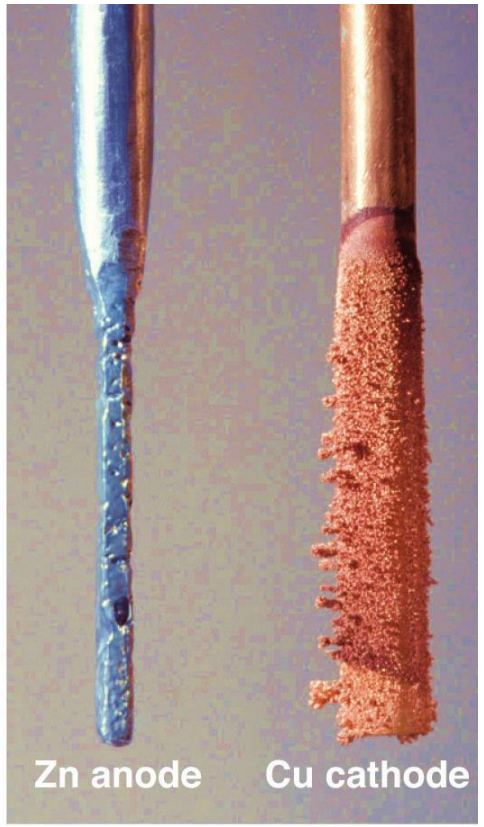
Electrolytic Cell



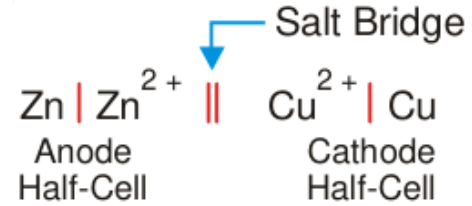
Non-spontaneous redox reaction forced to occur with external power source.

Galvanic(Voltaic) Cell



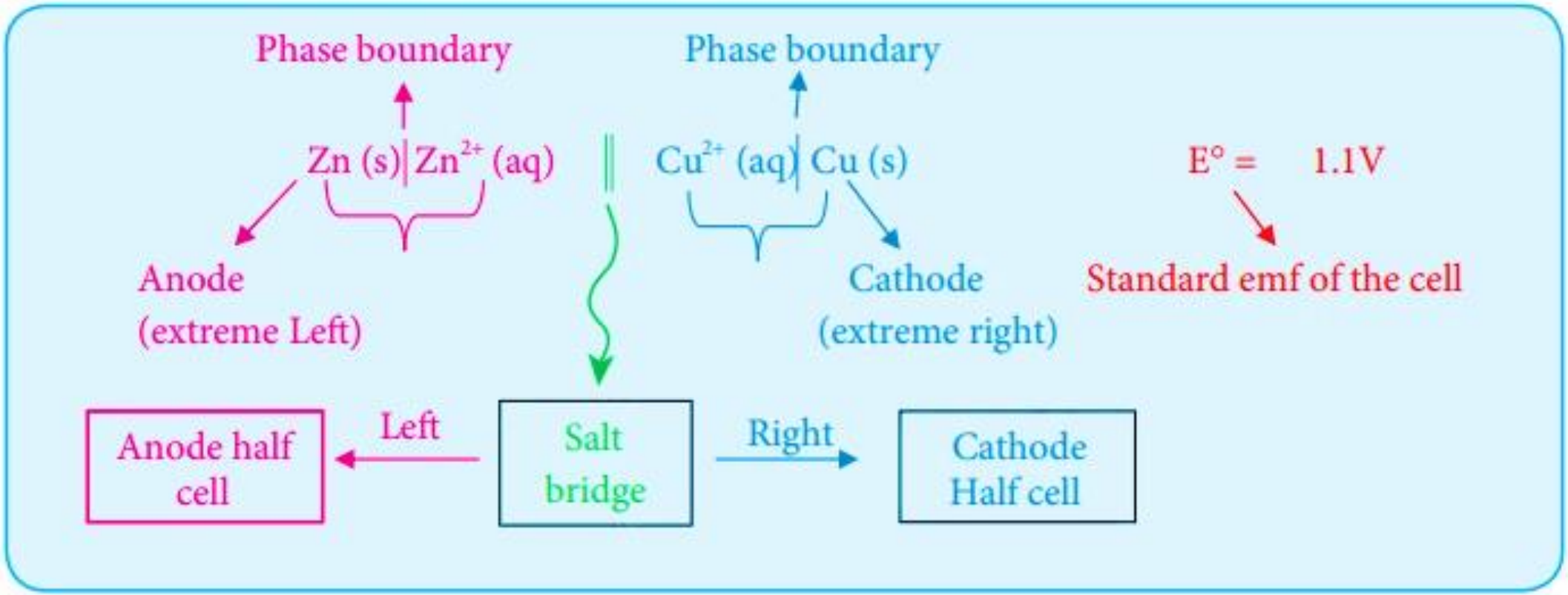


Cell diagram:



Cell diagram or Notation

A cell diagram is an abbreviated symbolic depiction of an electrochemical cell.
In 1953, IUPAC recommended the following conventions for writing cell diagrams.



Role of Salt Bridge

Charge balance is important because it is essential for the proper functioning of any electrochemical cell

The electrons flow from the anode to the cathode. The oxidation reaction that occurs at the anode generates electrons and positively charged ions.

The electrons move through the wire leaving the unbalanced positive charge in this vessel. In order to maintain neutrality, the negatively charged ions in the salt bridge will migrate into the anodic half cell.

A similar (but reversed) situation is found in the cathodic cell, where Cu^{2+} ions are being consumed, and therefore electroneutrality is maintained by the migration of K^{+} ions from the salt bridge into this half cell.

1 M: **KCl solution** **Agar gel** **Sodium sulfate solution** **Potassium nitrate solution** **Gelatin**

Role of Salt Bridge

Salt bridge :

1. It allows to flow of current by completing the circuit.
2. It maintains electrical neutrality of electrolytes in two half cells.

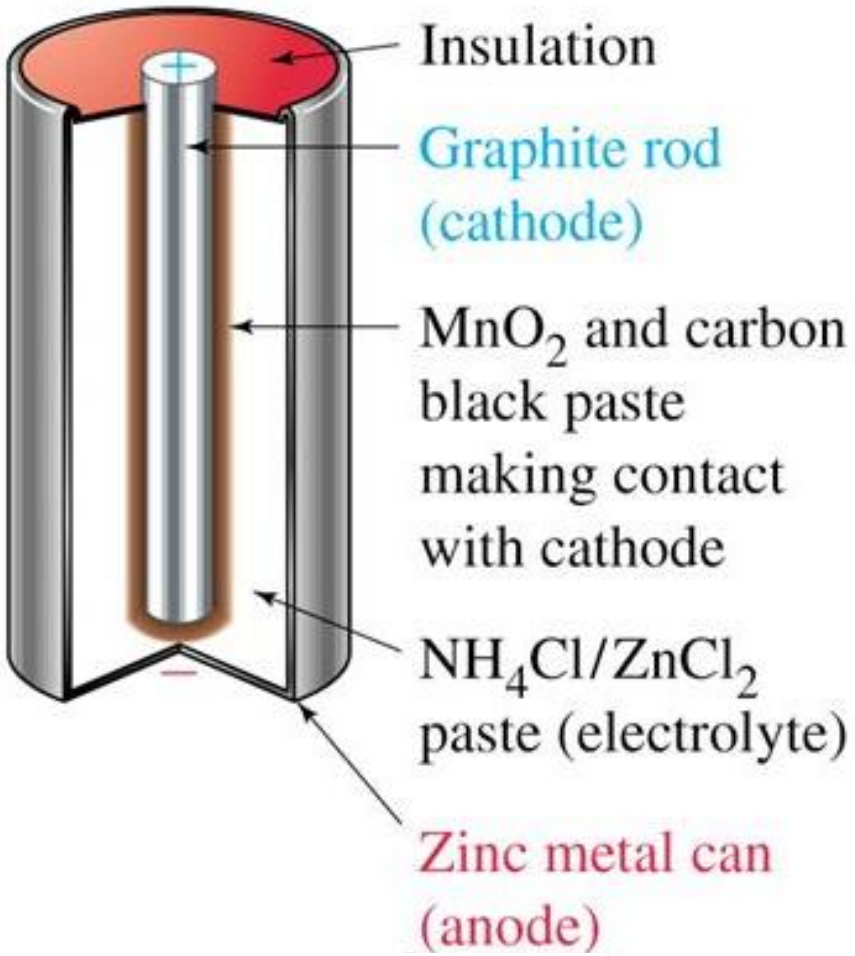
Characteristics of electrolyte used in salt bridge :

1. The electrolyte should be inert
2. The cations and anions of the electrolyte used should be of the same ionic mobility.

Toppersnotes

Types of Cell

Primary Cell/ Dry Cell/ Leclanché cell



Anode:

$$Zn\ (s) \rightarrow Zn^{2+}\ (aq) + 2\ e^-$$

Cathode:

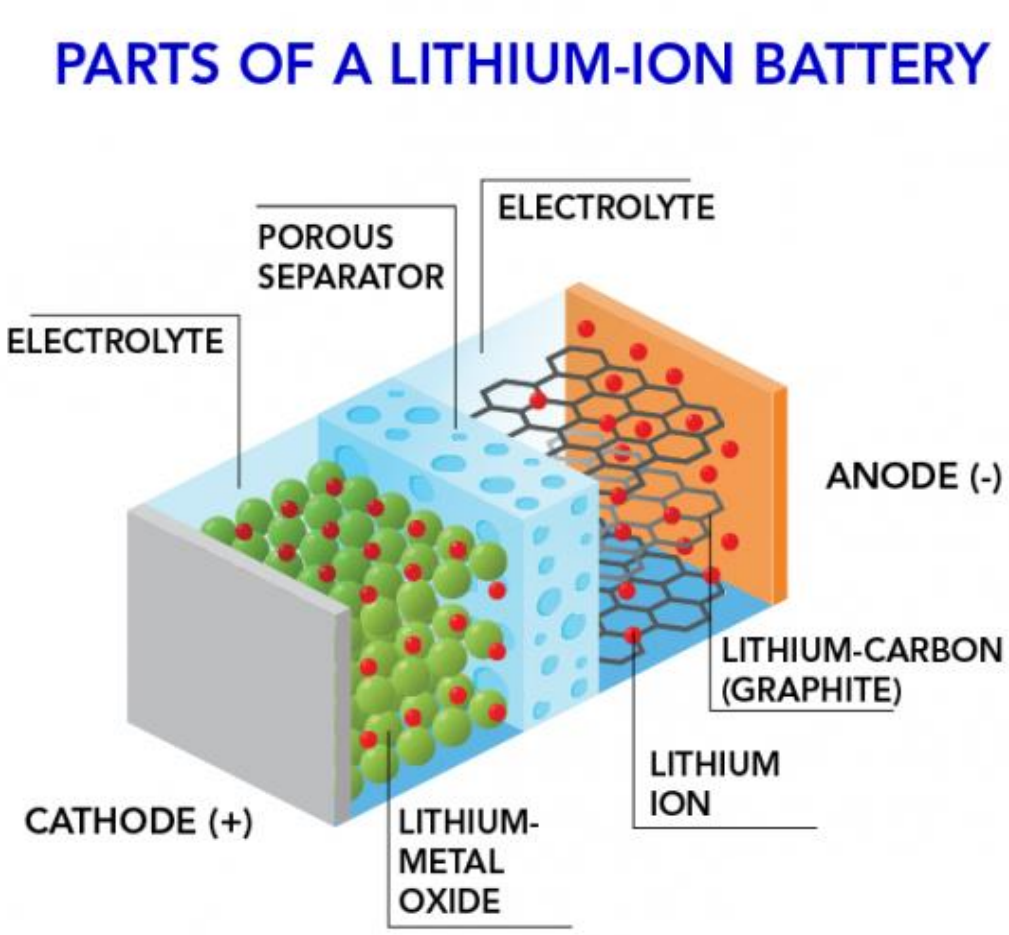
$$2MnO_2 + H_2O + 2e^- \rightarrow Mn_2O_3 + OH^-$$

Overall Reaction:

$$Zn + 2MnO_2 \rightarrow Zn^{2+} + Mn_2O_3 + OH^-$$

Types of Cell

Secondary Cell



Industrial Machinery

Electric carts

Electric forklifts

Elevators

Power tools

Uninterruptible Power Supply

Relay base stations for communication

Data centers

Mobile Device Field

IoT sensors

Wearable devices

Advanced Technology Field

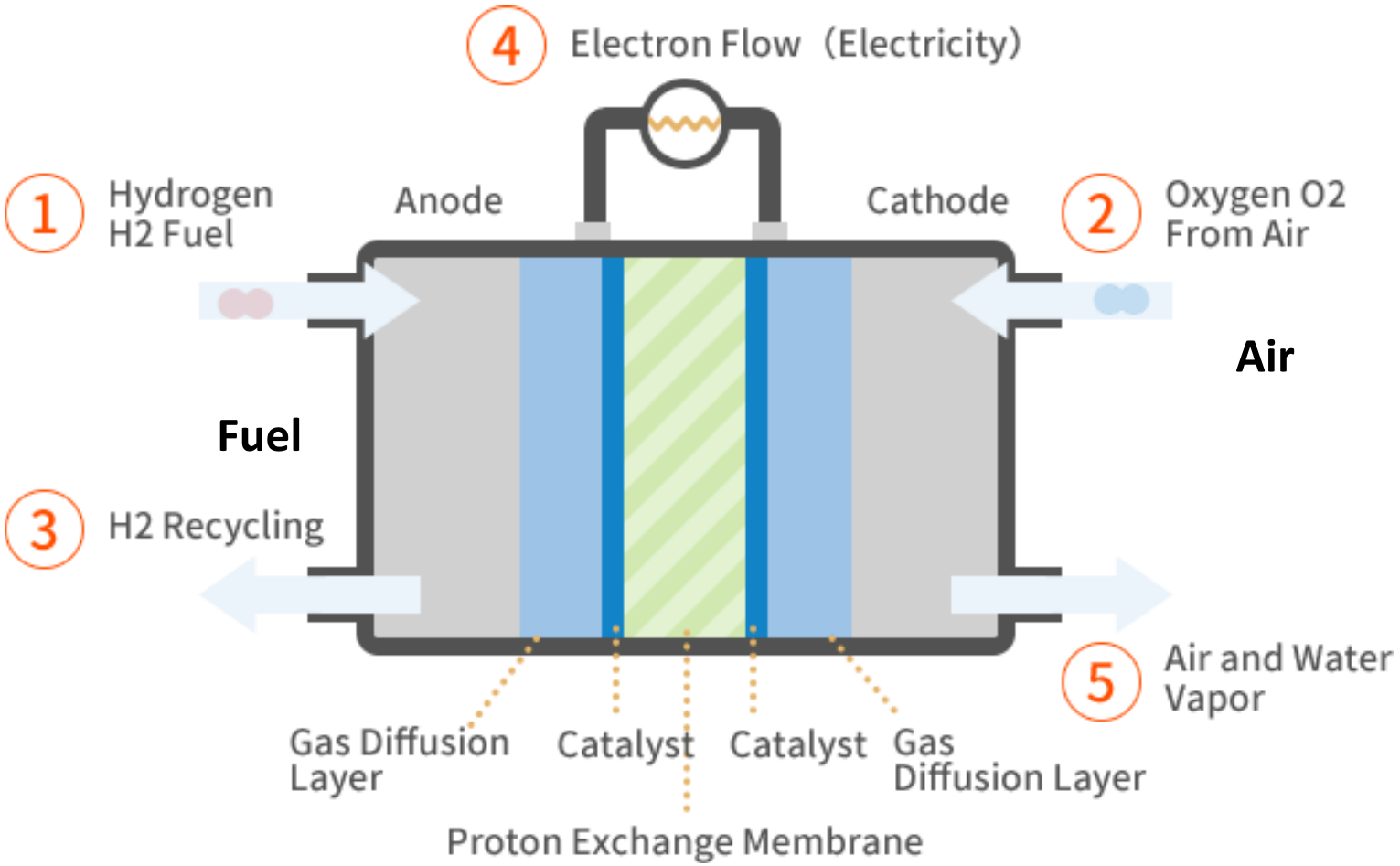
Satellites

Robots

Submarines

Fuel Cell

An electrochemical cell that converts chemical energy into electrical energy through redox reactions.



Anode side reaction:

$$2H_2 \rightarrow 4H^+ + 4e^-$$

Cathode side reaction:

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$$

Net reaction:

$$2H_2 + O_2 \rightarrow 2H_2O$$

CONDUCTANCE OF ELECTROLYTES

The power of electrolytes to conduct electric currents is termed conductivity or conductance. Like metallic conductors, electrolytes obey Ohm's law.

According to this law, the current I flowing through a metallic conductor is given by the relation.

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

where E is the potential difference at two ends (in volts); and R is the resistance measured in ohms (or Ω). The resistance R of a conductor is directly proportional to its length, l, and inversely proportional to the area of its cross-section, A. That is,

$$R \propto \frac{l}{A}$$

or

$$R = \rho \times \frac{l}{A} \qquad \ldots(1)$$

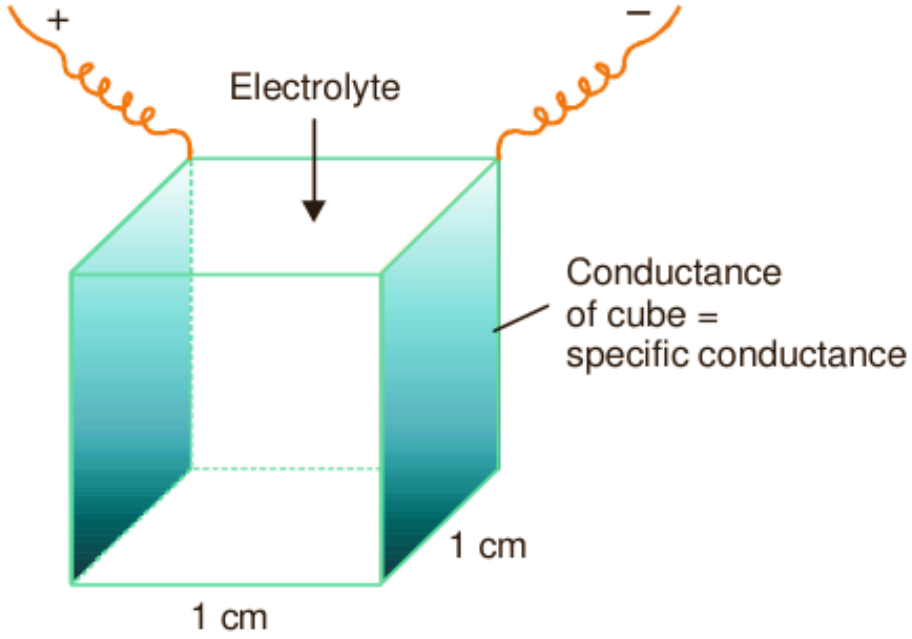
where ρ "rho" is a constant of proportionality and is called **resistivity** or **specific resistance.** Its value depends upon the material of the conductor. From (1) we can write

Specific Conductance

The conductance of one centimeter cube (cc) of a solution of an electrolyte.

The specific conductance is denoted by the symbol **κ (kappa).** Thus,

$$\kappa = \frac{1}{\rho} = \frac{1}{R} \times \frac{l}{A} = \frac{1}{\text{ohm}} \times \frac{\text{cm}}{\text{cm}^2} = \textbf{ohm}^{-1}\textbf{cm}^{-1}$$



The specific conductance increases with :
(i) ionic concentration, and (ii) speeds of the ions concerned.

In measuring the specific conductance of the aqueous solution of an electrolyte, the volume of water in which a certain amount of the electrolyte is dissolved is always measured in cubic centimeters (cc) and this is known as **dilution.** If the volume of a solution is V_{cc}, the specific conductance of the solution is written as κ.

Equivalent Conductance

The conductance of an electrolyte obtained by dissolving 1 gram-equivalent of it in V cc of water.

The equivalent conductance is denoted by **Λ** . It is equal to the product of the specific conductance, κ and the volume V in cc containing one gram-equivalent of the electrolyte at the dilution V.

$$\Lambda = \kappa \times V$$

Unit of Equivalent conductance

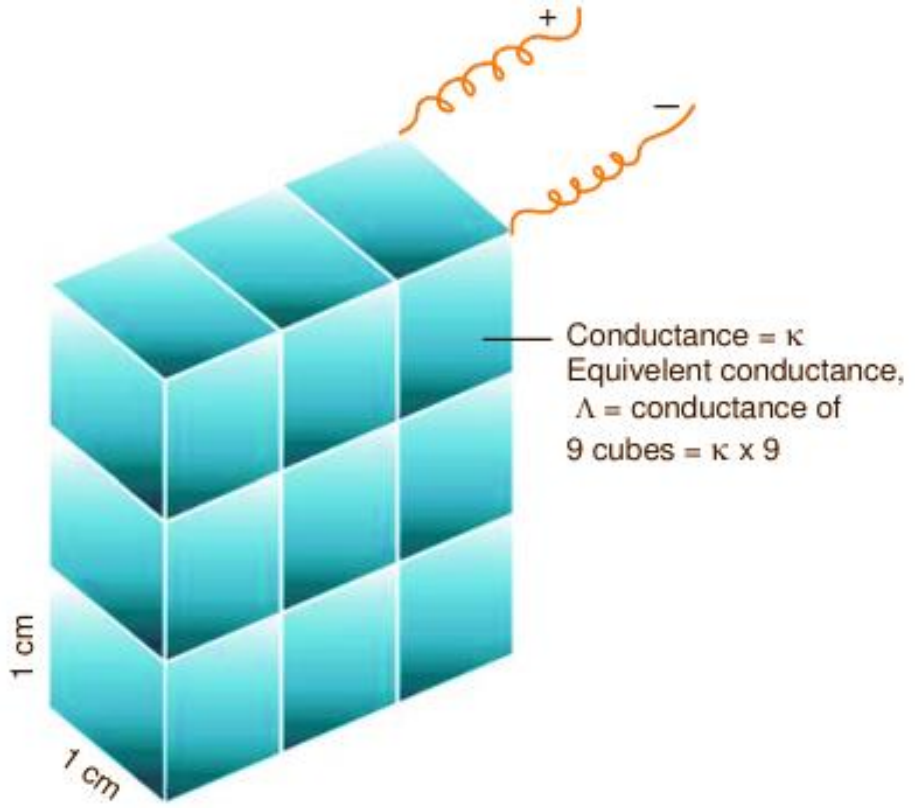
The unit of equivalent conductance may be deduced as follows :

$$\Lambda = \kappa \times V$$

$$= \frac{1}{R} \times \frac{l}{A} \times V$$

$$= \frac{1}{\text{ohm}} \times \frac{\text{cm}}{\text{cm}^2} \times \frac{\text{cm}^3}{\text{eqvt}}$$

$$= \text{ohm}^{-1}\,\text{cm}^2\,\text{eqvt}^{-1}$$



Solution of 1 g-eqvt. dissolved in 9 cc water between electrode plates 1 cm apart has L = κ x 9.

SOLVED PROBLEM 1. 0.5 Normal solution of a salt placed between two platinum electrodes, 20 cm apart and of area of cross-section 4.0 sq cm has a resistance of 25 ohms. Calculate the equivalent conductance of the solution.

SOLUTION

Calculation of specific conductance

$l = 20$ cm $\qquad A = 4.0$ sq cm $\qquad R = 25$ ohms

$$\text{Specific conductance } \kappa = \frac{1}{R} \times \frac{l}{A}$$

$$= \frac{1}{25} \times \frac{20}{4}$$

$$= 0.2 \text{ ohm}^{-1} \text{ cm}^{-1}$$

Calculation of Equivalent conductance

$$\text{Equivalent conductance } = \kappa \times \frac{1000}{\text{N}} = \frac{0.2 \times 1000}{0.5}$$

$$= \mathbf{400 \text{ ohm}^{-1} \text{ cm}^2 \text{ eqvt}^{-1}}$$

SOLVED PROBLEM 2. The resistance of a N/10 solution of a salt is found to be 2.5×10^3 ohms. Calculate the equivalent conductance of the solution. Cell constant = 1.15 cm^{-1}.

SOLUTION

Calculation of Specific conductance

$$\text{Specific conductance } \kappa = \frac{1}{R} \times \text{cell constant}$$

$$= \frac{1}{2.5 \times 10^3} \times 1.15$$

Calculation of Equivalent conductance

$$\text{Equivalent conductance} = \frac{\kappa \times 1000}{N}$$

$$= \frac{1.15 \times 1000}{2.5 \times 10^3 \times 0.1} = \frac{115}{25}$$

$$= \mathbf{4.60\ ohm^{-1}\ cm^2\ eqvt^{-1}}$$

Molar Conductance

The conductance of all ions produced when one mole of an electrolyte is dissolved in V cc of solution.

Molar conductance is denoted by **$\mu = k \times V$**

where V is the volume of the solution in cc containing one mole of the electrolyte.

$$\mu = \frac{1}{R} \times \frac{l}{A} \times V$$

$$= \frac{1}{\text{ohm}} \times \frac{\text{cm}}{\text{cm}^2} \times \frac{\text{cm}^3}{\text{mol}}$$

$$= \text{ohm}^{-1}\ \text{cm}^2\ \text{mol}^{-1}$$

Calculation of Molar conductance

Molar conductance can be calculated by using the relation :

$$\mu = \frac{\kappa \times 1000}{M}$$

where M is the number of moles of the electrolyte present in 1000 cc of solution.

CONDUCTANCE OF ELECTROLYTES

Upon dilution specific conductance decreases, while Equivalent conductance and Molar conductance increases.

- It is important to note that specific conductance decreases with dilution. It is the conductance of one cc of the solution. Upon diluting the solution, **the concentration of ions or no. of ions per cc decreases**. Hence the specific conductance falls.

- On the other hand, the equivalent and molar conductance show an increase as **the no. of ions is fixed as 1 equivalent or 1 mole**.

When solution becomes more and more dilute, the distance between the ions (or the "free path" available for movement of the ions) increases. So the ions can move faster without colliding with other ions on its way; therefore equivalent conduction or molar conductance increases **This results in an increase in the conductance of the solution.**

Factors influencing the conductivity of electrolytes

- Nature of electrolyte: Strong electrolytes ionize almost completely in the solution whereas weak electrolytes ionize to a small extent.
- Size of ions: larger the ion, smaller will be its conductance.
- Nature of solvent and viscosity: Greater the polarity of the solvent, greater is the conductance. Greater the viscosity, lesser will be the conductance.
- Concentration of solution: Higher the concentration of the solution, less is the conduction.
- Temperature: On increasing the T, the dissociation increases and the conduction increases.

Debye-Huckel Theory

Modern theory of strong electrolytes → Not Applicable to Weak Electrolyte

Debye and Huckel initially derived an equation to describe how the equivalent conductance of electrolytic solution changes on dilution. Later this equation was further improved by Onsager and now this equation is known as Debye huckel Onsager equation.

$$\Lambda_c = \Lambda_o - (A + B\Lambda_o)\sqrt{C}$$

Λ_c = equivalent conductance at a given concentration
Λ_o = equivalent conductance at infinite dilution
C = concentration
Where A and B are constant at a given temperature

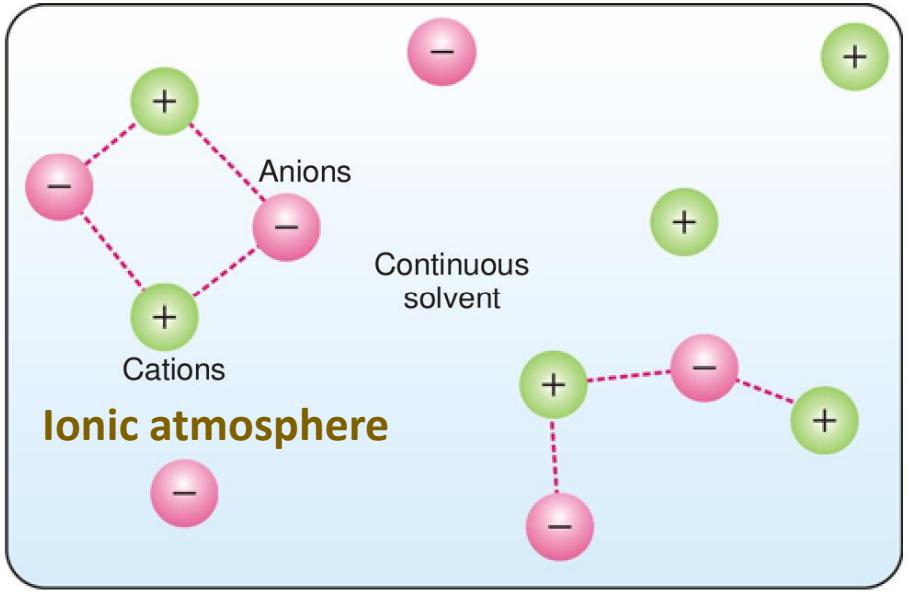
Brief outline of the main ideas of the theory

- The strong electrolyte is completely ionized (we should say 'almost completely ionised') at all dilutions.
- Equivalent conductance decreases with increase in concentration is due to fall in mobilities of the ions due to greater inter-ionic effect and vice-versa.

Debye-Huckel Theory

- Since oppositely charged ions attract each other, it suggests that anions and cations are not uniformly distributed in the solution of an electrolyte but that the cations tend to be found in the vicinity of anions and vice-versa.

- The ratio λ_v / λ_∞ does not correctly give the degree of dissociation, α for strong electrolytes but only the conductance or conductance coefficient f_c.



Ostwald's Law: $$\alpha = \frac{\lambda_v}{\lambda_\infty}$$

where λ_v and λ_∞ are the equivalent conductances at finite dilution V and infinite dilution respectively. Their values are found by conductance measurements and Kohlrausch's law.

- In spite of almost complete ionisation, λ_v is much less than λ_∞.

Variation of Equivalent conductance with Concentration (or Dilution)

The equivalent conductance of a solution does not vary linearly with concentration. The effect of concentration on equivalent conductance can be studied by plotting L values against the square root of the concentration.

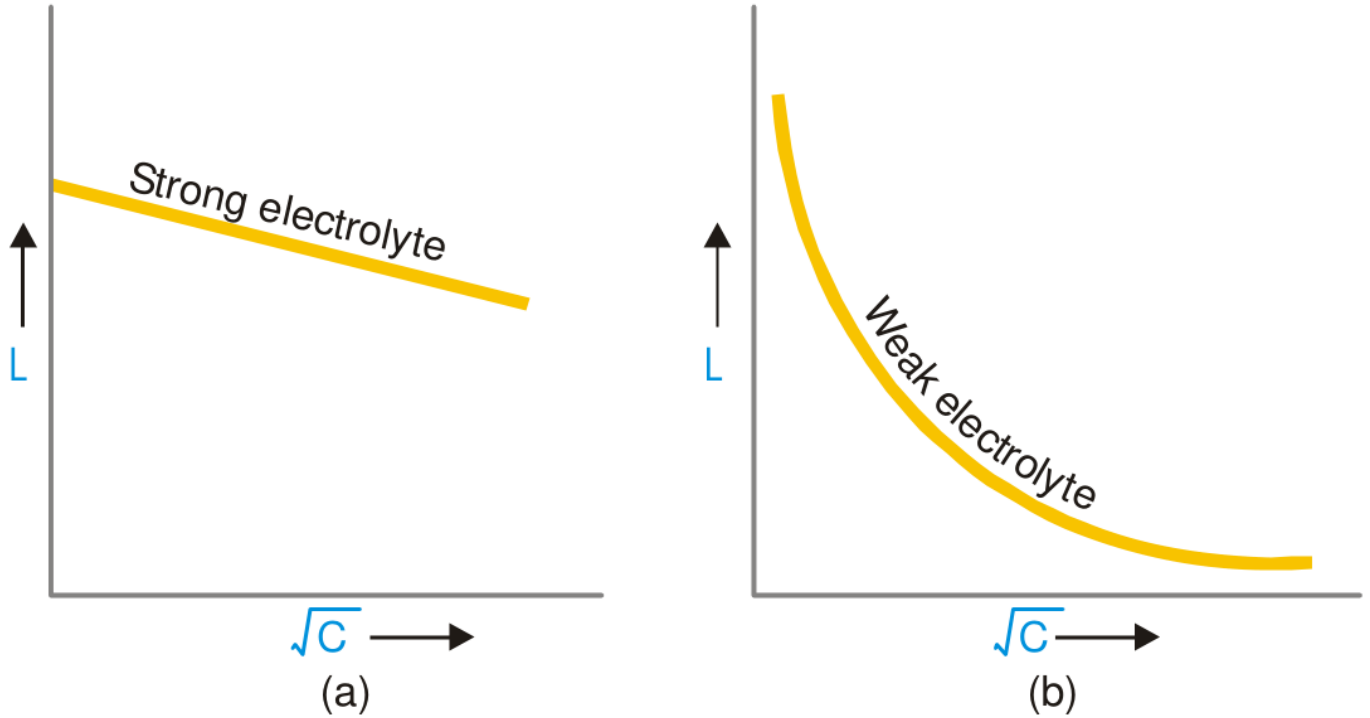


Figure 24.5
Variation of equivalent conductivity, L with $\sqrt{C}$:
(*a*) for strong electrolyte; (*b*) for weak electrolyte.

Kohlrausch's Law

The equivalent conductance of an electrolyte at infinite dilution is equal to the sum of the equivalent conductances of the component ions.

The law may be expressed mathematically as :

$$\lambda_{\infty} = \lambda_a + \lambda_c$$

where λ_a is the equivalent conductance of the anion and λ_c that of the cation.

For example, the equivalent conductance of NaCl at infinite dilution at 25°C is found to be 126.45. The equivalent conductance of Na^+ and Cl^- ion is 50.11 ohm^{-1} and 76.34 ohm^{-1} respectively. Thus,

$$\lambda_{\infty}(NaCl) = \lambda_{Cl^-} + \lambda_{Na^+}$$

or $$126.45 = 50.11 + 76.34$$

This is in conformity with the Kohlrausch's Law.

Transport Number

During electrolysis the current is carried by the anions and the cations. **The fraction of the total current carried by the cation or the anion is termed its Transport number or Hittorf's number.** If v_+ represents the speed of migration of the cation and v_- that of the anion,

$$\text{the transport number of cation} = \frac{v_+}{v_+ + v_-}$$

$$\text{the transport number of anion} = \frac{v_-}{v_+ + v_-}$$

The transport number of the cation is represented by t and that of the anion by t_-.

Thus $$t_+ = \frac{v_+}{v_+ + v_-} \quad \text{and} \quad t_- = \frac{v_-}{v_+ + v_-}$$

or $$\frac{t_+}{t_-} = \frac{v_+}{v_-} \quad \text{and} \quad t_+ + t_- = 1$$

If the speed ratio v_+/v_- be denoted by r, we have,

$$r = \frac{t_+}{t_-} = \frac{t_+}{1 - t_+}$$

and $$t_- = \frac{1}{1 + r}$$

Each ion has the same constant ionic conductance at a fixed temperature, no matter of which electrolyte it forms a part. It is expressed in $ohm^{-1}\ cm^2$ and is directly proportional to the speeds of the ions.

$$\lambda_a \propto v_- \quad \text{or} \quad \lambda_a = k \times v_-$$
$$\lambda_c \propto v_+ \quad \text{or} \quad \lambda_c = k \times v_+$$

where k is the proportionality constant.

Also $$\lambda_\infty \propto (\lambda_a + \lambda_c) = k\,(v_- + v_+)$$

$$\therefore \quad \frac{\lambda_a}{\lambda_\infty} = \frac{kv_-}{k(v_- + v_+)} = \frac{v_-}{v_- + v_+} = t_- \qquad ...(1)$$

and $$\frac{\lambda_c}{\lambda_\infty} = \frac{kv_+}{k(v_- + v_+)} = \frac{v_+}{v_- + v_+} = t_+ = 1 - t_- \qquad ...(2)$$

Dividing (1) by (2), we have

$$\frac{\lambda_a}{\lambda_c} = \frac{t_-}{1 - t_-} \qquad ...(3)$$

With the help of the expression (3), we can determine ionic conductances from the experimental values of the transport number of the ions.

(1) Calculation of λ_∞ for Weak electrolytes

Weak electrolytes do not ionise to a sufficient extent in solution and are far from being completely ionised even at very great dilution. The practical determination of λ_∞ in such cases is, therefore, not possible. However, it can be calculated with the help of Kohlrausch's law.

$$\frac{\lambda_a}{\lambda_c} = \frac{t_-}{1 - t_-}$$

$$\lambda_a - t_- \lambda_a = t_- \lambda_c$$

$$\lambda_a = t_- (\lambda_a + \lambda_c)$$

$$= t_- \lambda_\infty$$

Thus the ionic conductance of an ion is obtained by multiplying the equivalent conductance at infinite dilution of any strong electrolyte containing that ion by its transport number.

In this manner, the ionic mobilities of the two ions present in the weak electrolyte can be calculated. Thus we can get the equivalent conductance of the electrolyte at infinite dilution by adding up these two values.

Applications

Uses of Kohlrausch's law

- Calculation of molar conductivity at infinite dilution for weak electrolytes
- Calculation of degree of dissociation.
- Calculation of dissociation constant for a weak electrolyte
- Calculation of solubility of sparingly soluble salt.

Conductometric Titrations

Titrations in which conductance measurements are made in determining the end-point of acid-base reactions, precipitation reactions.

Conductance of a solution at a constant temperature depends upon the **number of ions** present in it and their mobility.





Conductometer

APPLICATIONS

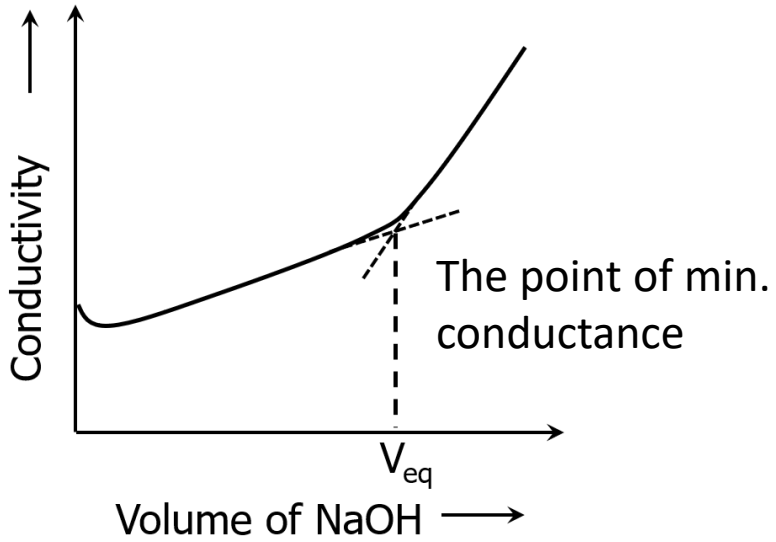
Commonly used particularly in acid-base, redox, and complexometric titrations, where the change in conductivity provides valuable information about the progress of the reaction.

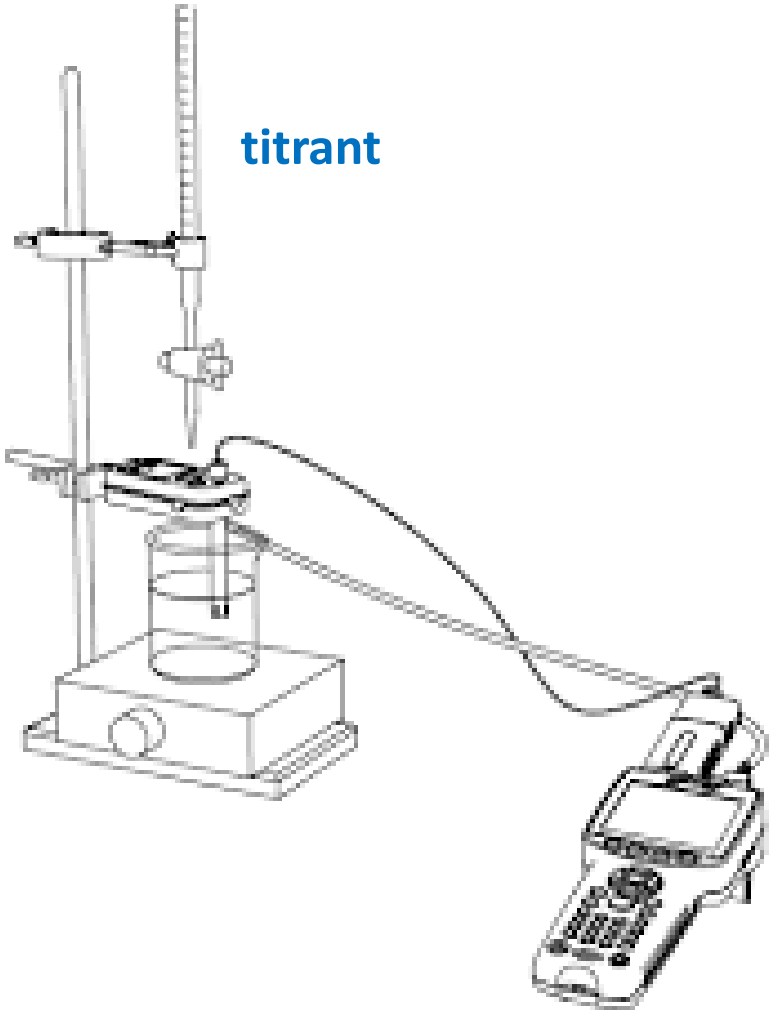
Conductometric Titrations

1. The titrant is added from a burette into a measured volume of the solution to be titrated in a conductance cell

2. The conductance readings corresponding to the various additions are plotted against the volume of the titrant

In this way two linear curves are obtained, the point of intersection of which is the end-point.





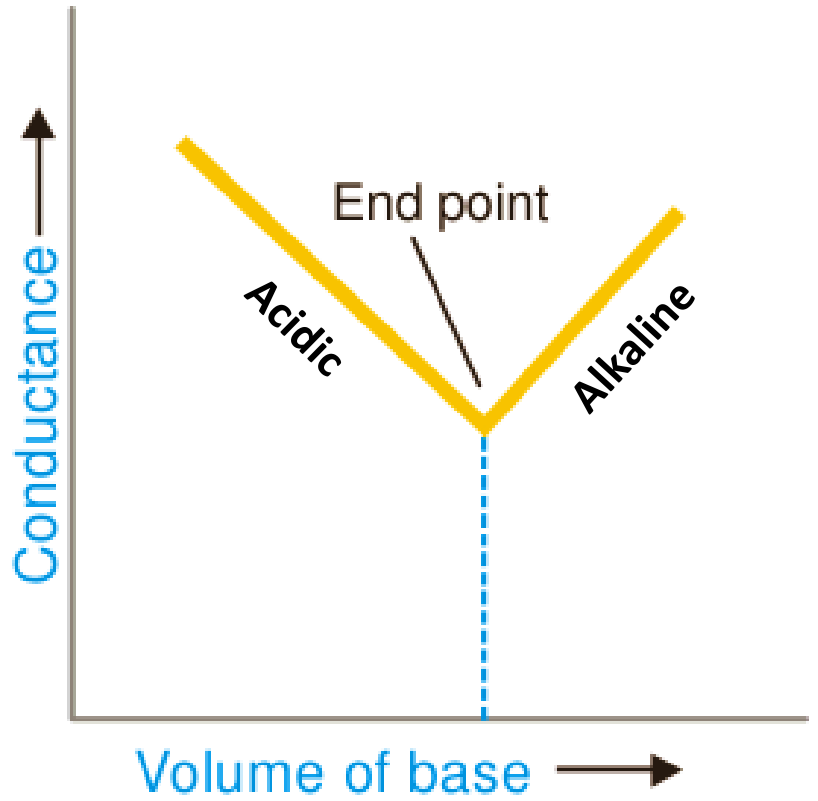
Conductometric Titrations

Titration of a Strong acid against a Strong base [HCl vs NaOH]

$$H^+ + Cl^- + Na^+ + OH^- \longrightarrow Na^+ + Cl^- + H_2O$$ **(Undissociated)**

- Before the addition of alkali, the conductance of the solution is due to presence of H^+ and Cl^- ions.
- As alkali solution is added, the hydrogen ions are removed by combination with the hydroxyl ions

Ion	$u_c \times 10^4$	Ion	$u_a \times 10^4$
H^+	36.30	OH^-	20.50
Li^+	4.01	Cl^-	7.91
Na^+	5.19	I^-	7.95
K^+	7.61	NO_3^-	7.40
Ca^{2+}	6.16	SO_4^{2-}	8.27
La^{3+}	7.21		



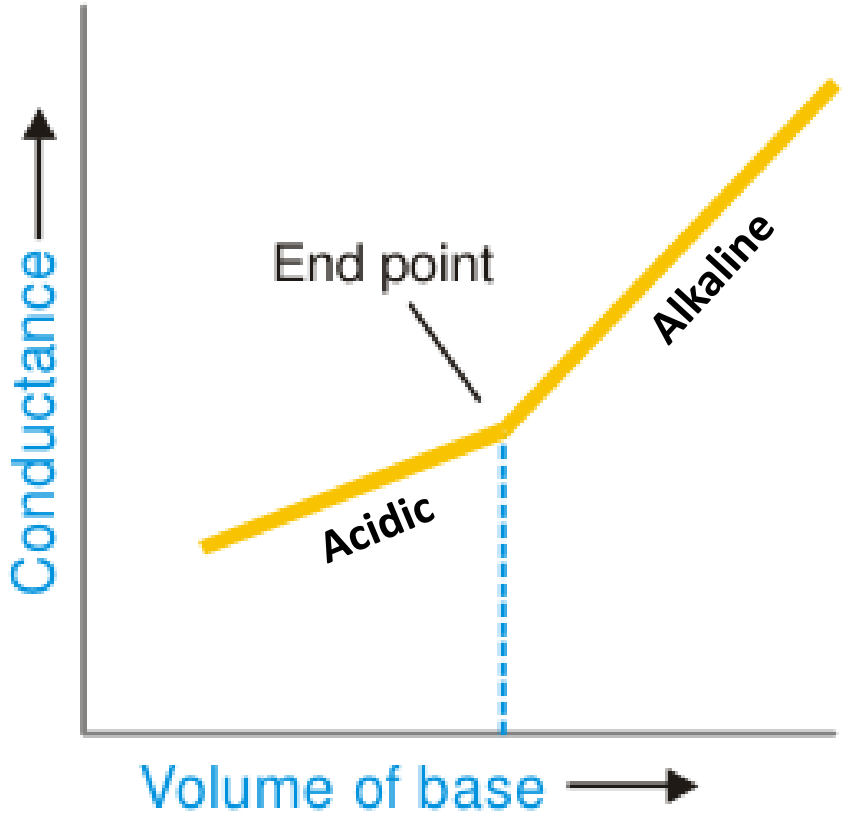
Conductometric Titrations

Titration of a Weak acid against a Strong alkali [CH_3COOH vs NaOH]

- The initial conductance is low because of the poor dissociation of the weak acid (**CH_3COOH**).
- On adding alkali, highly ionised **CH_3COONa** is formed.
- Initially, acetate ions tend to suppress the ionisation of acetic acid due to **Common Ion Effect.**

$$CH_3COOH + Na^+ + OH^- \longrightarrow CH_3COO^- + Na^+ + H_2O$$

- After a while, conductivity increases because of the conducting power of ionized salt than the weak acid.
- Further addition of alkali, conductivity booms due to the high mobility of OH^- ions.



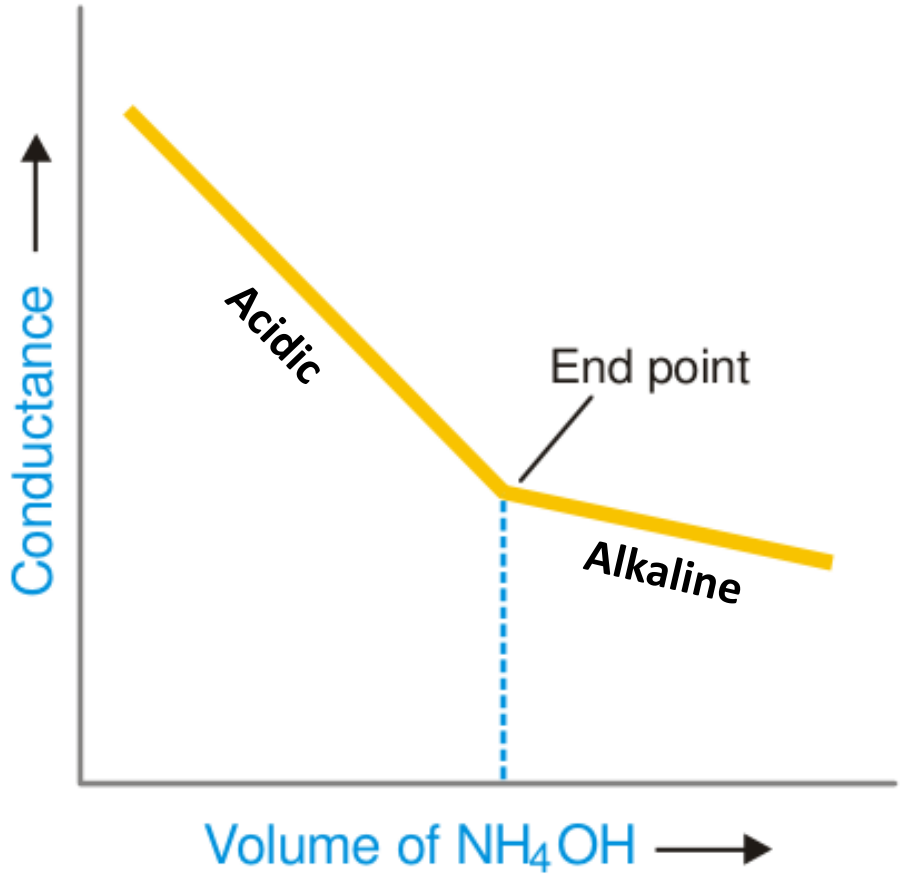
Conductometric Titrations

Titration of a Strong acid against a Weak base [HCl vs NH_4OH]

- The conductance of the solution will first decrease due to the decrease of the fast moving H^+ ions with the formation of H_2O and their replacement by slow moving NH_4^+ ions.

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

- After the end-point has been reached, the addition of ammonium hydroxide will not cause any appreciable change in conductance value as it is a weak electrolyte having low conductance.



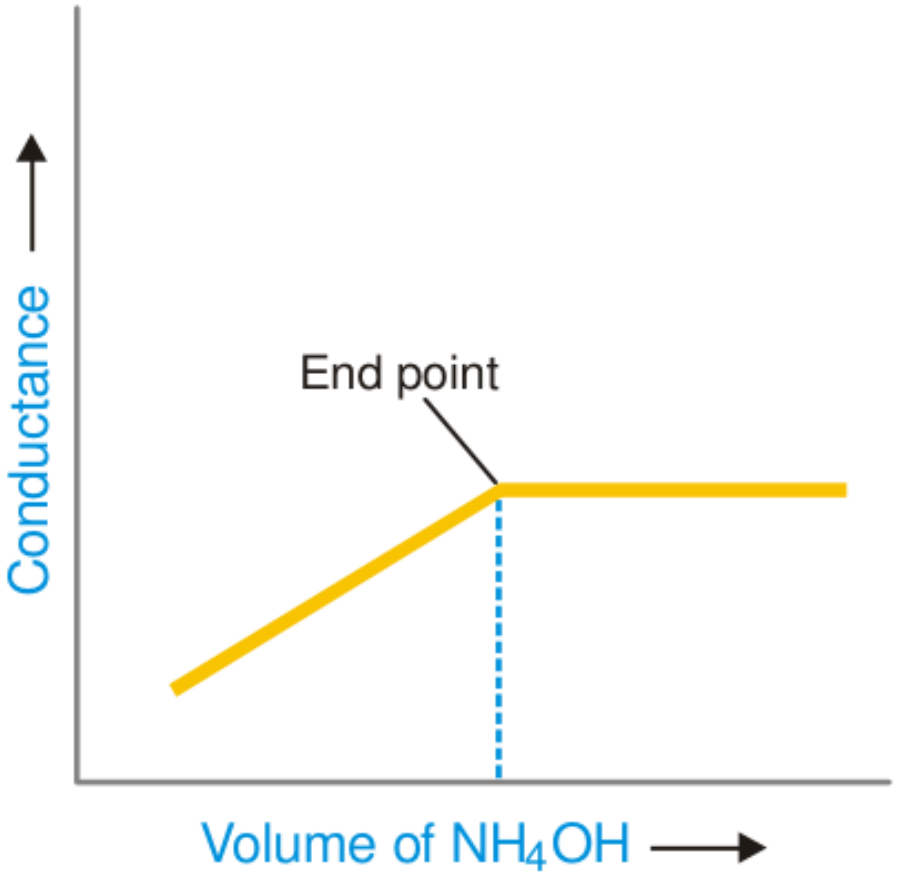
Conductometric Titrations

Titration of a Weak acid against a Weak base [CH_3COOH vs NH_4OH]

- The initial conductance of the solution is low due to the poor dissociation of the weak acid (**CH_3COOH**).

$$CH_3COOH + NH_4OH \rightarrow CH_3COONH_4 + H_2O$$

- It starts increasing as the highly ionized salt, CH_3COONH_4 is formed.
- After the end point, the conductivity remains almost constant because the free base NH_4OH is a weak electrolyte.



Conductometric Titrations

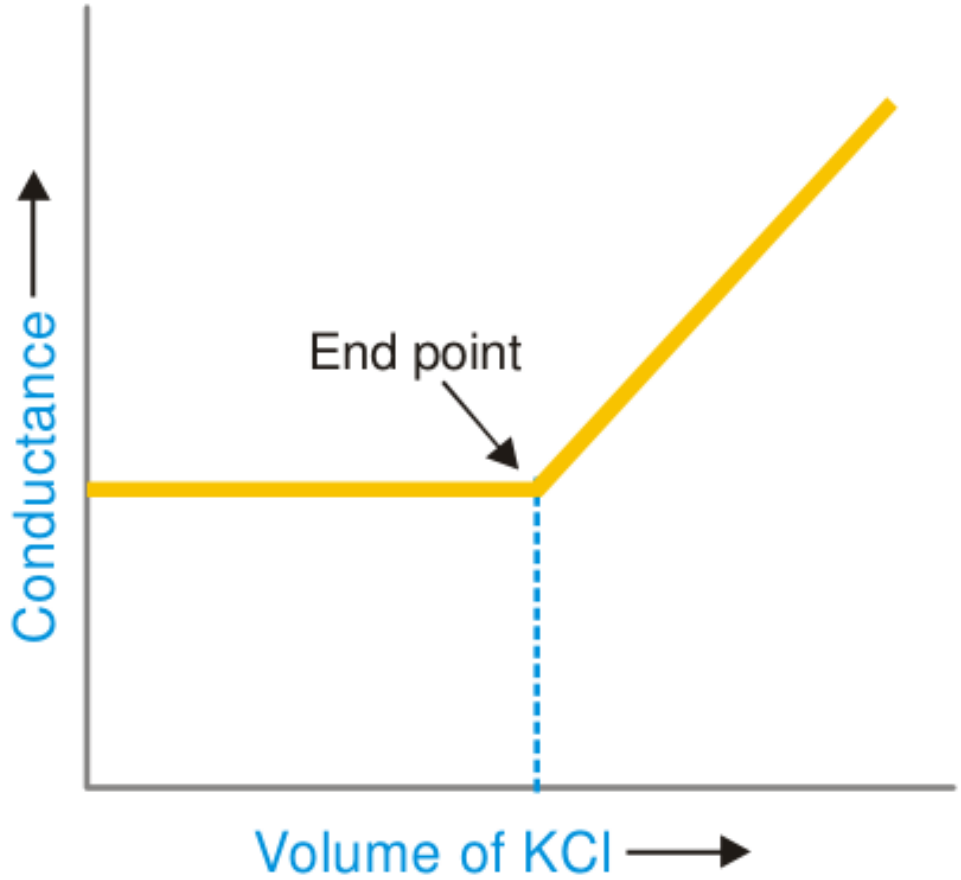
Precipitation reactions

[KCl vs $AgNO_3$]

- The change in conductance on the addition of **$AgNO_3$** is not much since the mobility of the potassium ion and the silver ion is merely same.

$$Ag^+ + NO_3^- + K^+ + Cl^- \longrightarrow K^+ + NO_3^- + AgCl\,(ppt)$$

- After the end-point, there is a sharp increase in conductance due to an increase in the number of free ions in solution.



Conductometric Titrations

Advantage of Conductometric Titrations

(1) Coloured solutions where no indicator is found to work satisfactorily can be successfully titrated by this method.

(2) This method is useful for the titration of weak acids against weak bases which do not give a sharp change of colour with indicators in ordinary volumetric analysis.

(3) More accurate results are obtained because the end -point is determined graphically.

Precautions. (*i*) It is necessary to keep the temperature constant throughout the experiment. (*ii*) In acid-alkali titrations, the titrant should be about 10 times stronger than the solution to be titrated so that the volume change is as little as possible.