CHEMISTRY STUDY MATERIALS FOR CLASS 12
(NCERT BASED NOTES OF CHAPTER -03)
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Electrochemistry

Electrochemical Cell and Gibbs Energy of the Reaction

Electrical work done in one second is equal to electrical potential multiplied by total charge passed.

Also the reversible work done by a galvanic cell is equal to decrease in its Gibbs energy. Therefore, if the emf of the cell is E and nF is the amount of charge passed,

then the Gibbs energy of the reaction, $\Delta G = -nFE_{cell}$

If the concentration of all the reacting species is unity, then $E_{cell} = E^0_{cell}$. So, $\Delta G^0 = -nFE^0_{cell}$

Thus, from the measurement of E^0_{cell}, we can calculate the standard Gibbs energy of the reaction.

Conductance of Electrolytic Solutions

Resistance (R): The electrical resistance is the hindrance to the flow of electrons. Its unit is ohm (Ω). The resistance of a conductor is directly proportional to the length of the conductor (l) and inversely proportional to the area of cross-section (A) of the conductor.

i.e. $R \alpha l/A$

or, R = a constant x l/A

or, $R = \rho \times l/A$,

where ρ (rho) is a constant called resistivity.

Its unit is ohm-metre (Ω m) or ohm-centimetre (Ω cm).

$1\ \Omega\ m = 100\ \Omega\ cm$, $1\ \Omega\ cm = 10^{-2}\ \Omega\ m$

Resistivity is defined as the resistance offered by a conductor having unit length and unit area of cross- section.

Conductance (G): It is the inverse of resistance. i.e. G = 1/R.

Its unit is ohm^{-1} or mho or Siemens (S)

Or, $G = \frac{1}{\rho} \times \frac{A}{l}$

Or, $G = \kappa \times A/l$ Where, ***κ*** is called ***conductivity***.

It is defined as the conductance of a conductor having unit length and unit area of cross-section.

Its unit is $ohm^{-1}\ m^{-1}$ or $mho\ m^{-1}$ or $S\ m^{-1}$.

$1\ S\ cm^{-1} = 100\ S\ m^{-1}$

$1\ S\ m^{-1} = 10^{-2}\ S\ cm^{-1}$

There are of two types of Conductance - electronic or metallic conductance and electrolytic or ionic conductance.

Electrical conductance through metals is called *metallic or electronic conductance* and it is due to the movement of electrons. It depends on the nature and structure of the metal, the no. of valence electrons per atoms and temperature. For electronic conductance, when temperature increases, conduction decreases.

The conductance of electricity by ions present in solutions is called electrolytic or ionic conductance. It depends on

i) The nature of electrolyte

ii) Size of the ion produced and their solvation

iii) The nature of the solvent and its viscosity

iv) Concentration of the electrolyte and

v) Temperature (As temperature increases electrolytic conduction also increases).

Note: Substances which allow the passage of electricity in molten state or in solution state are called electrolytes. On the passage of electricity, they undergo chemical decomposition.

Measurement of the conductivity of ionic solutions

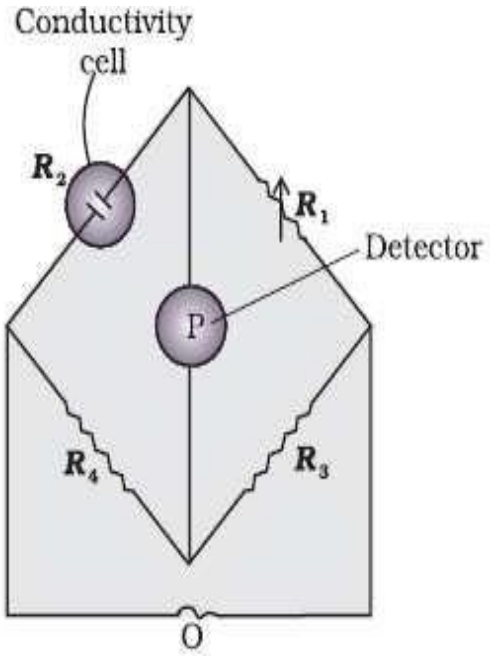
We know that, conductivity $G = k \times A/l$

So conductivity, $k = G \times l/A$,

The quantity l/A is called ***cell constant*** (G^*). It depends on the distance between the electrodes and their area of cross-section. Its unit is m^{-1}.

i.e. conductivity = conductance x cell constant

So in order to determine the conductivity of an electrolytic solution, first determine the resistance by using a Wheatstone bridge. 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. It is connected to an AC source (an oscillator, O) and a suitable detector (a headphone or other electronic device, P). Direct current (DC) cannot be used since it causes the decomposition of the solution.



The bridge is balanced, when no current passes through the detector.

Under this condition,

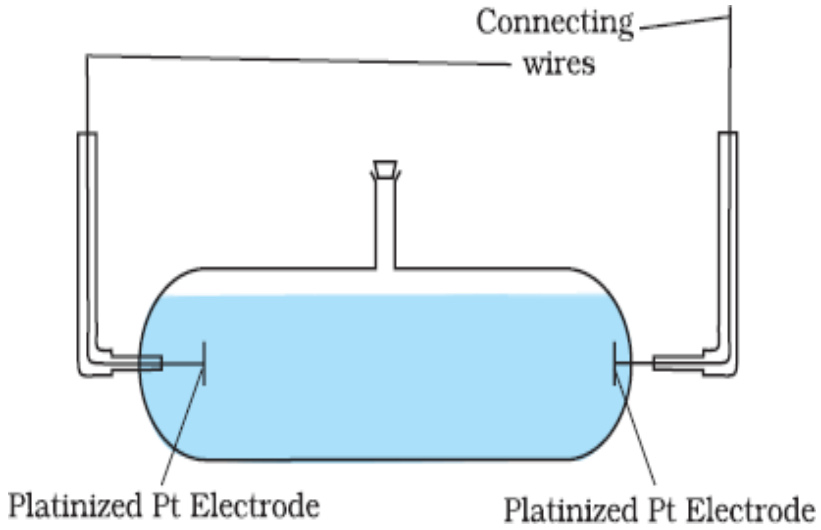
$$\frac{R_1}{R_2} = \frac{R_3}{R_4}$$

Therefore, the unknown resistance, $R_2 = \frac{R_1 R_4}{R_3}$

By knowing the resistance, we get the value of conductance and conductivity.

Conductivity cell

It consists of two platinum electrodes coated with platinum black. The electrodes are separated by a distance l and their area of cross-section is A.



The cell constant of a conductivity cell is usually determined by measuring the resistance of the cell containing a solution whose conductivity is already known (e.g. KCl solution).

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