

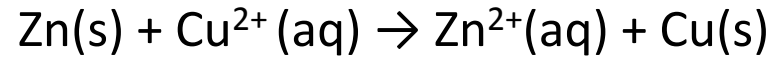
# Electrochemical cell and gibbs energy of the reaction

- Electrical work done in one second is equal to electrical potential multiplied by total charge passed. If we want to obtain maximum work from a galvanic cell then charge has to be passed reversibly. The reversible work done by a galvanic cell is equal to decrease in its Gibbs energy and therefore, if the emf of the cell is  $E$  and  $nF$  is the amount of charge passed and  $\Delta_r G$  is the Gibbs energy of the reaction, then

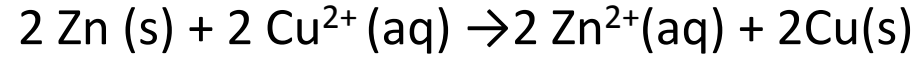
$$\Delta_r G = - nFE_{(\text{cell})}$$

- We know that  $E_{(\text{cell})}$  is an intensive parameter but  $\Delta_r G$  is an extensive thermodynamic property and the value depends on  $n$ .

Thus, if we write the reaction



$\Delta_r G = -2FE_{(\text{cell})}$  but when we write the reaction as



Then the equation becomes

$$\Delta_r G = -4FE_{(\text{cell})}$$

- If the concentration of all the reacting species is unity, then

$E_{\text{cell}} = E_{\text{cell}}^{\ominus}$  and we have

$$\Delta_r G^{\ominus} = -nFE_{\text{cell}}^{\ominus}$$

Thus, from the measurement of  $E_{\text{cell}}^{\ominus}$  we can obtain an important thermodynamic quantity,  $\Delta_r G^{\ominus}$ , standard Gibbs energy of the reaction. From the latter we can calculate equilibrium constant by the equation:

$$\Delta_r G^{\ominus} = -RT \ln K.$$

# Conductance of electrolytic cells

- The electrical resistance is represented by the symbol 'R' and it is measured in ohm ( $\Omega$ ) which in terms of SI base units is equal to  $(\text{kg m}^2)/(\text{S}^3 \text{ A}^2)$ .
- It can be measured with the help of a Wheatstone bridge. The electrical resistance of any object is directly proportional to its length,  $l$ , and inversely proportional to its area of cross section,  $A$ . That is,

we also know,  $R \propto l$   
 $R \propto \frac{1}{A} \quad \Rightarrow R = \rho \frac{l}{A}$

The constant of proportionality, is called resistivity (specific resistance).

- Its SI units are ohm metre ( $\Omega \text{ m}$ ) and quite often its submultiple, ohm centimetre ( $\Omega \text{ cm}$ ) is also.
- Physically, the resistivity for a substance is its resistance when it is one metre long and its area of cross section is one  $\text{m}^2$ . It can be seen that:

$$1 \Omega \text{ m} = 100 \Omega \text{ cm} \text{ or } 1 \Omega \text{ cm} = 0.01 \Omega \text{ m}$$

- The inverse of resistance,  $R$ , is called conductance,  $G$ , and we have the relation:

$$G = 1/R = A/\rho l = \kappa A/l$$

- The SI unit of conductance is siemens, represented by the symbol  $S$  and is equal to  $\text{ohm}^{-1}$  (also known as mho) or  $\Omega^{-1}$ .
- The inverse of resistivity, called conductivity (specific conductance) is represented by the symbol,  $\kappa$ .
- The SI units of conductivity are  $S \text{ m}^{-1}$  but quite often,  $\kappa$  is expressed in  $S \text{ cm}^{-1}$ .
- Conductivity of a material in  $S \text{ m}^{-1}$  is its conductance when it is 1 m long and its area of cross section is  $1\text{m}^2$ . It may be noted that  $1S\text{cm}^{-1} = 100S\text{m}^{-1}$ .

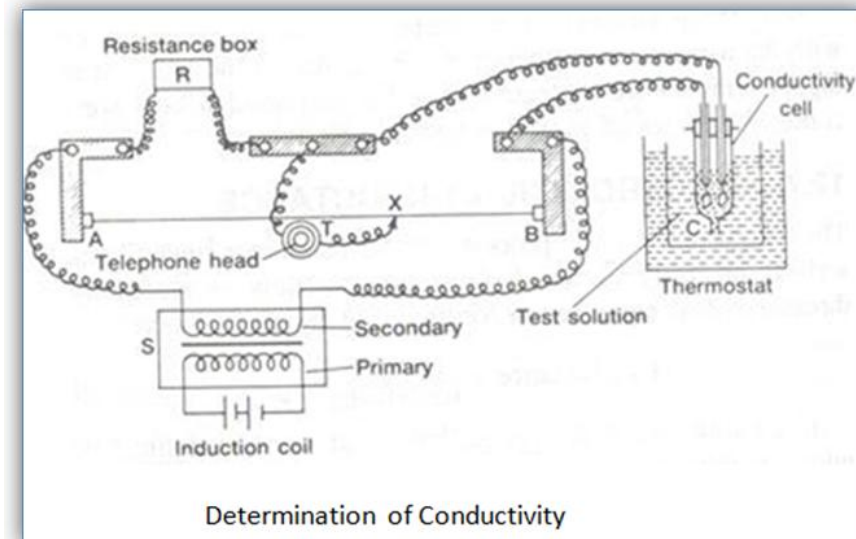
- The magnitude of conductivity varies a great deal and depends on the nature of the material. It also depends on the temperature and pressure at which the measurements are made. Materials are classified into conductors, insulators and semiconductors depending on the magnitude of their conductivity.
- Metals and their alloys have very large conductivity and are known as conductors. Certain non-metals like carbon-black, graphite and some organic polymers\* are also electronically conducting.
- Substances like glass, ceramics, etc., having very low conductivity are known as insulators. Substances like silicon, doped silicon and gallium arsenide having conductivity between conductors and insulators are called **semiconductors** and are important electronic materials. Certain materials called superconductors by definition have zero resistivity or infinite conductivity.
- Earlier, only metals and their alloys at very low temperatures (0 to 15 K) were known to behave as superconductors, but nowadays a number of ceramic materials and mixed oxides are also known to show superconductivity at temperatures as high as 150 K.
- Electrical conductance through metals is called metallic or electronic conductance and is due to the movement of electrons. The electronic conductance depends on
  - (i) the nature and structure of the metal
  - (ii) the number of valence electrons per atom
  - (iii) temperature (it decreases with increase of temperature).

- As the electrons enter at one end and go out through the other end, the composition of the metallic conductor remains unchanged. The mechanism of conductance through semiconductors is more complex.
- pure water has small amounts of hydrogen and hydroxyl ions ( $\sim 10^{-7}\text{M}$ ) which lend it very low conductivity ( $3.5 \times 10^{-5} \text{ S m}^{-1}$ ). When electrolytes are dissolved in water, they furnish their own ions in the solution hence its conductivity also increases.
- The conductance of electricity by ions present in the solutions is called electrolytic or ionic conductance. The conductivity of electrolytic (ionic) solutions depends on:
  - i) the nature of the electrolyte added
  - ii) size of the ions produced and their solvation
  - iii) the nature of the solvent and its viscosity
  - iv) concentration of the electrolyte
  - v) temperature (it increases with the increase of temperature).
- Passage of direct current through ionic solution over a prolonged period can lead to change in its composition due to electrochemical reactions

# Measurement of conductivity of ionic solutions

- A conductivity cell consists of two platinum electrodes coated with platinum black which has finely divided metallic Pt is deposited on the electrodes electrochemically. These have area of cross section equal to 'A' and are separated by distance 'l'. Therefore, solution confined between these electrodes is a column of length l and area of cross section A. The resistance of such a column of solution is then given by the equation:

$$R = \rho \frac{l}{A} = \frac{l}{kA}$$



- The quantity  $l/A$  is called cell constant denoted by the symbol,  $G^*$ .
- It depends on the distance between the electrodes and their area of cross-section and has the dimension of  $\text{length}^{-1}$  and can be calculated if we know  $l$  and  $A$ .
- Measurement of  $l$  and  $A$  is not only inconvenient but also unreliable. The cell constant is usually determined by measuring the resistance of the cell containing a solution whose conductivity is already known.
- For this purpose, we generally use KCl solutions whose conductivity is known accurately at various concentrations and at different temperatures. The cell constant,  $G^*$ , is then given by the equation:

$$G^* = l/A = Rk$$



- Once the cell constant is determined, we can use it for measuring the resistance or conductivity of any solution.
- It consists of two resistances  $R_3$  and  $R_4$ , a variable resistance  $R_1$  and the conductivity cell having the unknown resistance  $R_2$ .
- The Wheatstone bridge is fed by an oscillator O which is a source of a.c. power in the audio frequency range 550 to 5000 cycles per second.
- P is a suitable detector and the bridge is balanced when no current passes through the detector. Under these conditions:

$$\text{Unknown resistance } R_2 = \frac{R_1 R_4}{R_3}$$

- Once the cell constant and the resistance of the solution in the cell is determined, the conductivity of the solution is given by the equation:

$$\kappa = \frac{\text{cell constant}}{R} = \frac{G^*}{R}$$

- The conductivity of solutions of different electrolytes in the same solvent and at a given temperature differs due to charge and size of the ions in which they dissociate, the concentration of ions or ease with which the ions move under a potential gradient.
- It, therefore, becomes necessary to define a physically more meaningful quantity called molar conductivity denoted by the symbol  $\Lambda_m$ . It is related to the conductivity of the solution by the equation:

$$\text{Molar conductivity} = \Lambda_m = \frac{\kappa}{C}$$

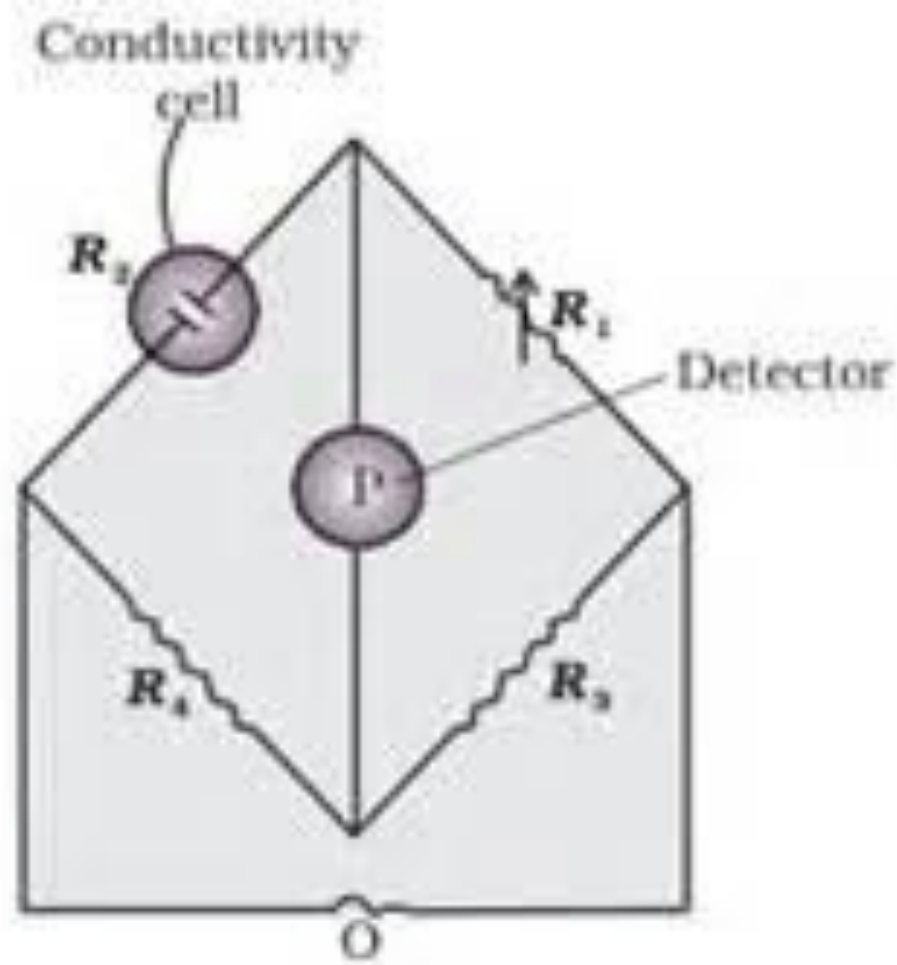


Fig. 3.5: Arrangement for measurement of resistance of a solution of an electrolyte.

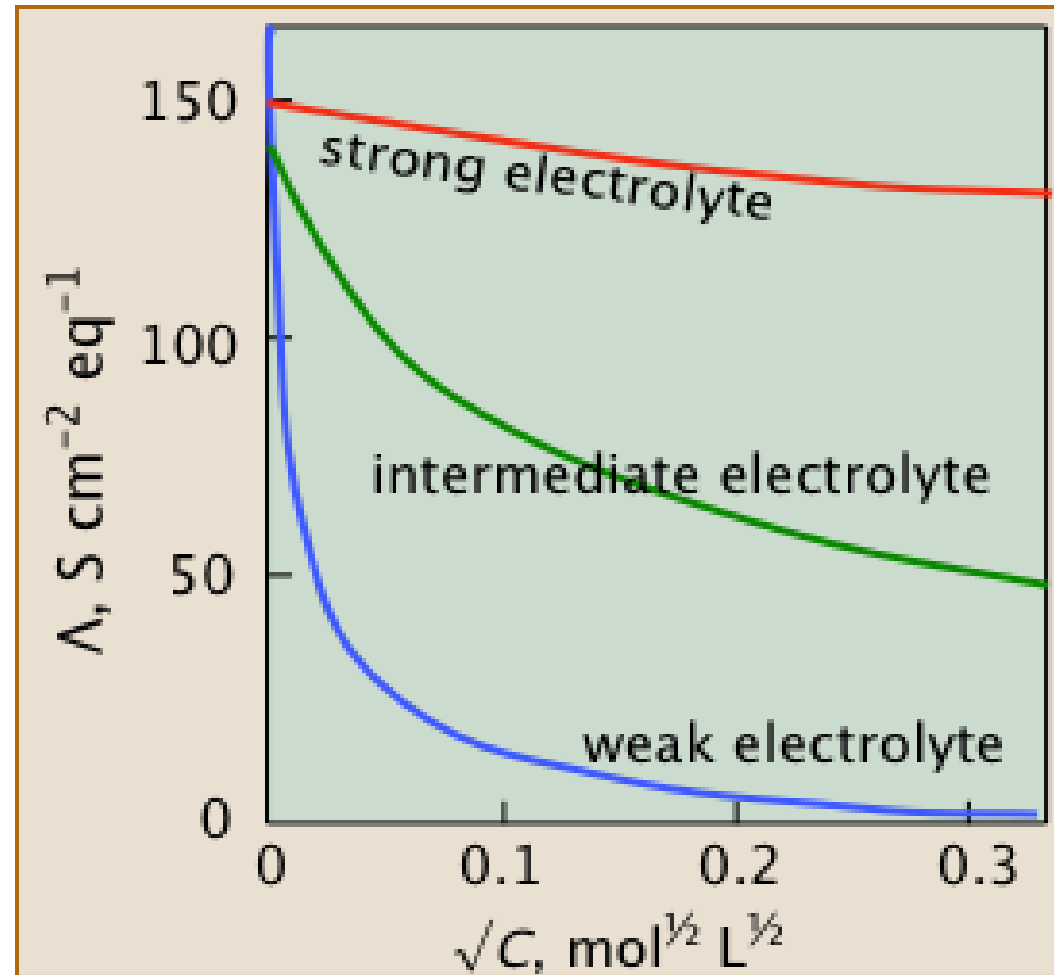
In the above equation, if  $\kappa$  is expressed in  $\text{S m}^{-1}$  and the concentration,  $c$  in  $\text{mol m}^{-3}$  then the units of  $\Lambda_m$  are in  $\text{S m}^2 \text{mol}^{-1}$ .

$$1 \text{ S m}^2 \text{mol}^{-1} = 10^4 \text{ S cm}^2 \text{mol}^{-1} \text{ or } 1 \text{ S cm}^2 \text{mol}^{-1} = 10^{-4} \text{ S m}^2 \text{mol}^{-1}.$$

# Variation of conductivity and molar conductivity with concentration

- Both conductivity and molar conductivity change with the concentration of the electrolyte. Conductivity always decreases with decrease in concentration both, for weak and strong electrolytes.
- This can be explained by the fact that the number of ions per unit volume that carry the current in a solution decreases on dilution.
- The conductivity of a solution at any given concentration is the conductance of one unit volume of solution kept between two platinum electrodes with unit area of cross section and at a distance of unit length.
- If  $A$  and  $l$  are unity then  $G^* = k$

- Molar conductivity of a solution at a given concentration is the conductance of the volume  $V$  of solution containing one mole of electrolyte kept between two electrodes with area of cross section  $A$  and distance of unit length. Therefore,
  - $\Lambda_m = \frac{\kappa A}{l} = \kappa$  ( $A=V$  and  $l$  are containing 1 mole of electrolyte)
- Therefore  $\Lambda_m = \kappa V$ .



- Molar conductivity increases with decrease in concentration. This is because the total volume,  $V$ , of solution containing one mole of electrolyte also increases. It has been found that decrease in  $\kappa$  on dilution of a solution is more than compensated by increase in its volume.
- At a given concentration,  $\Lambda_m$  can be defined as the conductance of the electrolytic solution kept between the electrodes of a conductivity cell at unit distance but having area of cross section large enough to accommodate sufficient volume of solution that contains one mole of the electrolyte.
- **When concentration approaches zero, the molar conductivity is known as limiting molar conductivity and is represented by the symbol  $\Lambda_m^\circ$ .**

