

CONDUCTOMETRIC TITRATIONS

These are based on measurement of electrical conductivity of a solution, due to the movement of ions. The ions are in movement due to influence of imposed force, electrical field, conc. gradient.

Factors that affect movement of ions are charge, size, mass, degree of solvation.

The electrolytic mobility is directly proportional to net charge of particle

Pure water has Conductance – 0.055µs/cm

Distilled water has Conductance – 0.5µs/cm

De-mineralized water has Conductance – 5µs/cm

Important terms:

Ohm's Law: It is obeyed by metallic/electrolytic conductors.

It states that Strength of current (I) through a conductor is directly proportional to applied electromotive force (EMF)/Potential difference (E) and inversely proportional to resistance R of conductor.

$$I(\text{current}) = \frac{E(\text{volt})}{R(\text{ohm})}$$

Conductance : Conductance is the property of conductor. It is an ease with which the current flows through the conductor. It is the ability of a substance to conduct electric current.

$$C = \frac{1}{R} (\text{mhos or siemens or ohm}^{-1})$$

Specific Resistance: Resistance R depends on the size of conductor as well as composition.

R of a conductor of uniform cross section is directly proportional to its length (l) & inversely proportional to cross section area (a).

$$R \propto l \quad \& \quad R \propto \frac{1}{a} \quad R \propto \frac{l}{a} \quad R = \rho \frac{l}{a}$$

ρ is a constant called as **resistivity or specific resistance**. ρ is defined as resistance in ohms of a specimen of 1 cm in length and 1 sq. cm cross section area.

$$\rho = \frac{R a}{l} = \frac{\text{ohm} \times \text{cm}^2}{\text{cm}} = \text{ohm} \cdot \text{cm}$$

Specific conductance: Specific conductance of any conductor is reciprocal of **specific resistance** and is denoted by κ

$$R = \rho \frac{l}{a} \quad \text{or} \quad R = \frac{1}{\kappa} \cdot \frac{l}{a} \quad \text{or} \quad \kappa = \frac{1}{R} \cdot \frac{l}{a} \quad \text{ohm}^{-1} \text{cm}^{-1}$$

If $l = 1\text{cm}$, $a = 1\text{sq.cm}$,

Then $\kappa = \frac{1}{R}$ mhos/cm or seimens/m

Therefore, **specific conductance = conductance**

Conductivity : Conductivity of 1 cm cube of solution of an electrolyte expressed in Mhos or reciprocal ohms.

$$\text{Conductivity } \sigma = \frac{1}{\rho(\text{resistivity})}$$

Units : seimens/m

Equivalent conductivity: It is Conductance of a solution containing 1 g equivalent of an electrolyte when placed between 2 sufficiently large electrodes which are 1 cm apart. It is denoted by λ_v . Where v is volume in c.c. containing 1 g equivalent of electrolyte dissolved in it and is measured in reciprocal of ohms or mhos.

Molecular conductivity: It is Conductance of a solution containing 1 g mole of solute/ electrolyte when placed between 2 sufficiently large electrodes which are exactly 1 cm apart. It is denoted by μ_v

Effect of dilution on conductance:

On dilution, the equivalent conductivity and the molar conductivity increases. This is because the degree of dissociation and the total number of ions increases. However the conductivity decreases as the number of ions per unit volume decreases.

Depending upon the nature of molecules involved in electrical conductance, conductance is of 2 types

Electrical conductance	Metallic conductance
Flow of current takes place due to migration of charged ions towards opposite electrode with chemical changes	Electricity produced due to free movement of electrons without any chemical changes
Transfer of matter takes place	No transfer of matter
Conductance increases with increase in temperature	Conductance decreases with increase in temperature
Ex. Solutions of acids, bases, salts in water, fused or molten salts	Metals, Graphite

Advantages :

- The end point of Highly dilute solutions/strongly colored solutions/ turbid mixtures can be determined
- No indicator is required
- Easy to operate. No need to determine the cell constant, specific conductance
- Incomplete reactions can also be titrated completely
- Graphical end point determination provides error minimization

Disadvantages:

- Less accurate
- Less satisfactory with increase in total electrolytic conductance

CONDUCTOMETRIC TITRATIONS

Measurement of conductance:

Conductivity cell:

Solution whose conductance is measured in a cell known as conductivity cell. It consists of 2 electrodes, which are firmly located in a constant geometry with respect to each other. Also known as Dipping cell in conductometric titrations.

Electrodes: It is made up of 2 parallel sheets of platinum foil. The platinum plates are coated with finely divided black platinum to reduce polarization effect.

Platinization: 2-3% solution of chloroplatinic acid & 0.02 TO 0.03g of lead acetate in the cell. Amount of solution should be enough to dip the electrode. Pass the current for 15-20 min. Electrolysis of chloroplatinic acid takes place and electrodes get blackened. Wash the electrode repeatedly with distilled water and finally with conductivity water. When not in use the electrodes are placed in conductivity water.

Conductivity water:

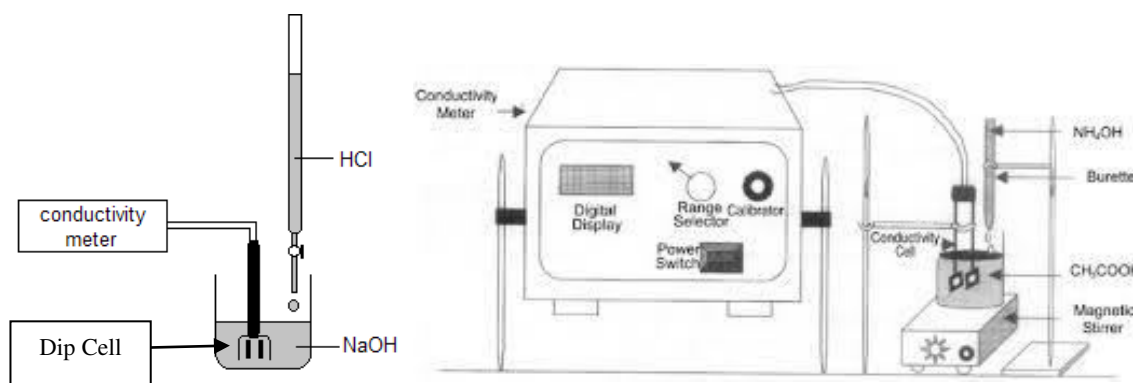
Conductivity water is water with high Degree of purity, with no conductance due to dissolved impurities. Ordinary water is not suitable because it contains dissolved CO_2 .

It is prepared by distilling distilled water containing small amounts of NaOH and KMnO_4 . Distillation is carried out in pyrex glass apparatus. Water is collected in a receiver fitted with a sodalime tube.

Titration Apparatus:

Conductivity bridge, detector cell (in contact with solution) or dip type cell.

Titrant is added and conductivities are measured. Plot Volume of titrant Vs Conductance
2 lines are obtained which intersect at a point, gives the end point.



Principle: In very dilute solutions, conductance is brought about by migration of ionic species i.e. anion and cations; both with varying degree of mobility towards charged electrodes. Therefore electrical current is produced and in-turn conductance.

When one electrolytic solution is mixed to another, the conductance of final solution is affected, which depends on whether the ionic reaction has taken place or not.

If no ionic reaction takes place, overall conductance of final solution is increased because all ions contribute.

Example: solution of NaNO_3 added to NaCl

If ionic reaction takes place, Conductance may be increased (due to replacement of ions of greater mobility) or decreased (due to replacement of ions of lower mobility).

Example: Solution of NaOH added to Acid HCl

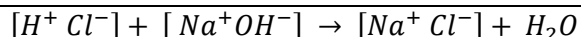
Replacement of greater mobility H^+ ions with that of Na^+ ions which are less mobile.

CONDUCTOMETRIC TITRATIONS

Conductivity Titrations:

Acid base titrations: Because of high conductance of OH^- and H_3O^+ , conductivity Titrations are well adapted.

1. Strong acid with a Strong base: (HCl Vs NaOH) Ionic conductance of H^+ is 350, OH^- is 199



At starting acid solution has high Conductivity due to mobile H^+ . Share of Cl^- is low.

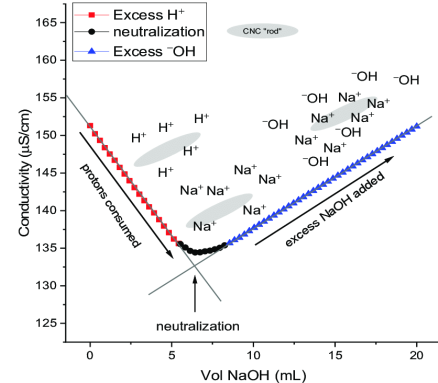
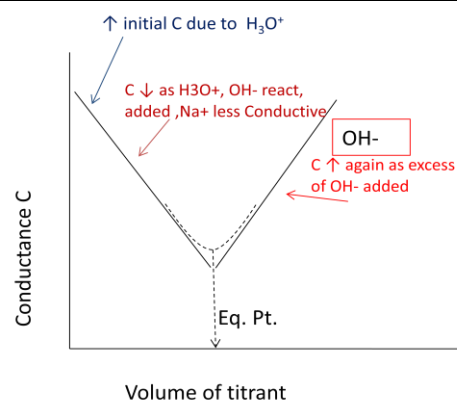
With addition of NaOH, highly mobile H^+ are replaced by low mobile Na^+ .

At end point, i.e. at neutralization only Na^+ and Cl^- are present. Therefore, the C decreases.

Then, with the further addition of NaOH, C increases due to OH^- , because OH^- have more mobility than Na^+ .

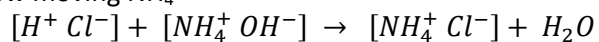
2 lines slightly curved are obtained due to

- Variation in temperature due to heat of neutralization
- Interionic effect
- Increase in volume of solution because of addition of strong acid
- In conductometric titration relative change in C is independent of conc. of st. acid, therefore, dilute solution are titrated with accuracy as compared to conc. solutions.



2. Strong acid with a weak base: (HCl Vs NH_4OH)

With the addition of NH_4OH to HCl Conductance decreases due to replacement of fast moving H^+ with slow moving NH_4^+ .



After the end point, addition of NH_4OH does not change conductance. Because NH_4OH is weakly ionized electrolyte, has very small conductance compared to

acid or its salt.	
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3. Weak acid with a Strong base: (CH_3COOH Vs NaOH)	
When small amount of NaOH is added to CH_3COOH, Conductance decreases initially and then increases with further addition of NaOH. $[\text{CH}_3\text{COO}^- + \text{H}^+] + [\text{Na}^+ \text{OH}^-] \rightarrow [\text{CH}_3\text{COO}^- \text{Na}^+] + \text{H}_2\text{O}$ Neutralization of acid completes, further addition of alkali produces excess of OH^-. Conductance of solution therefore starts increasing more rapidly.	

4. Weak acid Vs Weak Base $\text{NH}_4\text{OH} + \text{CH}_3\text{COOH} \leftrightarrow \text{NH}_4^+ + \text{CH}_3\text{COO}^- + \text{H}_2\text{O}$	
The reaction is between almost 2 neutral molecules, as their dissociation is too less. Initially CH_3COOH dissociates in less amt. So, the conductivity is very less. After the addition of NH_3, the dissociation takes place to a slight extent. So, the conductivity increases. After reaching equivalence point, over-adding of NH_3 as only slight dissociation takes place and there is little change in ion conc.	