

## 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).

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

$\rho$  is a constant called as **resistivity or specific resistance**.  $\rho$  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  $\kappa$

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

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  $\lambda_v$ . 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  $\mu_v$

**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

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

**Example:** solution of  $\text{NaNO}_3$  added to  $\text{NaCl}$

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  $\text{NaOH}$  added to Acid  $\text{HCl}$

Replacement of greater mobility  $\text{H}^+$  ions with that of  $\text{Na}^+$  ions which are less mobile.