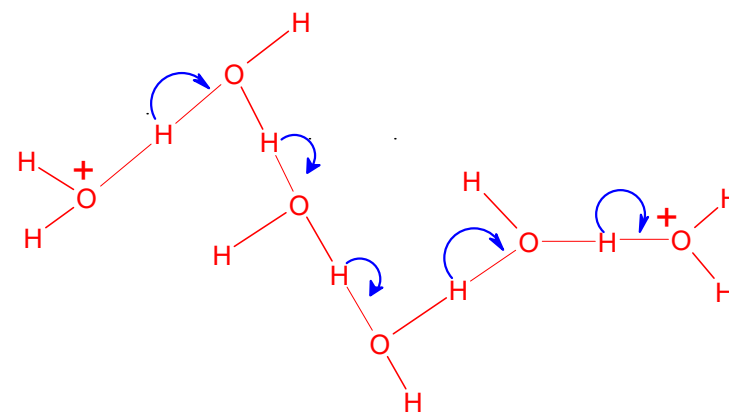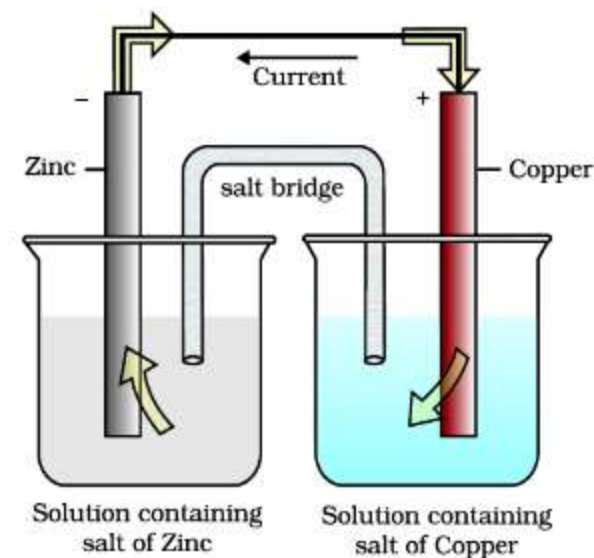# *Electrochemistry*

- Migration of ions
- Molar, specific, and equivalent conductance
- Transference (transport) number
- Determination of transference number by Hittorf's method
- Conductometric titrations
- Types of electrode: calomel and glass electrode
- Liquid junction potential
- Potentiometric titrations

Electrochemistry is the branch of chemistry that deals with the relation between chemical action and electricity. It deals with the study of electrical properties of electrolytes   and also the chemical changes brought about by passage of electricity.

Or

Electrochemistry is the study of production of electricity from energy released during spontaneous chemical reactions and the use of electrical energy to bring about non-spontaneous chemical transformations.

Electrical Conductance

❖ Substances that allow the passage of current through them are called conductors and the phenomenon is called electrical conductance.

❖ Conductors are further divided into two categories, namely, **metallic and electrolytic conductors**.

Metallic *vs* electrolytic conductors

1. In **metallic conductors**, the conduction is only due to the presence of free mobile electrons. Hence, these are referred to as electronic conductors.

2. The substances which conduct electricity both in the fused state and in the aqueous solution are called **electrolytic conductors or electrolytes.** These substances dissociate in molten state or aqueous solution to furnish ions. The conduction is due to the presence of these mobile ions. For example, molten or aqueous solution of sodium chloride.

Types of Electrolytes

Electrolytes are classified into two types :

1. **Strong electrolytes :** Those which are almost completely dissociated in their aqueous solutions and have a large value of conductance. For example, HCl, HNO_3, NaOH, KOH, NaCl and KCl

2. **Weak electrolytes :** Those which do not undergo complete dissociation even in their dilute aqueous solutions and have low value of conductance. In the solution of a weak electrolyte, there exists an equilibrium between the undissociated molecules and their ions. For example, CH_3COOH, HCOOH and NH_4OH.

❖ **Conductivity Cell:**

Conductance (G):

The reciprocal of solution resistance (1/R) is called Conductance, G.
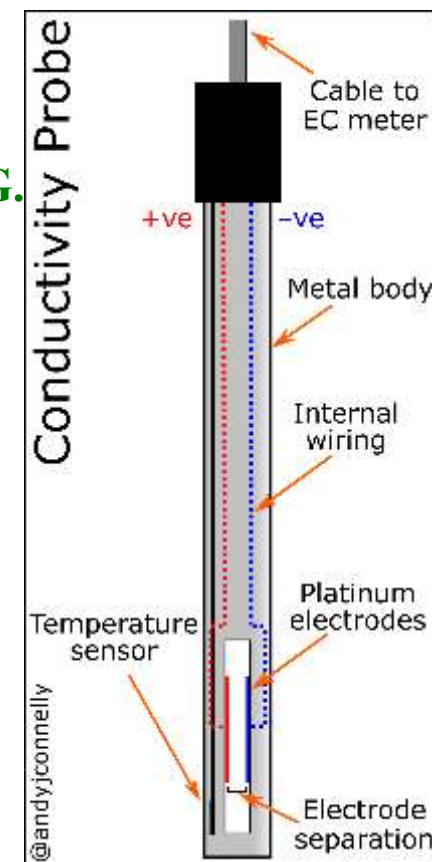
$$G = \frac{1}{R} = \frac{\kappa A}{l}$$

It is expressed in the unit called reciprocal ohm (ohm^{-1} or Ω^{-1})

In SI system, the unit of conductance is Siemen, S

Where,   **A = surface area of each electrode**

l **= distance between electrode**

κ **= conductivity**

Conductivity Probe

Cable to EC meter

+ve   −ve

Metal body

Internal wiring

Platinum electrodes

Temperature sensor

Electrode separation

@andyjconnelly

Specific Conductance

The resistance of any conductor varies directly as its length (l) and inversely as its cross-sectional area (a), i.e.

$$R \propto l/a$$

or
$$R = \rho \, (l/a)$$

Where ρ is a constant depending upon the nature of the material and is called specific resistance of the material.

- If, l =1cm and a =1cm^2, then ρ = R

- Specific resistance is defined as the resistance in ohms of a specimen 1 cm in length and 1 cm^2 cross-section (1 cm^3 of the material).

- The reciprocal of specific resistance, i.e., $1/\rho$ is called specific conductance.

Specific Conductance (κ):

From equation of specific resistance

$$\rho = R\,(a/l)$$

$$c = 1/\rho = (l/a)\,(1/R)$$

$$= (l/a) \times (conductance)$$

Since, conductance is measured in Ω^{-1}, length in cm and area in cm^2, hence,

$$\kappa = \Omega^{-1} \times (cm/cm^2) = \Omega^{-1}\,cm^{-1}$$ - units of specific conductance

In SI system, the units of specific conductance are Sm^{-1} where S stands for Siemen.

Equivalent Conductance (Λ_{eq}):

It is defined as the conducting power of all the ions produced by one gram equivalent of an electrolyte in a given solution.

Relation Between Specific Conductance and Equivalent Conductance

- Imagine 1 cc of a solution of an electrolyte placed between two large electrodes 1cm apart. The cross-sectional area of the solution will be 1cm^2.

- The conductance of the solution will evidently be its specific conductance because we are having one cc of solution.

- Further, If 1 cc of the solution contains 1gm equivalent of electrolyte dissolved in it.

- Then according to the definition, the conductance of the solution will be equal to the equivalent conductance (Λ)

- i.e., Conductance (G) = Specific conductance (κ) = Λ_{eq}

  = Equivalent conductance

<u>Molar Conductance</u> (Λ_m):

Conducting power of all the ions produced by one mole of the electrolyte in a given solution

Molar conductance is related to specific conductance by the relation

$$\Lambda_m = \kappa / c$$

Where c = concentration of the solution in moles/m^3

SI Units κ : S m^{-1}

c : mol/m^3

Λ_m : S m^2 mol^{-1}

Variation of Molar Conductance with dilution

Dilution ↑ ⟶ Molar conductance↑ ⟶ degree of dissociation of the electrolyte ↑.

Degree of dissociation is defined as the fraction of the total electrolyte in solution which exists in the form of its ions.

On dilution, the same amount of electrolyte is capable of furnishing a larger number of ions

However, the increase in number of ions on dilution is much lesser than increase in the volume of the solution
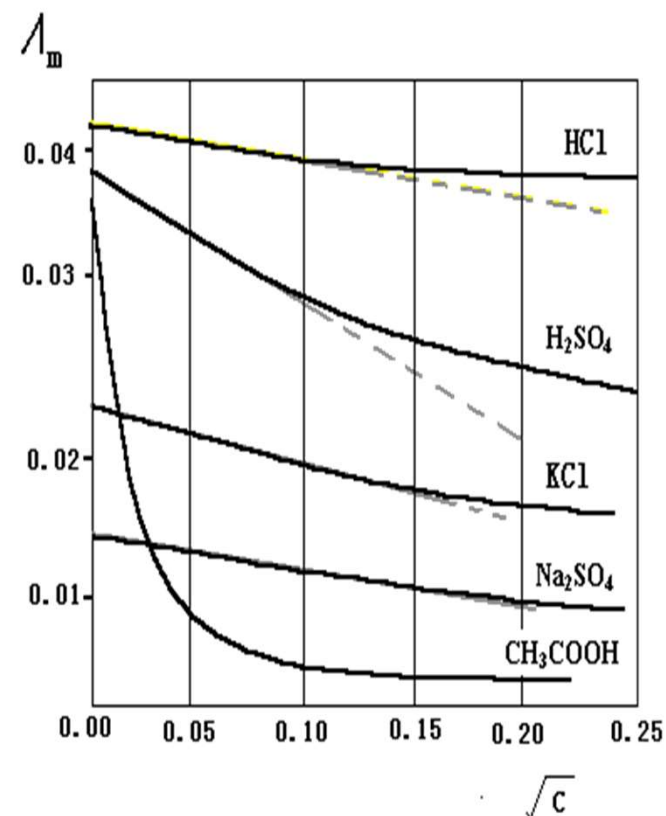
Therefore, the number of ions per unit volume (per cc) actually decreases. Hence, the *specific conductance decreases* although with *molar conductance increases* on progressive dilution.

Molar Conductance at Infinite Dilution (Λ_m°):

$$\alpha = \Lambda_m / \Lambda_m^{\circ}$$

Ionic Mobility

- Although, at infinite dilution, all electrolytes are completely dissociated, their molar conductance differ vastly from one another

- This is because of differences in speeds of the ions.

- Ex. The molar conductance at *infinite dilution of HCl* is more than *three times as high as that of NaCl.* Since chloride ion is common, it follows that the speed of hydrogen ion is more than three times of the speed of sodium ion.

- Speed of an ion varies with the potential applied.

- **Ionic mobility is defined as the distance travelled by an ion per second under potential gradient of 1 volt per meter**
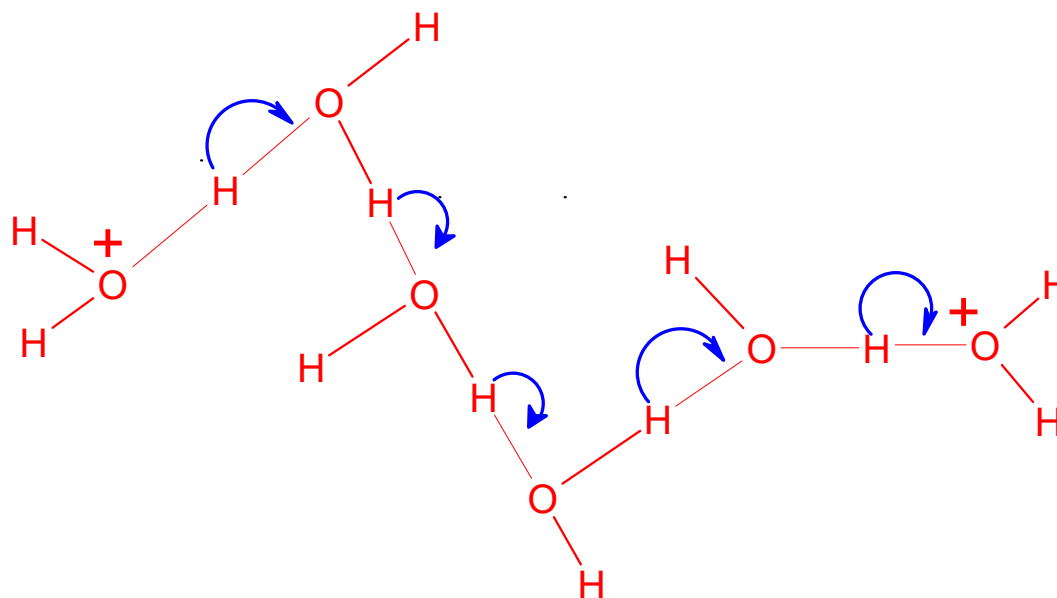
- **Ionic Mobility**
- The ionic mobility is extremely small as compared to the speed of gaseous molecules which is about 10^2 ms^{-1}. The low mobility of ions is due to the fact that there are frequent collisions between the ions and the solvent molecules since the mean free path of molecules in the liquid is very small.
- The ionic mobility of H$^+$ ion is found to be <u>five to ten times</u> that of other ions, except OH$^-$ ion
- H$^+$ ion in aqueous solutions is hydrated to form H$_9$O$_4^+$ ion, i.e., a trihydrate of hydronium ion, viz., H$_3$O$^+$. 3H$_2$O, having the following structure
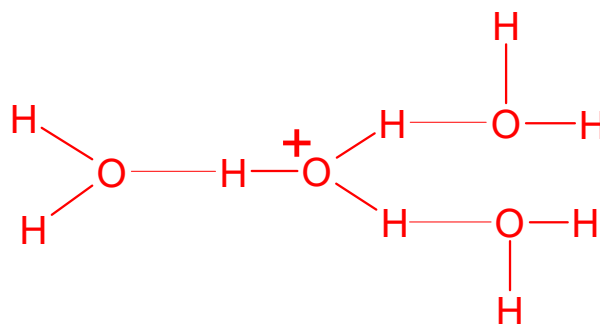
- **Ionic Mobility**
- The high mobility in hydroxylic solvents such as water can be explained by *Grotthus type* mechanism in which the proton moves rapidly from H_3O^+ to a hydrogen bonded water molecule and is transferred further along a series of hydrogen bonded water molecules by a rearrangement of hydrogen bonds.
- This accounts to high mobility of hydrogen ions in water.

**Grotthus-type Mechanism for High mobility of H^+ ions**

- **Ionic Mobility**
- Grotthus model also explains as to <u>why H$^+$ ions move about 50 times more rapidly through ice than through liquid water</u>
- Ice has tetrahedral structure with each oxygen atom surrounded by four hydrogen atoms


Covalent bond

Hydrogen bond
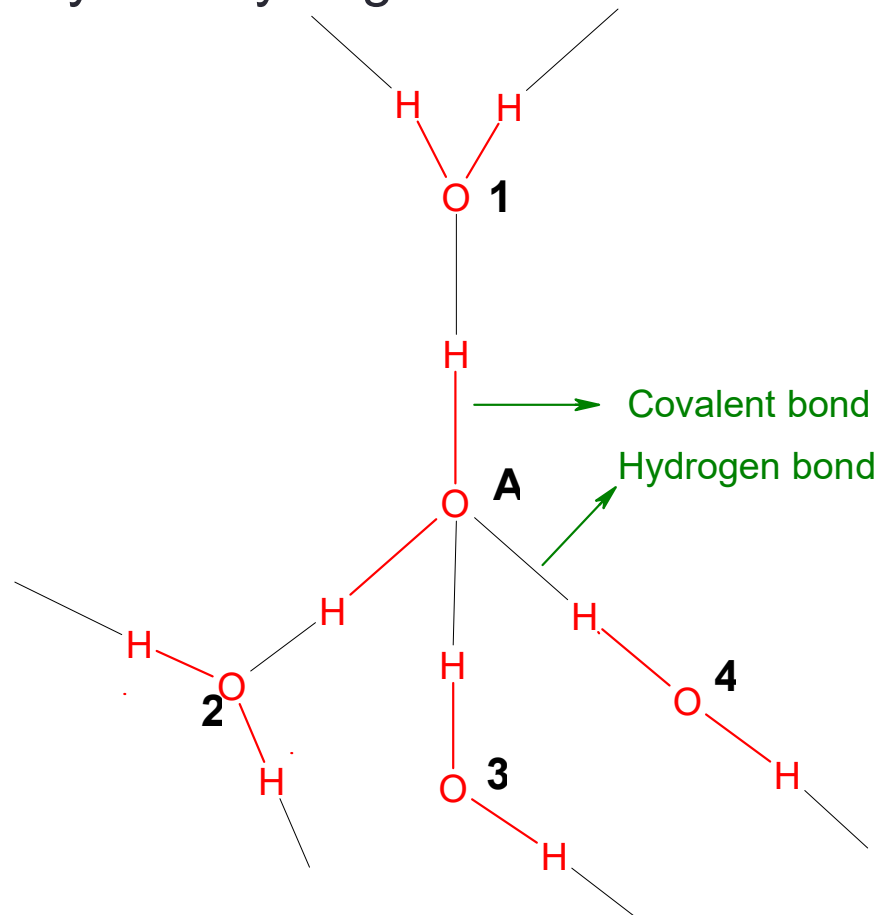
The central oxygen atom A is surrounded tetrahedrally by the atoms marked 1,2,3 and 4

- Each hydrogen atom lies on the center of line joining of the oxygen atoms.

- When water molecules are oriented properly, as in the case of ice, the hydrogen ions can move rapidly through its tetrahedral structure
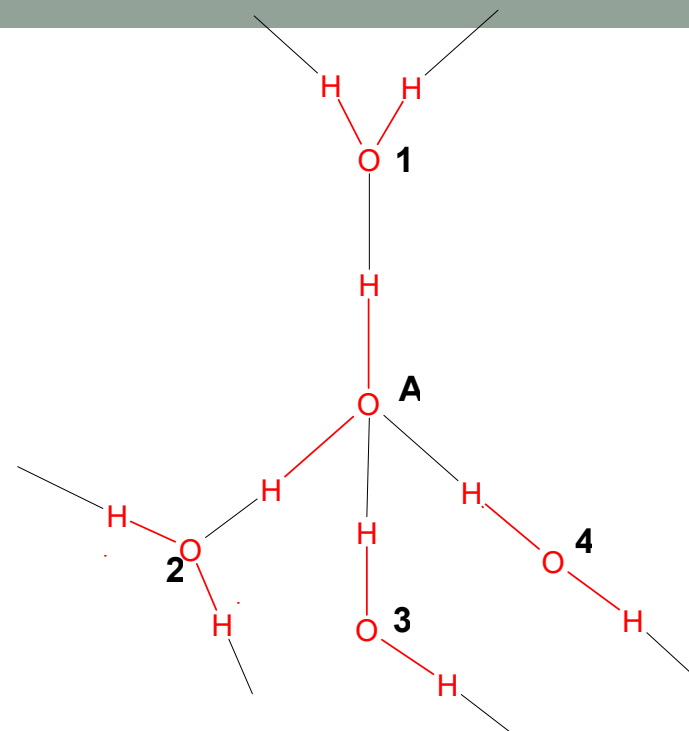
- Lithium and sodium ions have comparatively lower ionic mobilities

- *This is due to the higher charge density around these ions because of their small radii*

- The higher density causes these ions to be *more highly hydrated* by ion-dipole interactions than the larger ions

- Since *hydrated ions has to drag along a shell of water* as it moves through the solution, its mobility is naturally less than that of an unhydrated ion

- Ionic mobilities increase with temperature, the temperature coefficients being very nearly the same for all the ions in a given solvent.

- Thus, ionic mobilities increase by about 2% per degree in the vicinity of 25 °C
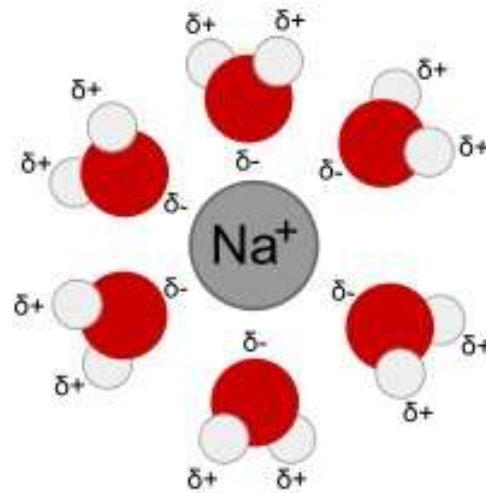
Take Home Message

- Grotthus Mechanism

- Conductance and Units

- Cell Constant

- Effect of Dilution: molar ↑ and specific ↓

- mobilities of H^+, Li^+, and Na^+

Migration of ions

- The migration of ions with different speeds can be demonstrated by a simple experiment devised by Noyes

  - The U tube is filled with 3/4th with dilute solution of agar-agar containing KCl and a little phenolphthalein.

  - A drop of dilute solution of NaOH is added to the right limb and drop of HCl to the left limb.

  - As a result, the soln. of agar-agar is coloured pink in the right limb and remains colourless in the left limb

A

HCl   NaOH

C   C

Solution colourless   Solution Pink

Phenolphthalein

Agar-Agar + KCl soln.
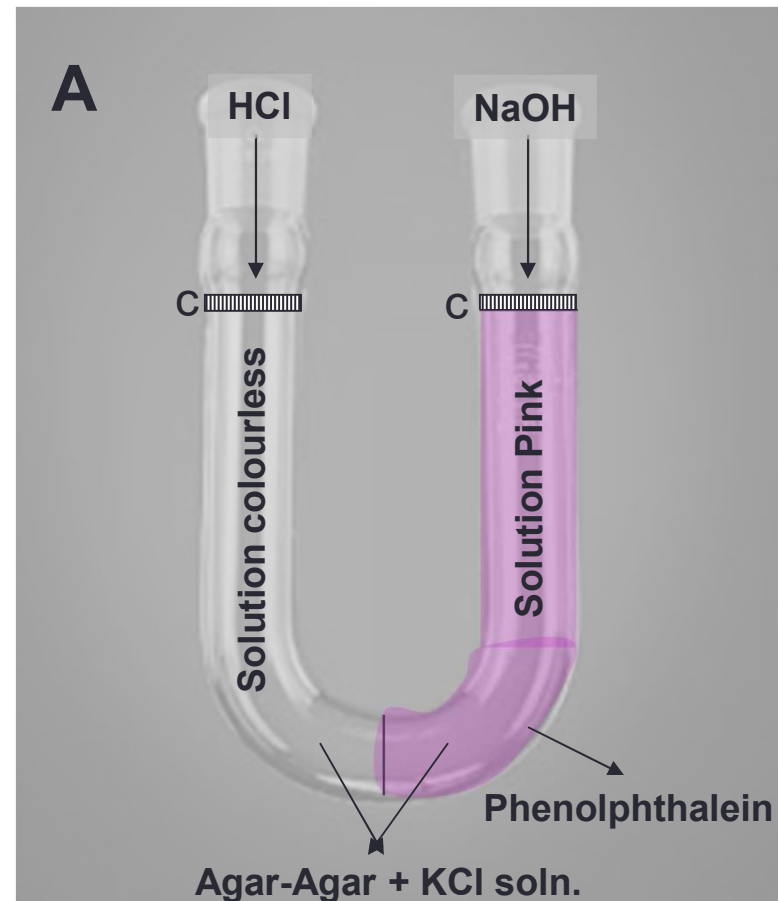
- The agar-agar solution is then allowed to set into a jelly by placing U tube in an ice-bath for few minutes A small amount of powdered charcoal marked CC is scattered on the surface of the solution on each side to mark the position of the boundary.

- A solution of HCl and CuCl$_2$ is poured gently over the charcoal boundary on the right side and a solution of NaOH is poured over the charcoal boundary on the left side.
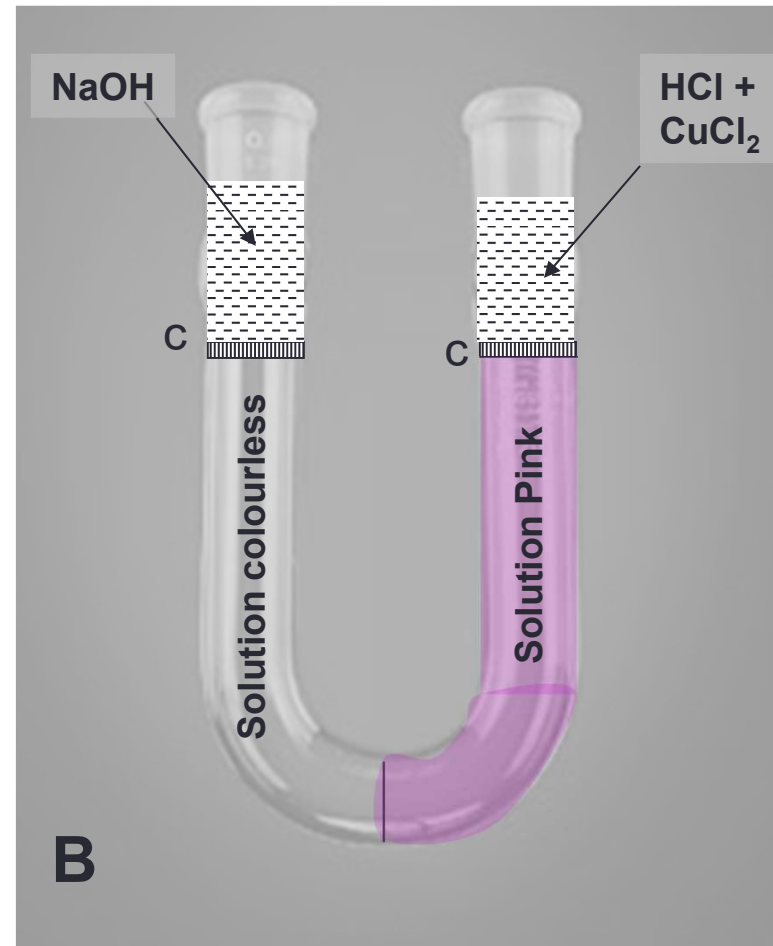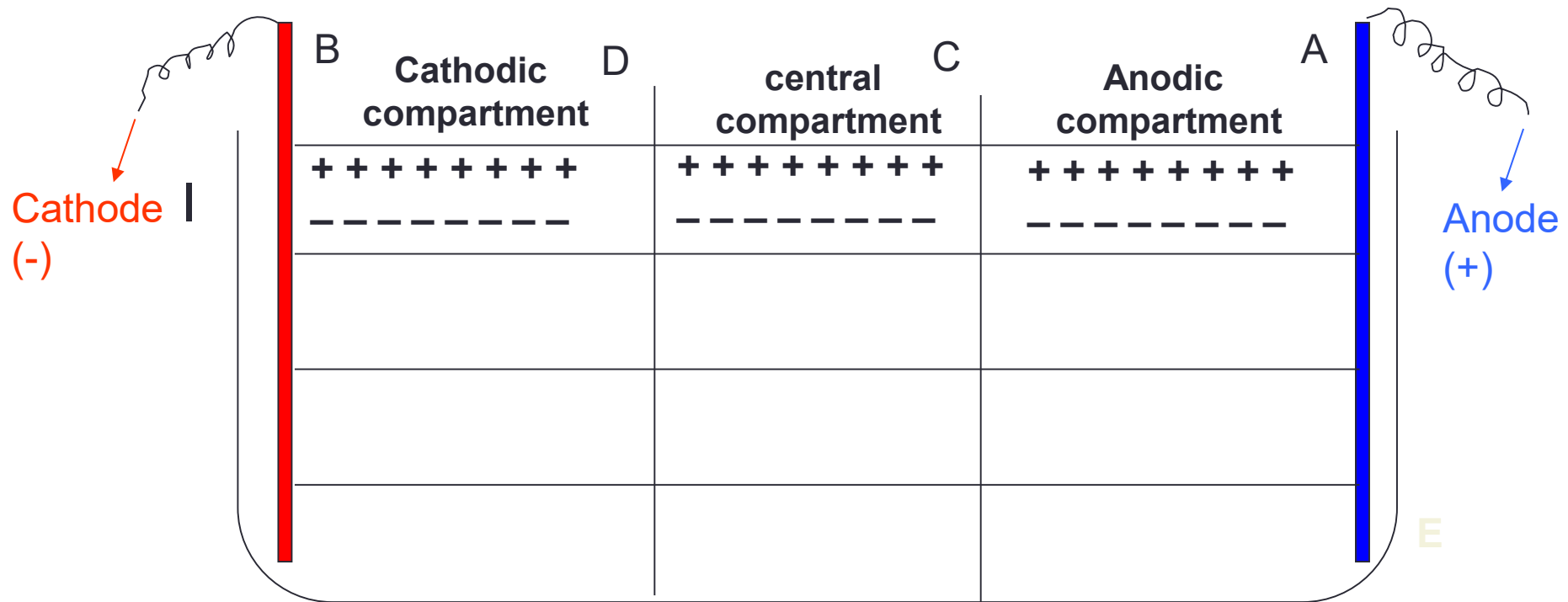
- Current is allowed to flow by inserting a metal electrode in each limb, the anode on the right limb and cathode on the left.

- As a result, the hydrogen and cupric ions move towards left limb while hydroxyl ions move towards the right limb

- The movement of hydrogen ions is indicated by the disappearance of the pink colour and that of the cupric ions by the development of blue colour in the solution on the right side.

- The movement of the hydroxyl ions is indicated by the appearance of pink colour of solution on the left
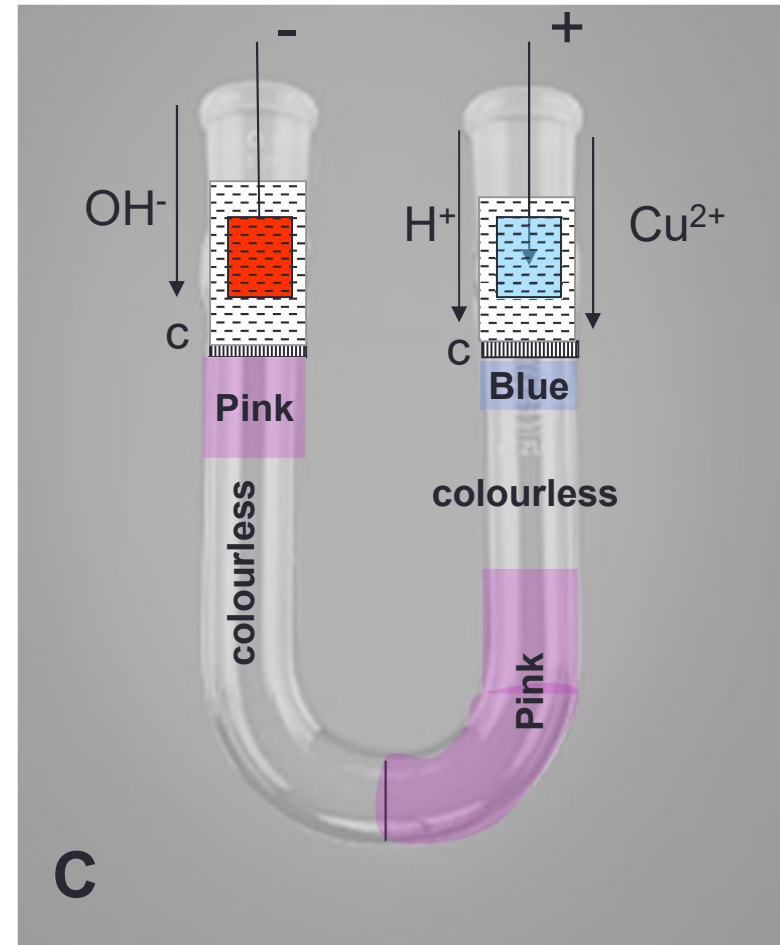
Experimental results show that if in a given time, the hydrogen ions move through a distance of 5 cm, the Cu^{2+} ions move through a distance of 0.91cm while OH^- ions move through a distance of 2.83cm

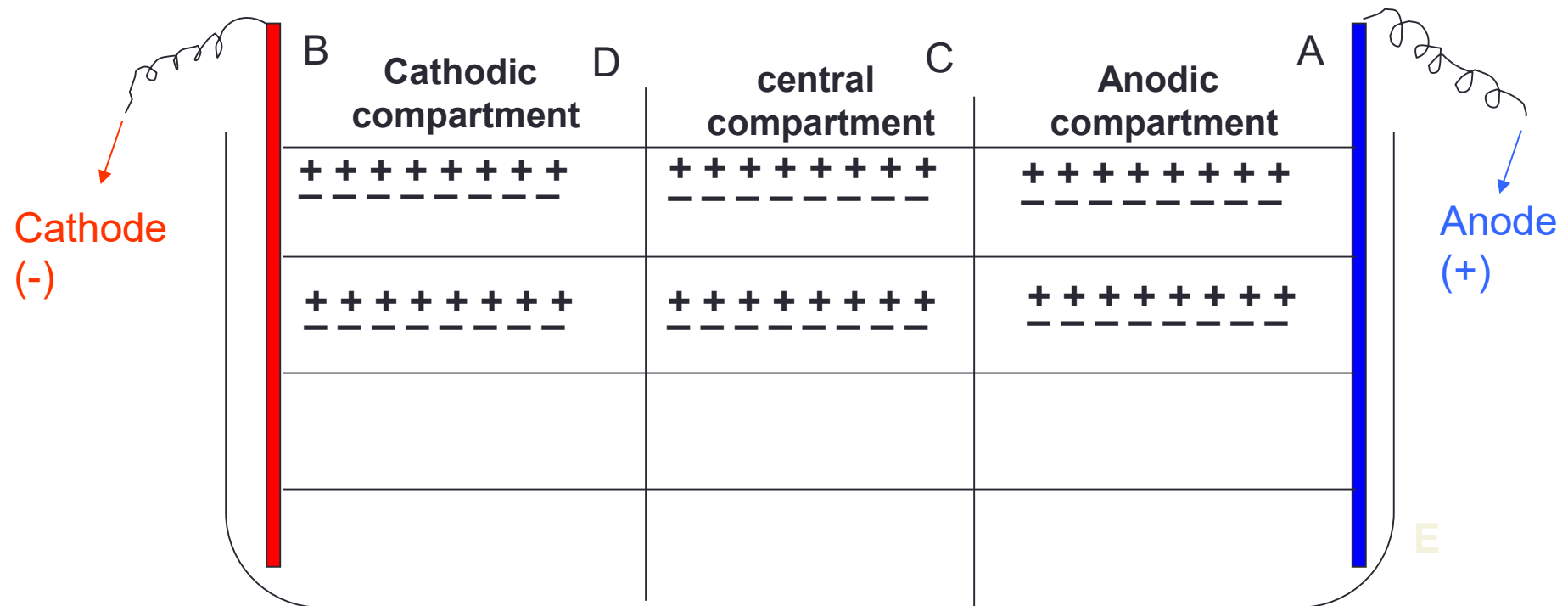## Discharge of ions on electrolysis: Hittorf's Theoretical Device

B   **Cathodic compartment**   D   **central compartment**   C   **Anodic compartment**   A

Cathode (-)

\+ + + + + + + +
\- - - - - - - -

\+ + + + + + + +
\- - - - - - - -

\+ + + + + + + +
\- - - - - - - -

Anode (+)

E

- The ions move with different speeds in the solution i.e. their ionic mobility is different

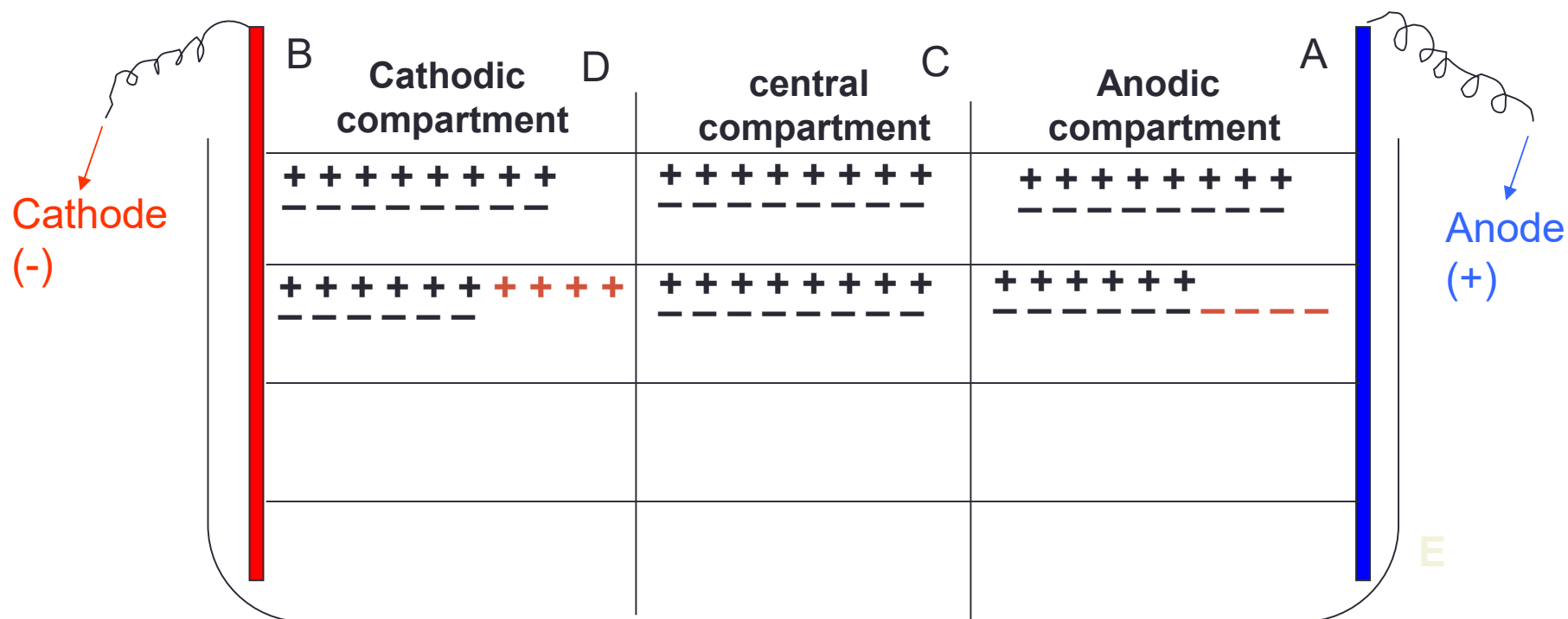- But the number of ions discharged at anode and cathode are equal

HOW ??
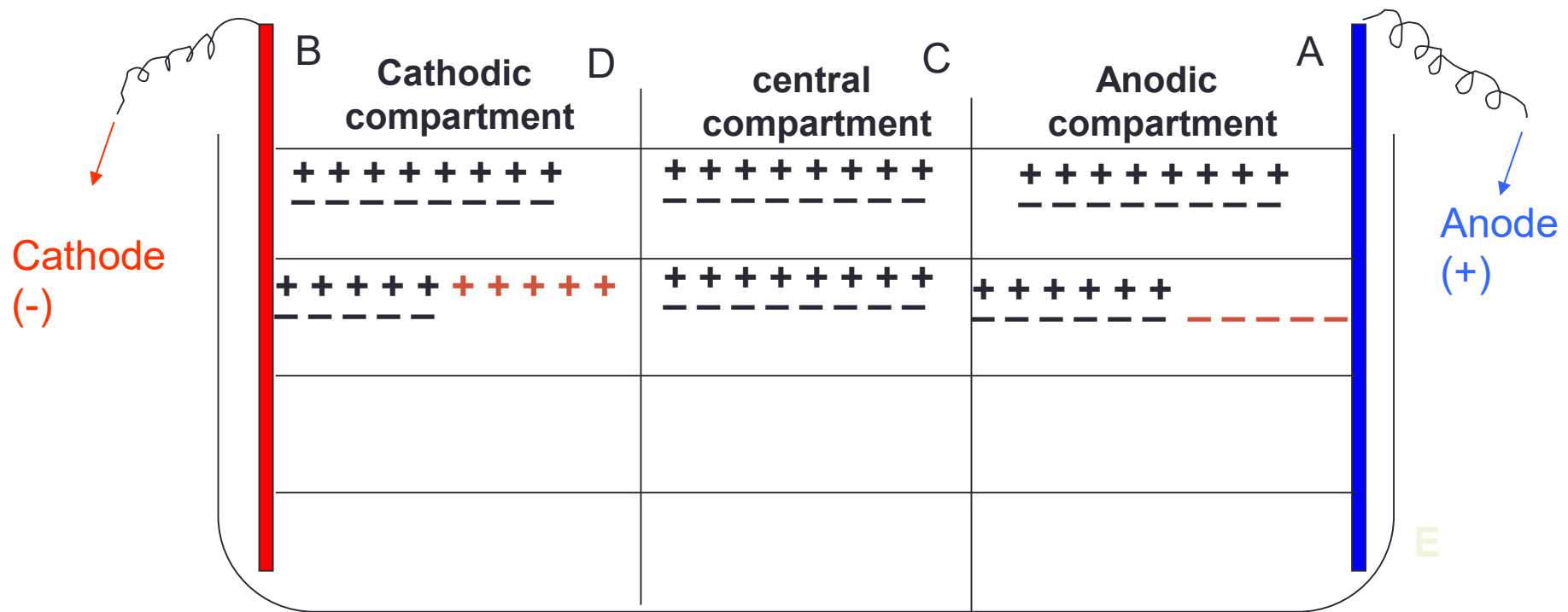
Case I: when neither cations move nor the anions

- Cations discharged at cathode: Zero

- Anions discharged at anode: Zero

Case II: 2 cations and 2 anions move in the given time (i.e. ions have equal mobility)

B **Cathodic compartment** D **central compartment** C **Anodic compartment** A

Cathode (-)

Anode (+)

- Cations discharged at cathode: 4

- Anions discharged at anode: 4

Case III: 2 cations and 3 anions move in the given time (i.e. ions have unequal mobility, anion moves faster)
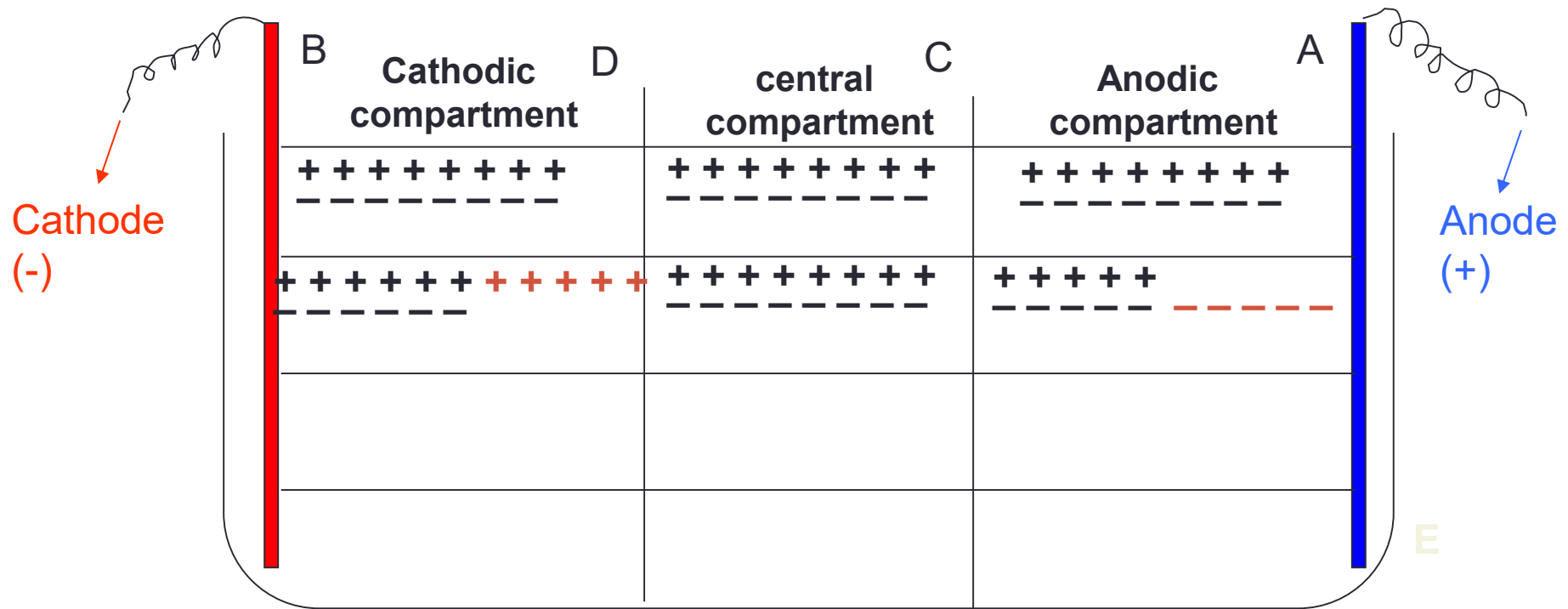

- Cations discharged at cathode: 5

- Anions discharged at anode: 5

Case IV: 3 cations and 2 anions move in the given time (i.e. ions have unequal mobility, cation moves faster)

Cathode (-)

Anode (+)

B	Cathodic compartment D	central compartment C	Anodic compartment	A
	+ + + + + + +	+ + + + + + + +	+ + + + + + +	
	– – – – – – –	– – – – – – – –	– – – – – – – –	
	+ + + + + + + + + + +	+ + + + + + + +	+ + + + + – – – – – –	
	– – – – – –	– – – – – – –	– – – – – –	

- Cations discharged at cathode: 5

- Anions discharged at anode: 5

Transport Number

- From Hittorf's theoretical device, it is also evident that the number of ions discharged at electrode depends upon the speeds or mobilities of two ions although number of ions discharged at each electrode are same.

- In first case when only two cations and two anions could move in a given time, the number of ions discharged at each electrode was also four

- In another case, when 2 cations and 3 anions moved in a given time the no. of ions discharged at each electrode was equal to five

- According to Faraday's first law of electrolysis, the number of ions discharged at a electrode is proportional to the total quantity of electricity passed through the solution, hence it follows that:

  - *Total quantity of electricity that passes through the solution is proportional to sum of the mobilities of the ions*

  - *The quantity of electricity carried by a particular ions is proportional to the mobility of that particular ion*

Transport Number

- The fraction of the total current carried by each ion is called its **Transport Number**

- Thus, if u_+ is the mobility of cation and u_- that of the anion then

  Transport number of the cation, t_+ = $\dfrac{current\ carried\ by\ the\ cation}{total\ current}$

$$= u_+ / [\ u_+ + u_-\ ]$$

  Transport number of the anion, t_- $= u_- / [\ u_+ + u_-\ ]$

  Further since $t_+ + t_- = 1$

  By Hittorf's theoretical device, it is possible to show that

  [mobility of cation / mobility of anion] =

$$\frac{fall\ of\ concentration\ around\ anode}{fall\ of\ concentration\ around\ cathode}$$

Transport Number

- Ex. In the case in Hittorf's theoretical device, 2 cations moved towards the cathode while 3 anions moved towards the anode in the same time.

- Thus mobility of cations/mobility of anions is 2/3.

- As given in Hittrof's device, the concentration round anode has fallen by 2 (from 8 to 6 ions) while that around cathode has fallen by three (8 to 5 ions)

- Thus, the fall of concentration round anode/fall of concentration round cathode is also 2/3

Transport Number

$$t_+ = \frac{\text{fall of concentration around anode}}{\text{(fall of concentration around cathode + fall of concentration around anode)}}$$

$$t_+ = \frac{\text{fall of concentration around anode}}{\text{(Ions discharged at electrode)}}$$

$$t_+ = \frac{\text{fall of concentration (g eq) around anode}}{\text{(gram equivalent of copper deposited)}}$$

Transport Number and Mobility

- Transport numbers of the 3 alkali ions, viz., Li^+, Na^+ and K^+ ions in their chlorides increases in the order of their mention.

- Since chloride ion is common in each case, it means that the speed of the cations increases in the order of $Li^+ < Na^+ < K^+$

- Speed of K ions in aqueous solution is the maximum and that of lithium ion is the minimum

Conductometric Titrations
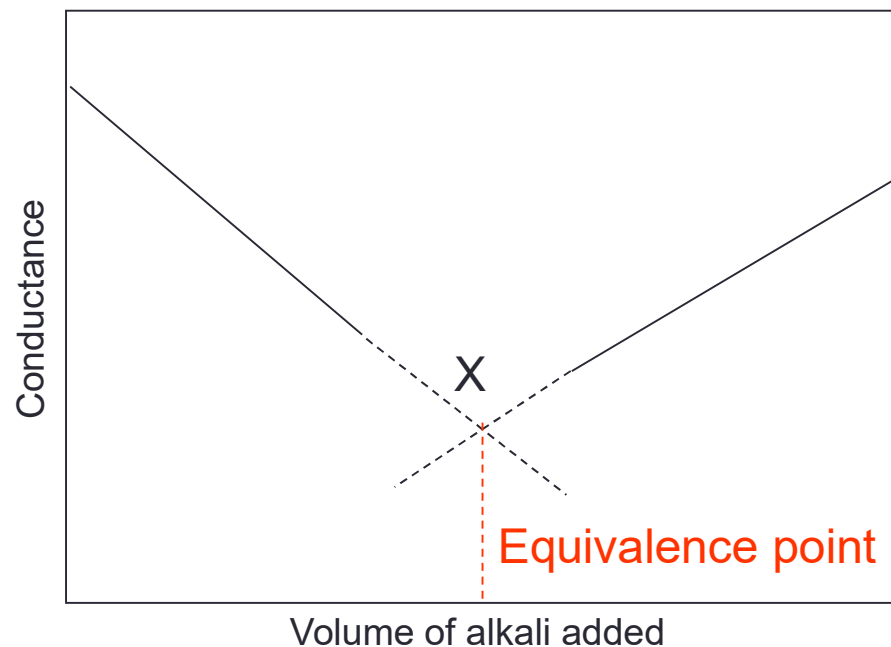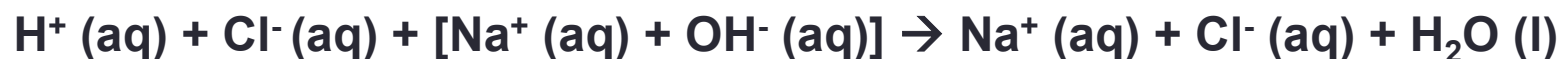
<u>Principle:</u>

The principle of conductometric titration is based on the fact that during the titration, *one of the ions is replaced by the other* and invariably these two ions differ in the ionic conductivity with the result that conductivity of the solution varies during the course of titration. The equivalence point may be located graphically by plotting the change in conductance as a function of the volume of titrant added.

Conductance depends upon:
I. Nature of ion
II. Number of ions present (concentration)

Conductometric Titrations

- e.g. Titration of strong acid (HCl) with a strong base (NaOH) with acid in conducting vessel and alkali in burette – the conductance of HCl is due to the presence of hydrogen and chloride ions.

$$H^+ (aq) + Cl^- (aq) + [Na^+ (aq) + OH^- (aq)] \rightarrow Na^+ (aq) + Cl^- (aq) + H_2O (l)$$

X

Equivalence point

Conductance

Volume of alkali added

- On addition of NaOH, the *conductance first decreases due to consumption of H^+ ions* and then after all H^+ ions are consumed, equivalence point, it increases due to addition of Na^+ and ^-OH ions.
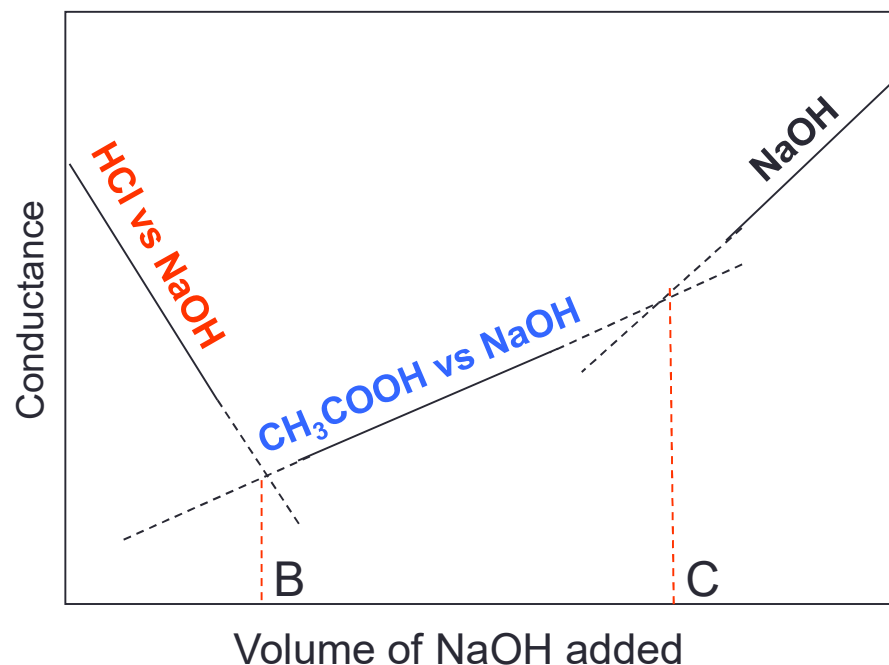
Conductometric titrations

- If a weak acid (such as acetic acid) is titrated against a strong alkali (such as NaOH), the conductance of acid will be low on account of poor dissociation.

- On adding alkali, highly ionized sodium acetate is formed and hence the conductance begins to increase

- CH_3COOH (aq) + [Na^+ (aq) + OH^- (aq)] $\rightarrow$ Na^+ (aq) + CH_3COO^- (aq) + H_2O (l)

- When the acid is completely neutralized, further addition of alkali introduces excess of fast moving ^-OH ions
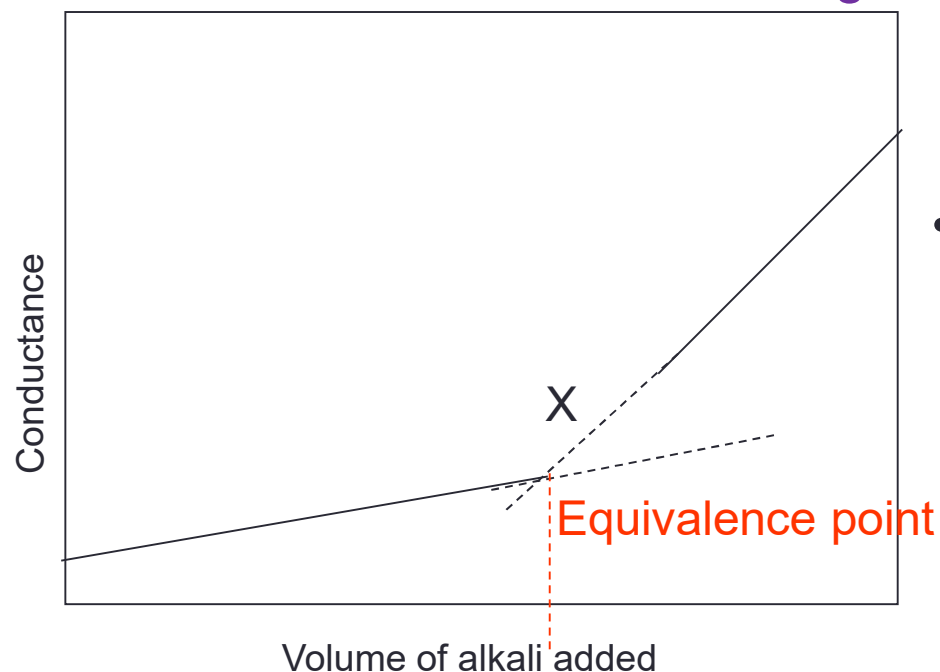
- The conductance of solution begins to increase even more sharply than earlier case.

Conductometric titrations

- When a mixture of a *strong and a weak acid* is to be titrated against a strong alkali a combination of earlier curves is obtained.

- If a mixture of HCl and CH_3COOH is to be titrated against NaOH, HCl will get titrated first, and the titration of acetic acid will commence only after HCl has been completely neutralized


HCl vs NaOH

CH_3COOH vs NaOH

NaOH

Conductance

B   C

Volume of NaOH added

- Point B corresponds to the neutralization of HCl, the point C corresponds to the neutralization of CH_3COOH

- **Conductometric titrations**

- If a strong acid like HCl is titrated against a weak base, like NH_4OH, the conductance will fall at first due to replacement of fast moving H^+ ions by slow moving NH_4^+ ions

- $H^+ (aq) + Cl^- (aq) + [NH_4OH (aq)] \rightarrow NH_4^+ (aq) + Cl^- (aq) + H2O (l)$

- After neutralization of the acid, further addition of weakly ionised ammonium hydroxide will not cause any appreciable change in the conductance

Conductance vs. Volume of NH_4OH added, with Equivalence point marked at X.
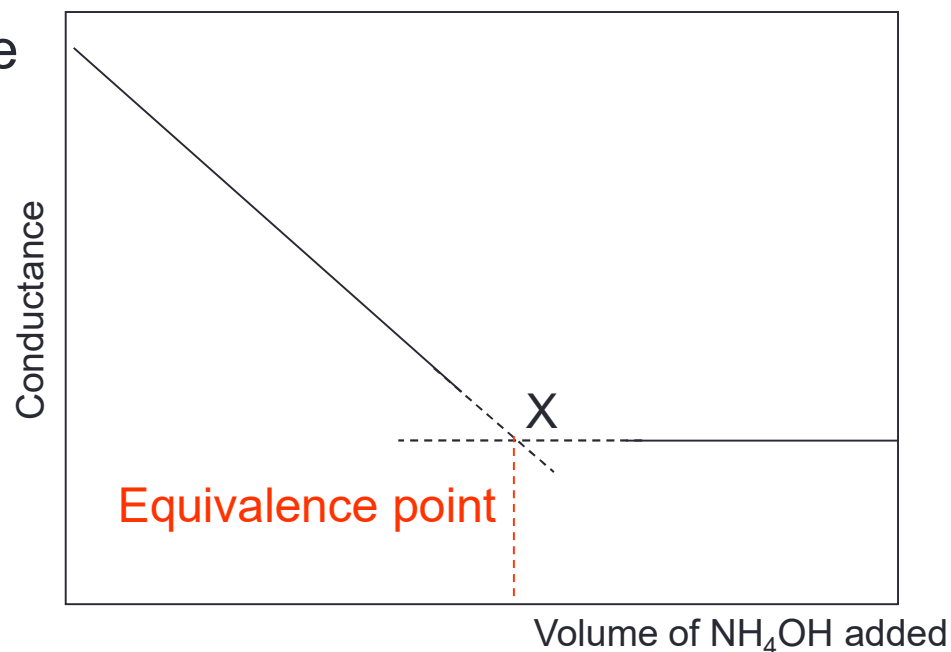
Precipitation titrations

- Titration of silver nitrate against potassium chloride

- Ag^+ (aq) + NO_3^- (aq) + K^+ + Cl^- $\rightarrow$ K^+ (aq) + NO_3^-(aq) + AgCl(s)

- Since the mobility of K^+ ion in more than that of silver ion which it replaces, the conductance will increase slowly and will begin to increase sharply only after the equivalence point.
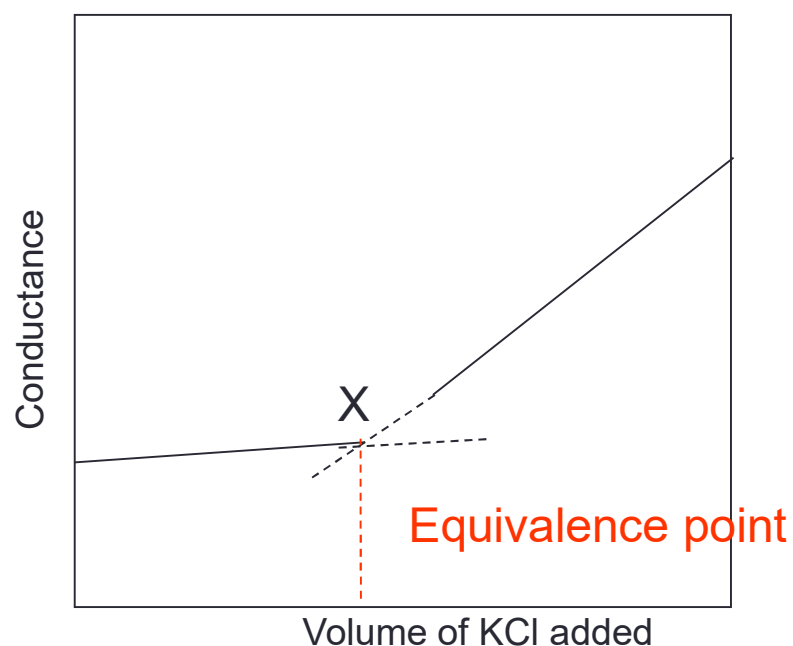
- The change in the volume during the titration should be as small as possible

- *For this purpose, the titration solution in the burette should be five to ten times stronger than solution taken in the conducting vessel*

Advantages of Conductometric titrations over volumetric titrations

- Coloured solutions which cannot be titrated by ordinary volumetric methods with help of indicators, can be successfully titrated conductometrically

- The method can also employed in the case of very dilute solutions and also for weak acids and bases.

- No special care is necessary near the end point as it is determined graphically.

Disadvantages of Conductometric Titrations

1. More concentrated solution needs to be taken in burette to avoid change in conductance due to dilution effects.

2. If salt concentrations are higher, then results tend to be less reliable and less accurate.

3. Perfect control of temperature is required since conductance changes with temperature.

4. Large concentrations of hydronium ions can affect the accuracy by masking change in conductance due to change in concentration of analyte ions as ionic mobility of hydronium ion is very high.

5. Usually dilute solution are used in conductometric titrations. Hence for conductometric titrations, highly concentrated solutions needs to be diluted.

- Two more limitations are: it required an instrument and for that electricity is required.