

**Effect of Dilution are as follows:**

- (i) The conductivity of solution increases on dilution.
- (ii) The specific conductivity decreases on dilution (as number of ions decreases w.r.t. to volume).
- (iii) The equivalent and molar conductivities increase with dilution.
- (iv) The equivalent and molar conductivities tend to acquire maximum value with increasing dilution. [Maximum at  $\infty$  dilution]
- (v) Variation of molar conductance with concentration: For a strong electrolyte it is shown by Debye-Huckel Sagar equation as follows:

$$\Lambda_m = \Lambda_m^0 - b\sqrt{c}$$

In place of  $\Lambda^0$  we can also use  $\Lambda^\infty$

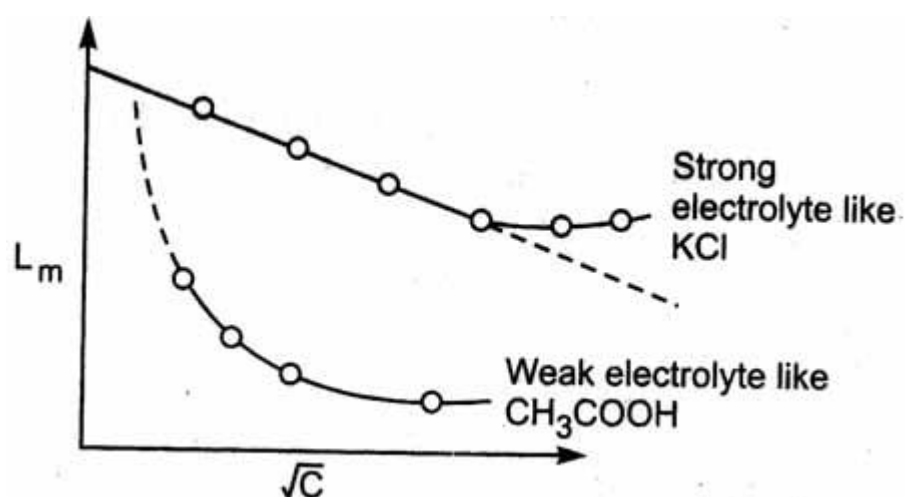
Here,  $\Lambda_M^0$  = molar conductance at infinite.

dilution (Limiting molar conductance)

$\Lambda_m$  = Molar conductance at V-dilution

b = It is a constant which depends upon nature of solvent and temperature

c = concentration



Effect of dilution

- $\Lambda M$  increases on dilution as inter-ionic attraction also decreases along with dilution.

At higher concentration these attractions are stronger so less deviations are observed in the value of  $\Lambda M$  with dilution.

In case of weak electrolytes  $\Lambda M$  increases as dissociation takes place on dilution. In case of strong electrolyte  $\Lambda^\infty$  can be observed by extrapolating concentration to zero. However in case of weak electrolytes it is possible.

### **Determination of cell constant**

In order to find out the cell constant, the cell is filled with 0.1 N solution of chemically pure KCl. The specific conductivity of 0.1 N KCl solution as determined accurately by Kohlraush is  $0.002765 \text{ mho cm}^{-1}$  at  $25^\circ \text{C}$  and the resistance of the solution is determined experimentally. Substituting the value of specific conductivity (0.002765) and offered by potassium chloride solution, the value of cell constant,  $x$  is calculated as follows:

$$\therefore \text{Specific Conductivity} = \frac{\text{Cell constant, } x}{\text{Resistance}}$$

$$\therefore \text{Cell constant, } x = \text{Sp. Conductivity} \times \text{resistance}$$

$$\text{or } x = 0.002765 \times \text{resistance}$$

### **Determination of conductivity of the solution**

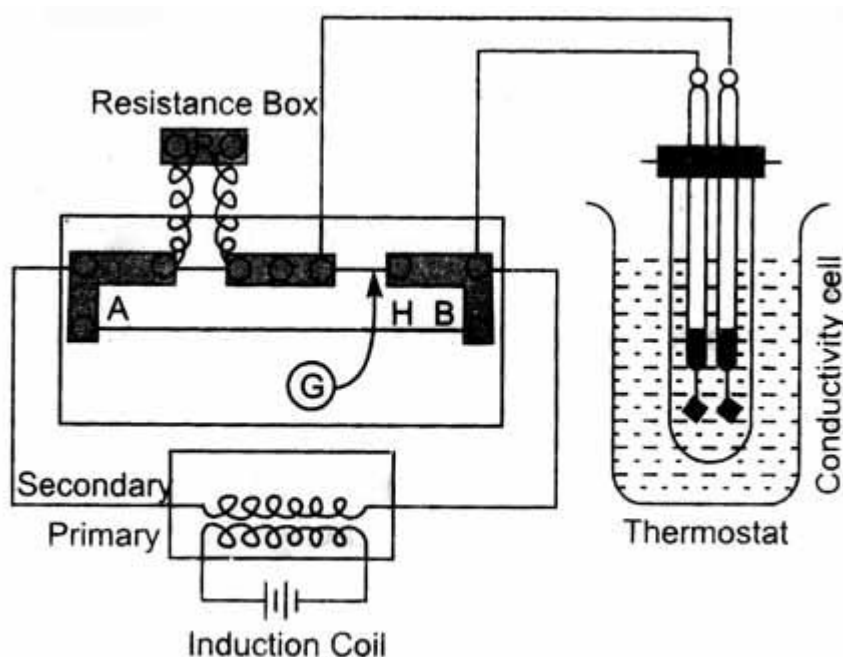
We know that conductivity is the reciprocal of resistance and the resistance is more frequently determined by means of some form of Wheatstone bridge circuit. But, when direct current is passed through the solution following difficulties arise:

- (i) The concentration of the charges,
- (ii) The polarisation set in due to the substance liberated at electrodes. With the result, a back E.M.F. is set up and the resistance of the electrolyte is altered. Kohlrausch (1868) avoided these difficulties as follows:
  - (a) *By using an alternating current:* The polarising effects of the deposition of substances due to the current in one direction is neutralised by the effect of current in the other direction.
  - (b) *By increasing the surface of electrodes:* Polarisation is decreased further if the surface of the electrodes is increased. This is done by coating electrodes in the cell with finely divided platinum.

(c) *By using headphone:* Since, with the passage of an alternating current, the ordinary galvanometer in Wheatstone bridge cannot be employed to determine the null point, it is replaced by a headphone.

(d) *By using an oscillator:* To obtain still better results the induction coil is replaced by an oscillator having a frequency of 2000-4000 cycles per second.

**Method:** The solution of an electrolyte whose conductivity is to be determined is taken in a special type of cell known as conductivity cell. This is made of pyrex glass and is fitted with platinum electrodes. The electrodes usually consist of stout platinum plates sealed into glass tubes which pass through mercury placed in the tubes. The relative positions of the electrodes are fixed by cementing the tubes to the ebonite cover. The electrodes are coated with finely divided platinum. To maintain definite temperature it is placed in a thermostat. Copper wires are dipped in mercury placed in glass tube to make connections.



### Determination of specific conductivity

Determination of specific conductivity

The cell is connected to resistance box, R on one side and thin uniform wire AB of meter bridge on the other secondary of induction coil is connected to the ends of the V bridge while the primary is connected to a battery. The headphone, G is connected to a sliding key, P and the binding screw in between the cell and resistance box.

The sliding key, P is placed near the middle. When the circuit is complete, a buzzing sound is heard in the headphone. Plugs are taken out from the resistance box. The sliding key is moved along the wire until the sound in the headphone is

reduced to a minimum. Thus point H is recorded. The observed conductivity of solution is then calculated by applying the following formula:

$$\frac{\text{Resistance of solution}}{\text{Resistance R}} = \frac{\text{Resistance of BH}}{\text{Resistance of AH}} = \frac{\text{length of BH}}{\text{Length AH}}$$

$$\text{or Resistance of solution} = \frac{BH}{AH} \times \text{Resistance, } R$$

$$\text{or } \frac{1}{\text{Obs. Conductivity}} = \frac{BH}{AH} \times \text{resistance}$$