Electrochemistry

Section - A

B.Sc 2nd Sem.

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Chemical Kinetics :→

The Branch of Chemistry which deals with the study of reaction rate and the factor affecting of rate of reaction.

Example :- Corrosion is a slow process
Combustion is a fast process

or we can say combination of corrosion and combustion is also called chemical kinetics (which consist of slow and fast process.

* Rate of Reaction :→

The rate of reaction may be defined as the changes in the concentration of any one of the reactants or product per unit time.

$$\text{Rate of Reaction} = \frac{\text{Change in Conc.}}{\Delta t}$$

Eg $A \rightarrow B$ Rate of $Rx^n = -\frac{[\Delta A]}{\Delta t} = +\frac{[\Delta B]}{\Delta t}$

* LAW OF MASS ACTION :→

At a given temperature the rate of chemical reaction is directly proportional to the product of the molar concentrations of the reactants.

$$aA + bB \rightarrow \text{Product}$$

$$\text{Rate} = K[A]^a[B]^b$$

where K is rate constant

[A] + [B] are molar concentration

Rate Constant of a reaction at a given may be defined as the rate of the reaction when the concentration of each of the each of reactants is unity. Hence, the rate constant is also called specific reaction rate.

Unit = $Mol\ Lt^{-1}\ time^{-1}$

* AVERAGE RATE OF REACTION :→

Average Rate of reaction is an average rate, obtained by taking the change in concentration over a time period

$$\frac{0.3\ M}{15\ \text{minutes}}$$

* INSTANTANEOUS RATE OF REACTION :→

It is defined as the change in the concentration of any one of the reactants or products per unit time at that particular instant of time.

* FACTORS INFLUENCING RATE OF REACTION :→

1. Concentration of the reactants
2. Nature of the reactants
3. Temperature of the system
4. Presence of a catalyst
5. Presence of radiations
6. Surface area of reactants

1. Concentration of the reactants :→

The concentration of the reactants go on decreasing with the passage of time. Since, the rate of reaction also decreases with time.

On the basis of collision theory, with the increase in concentration of the reactants, the number of molecular collisions increases & rate of rxn also increas

RBF

② Nature of the reactants :→

The nature of the reactants play an important role in influencing the rate of a reaction. For example, in the oxidation of nitric oxide and carbon monoxide by air, the first order reaction is much faster than the second at the same temperature.

$$2NO + O_2 \rightarrow 2NO_2 \quad \text{(fast)}$$

$$2CO + O_2 \rightarrow 2CO_2 \quad \text{(slow)}$$

In both reactions, the oxidising agent is same but in the first case it is nitric oxide which is to be oxidised whereas in the second case it is carbonmonoxide which is to be oxidised and hence the difference in the rate of reactions.

③ Temperature of the System :→

The rate of a reaction increases with a rise of temperature and its molecular energy also increases.

In most of the cases, a rise of 10K in temperature doubles and in some cases trebles the rate of a reaction. This is generally termed as temperature coefficient

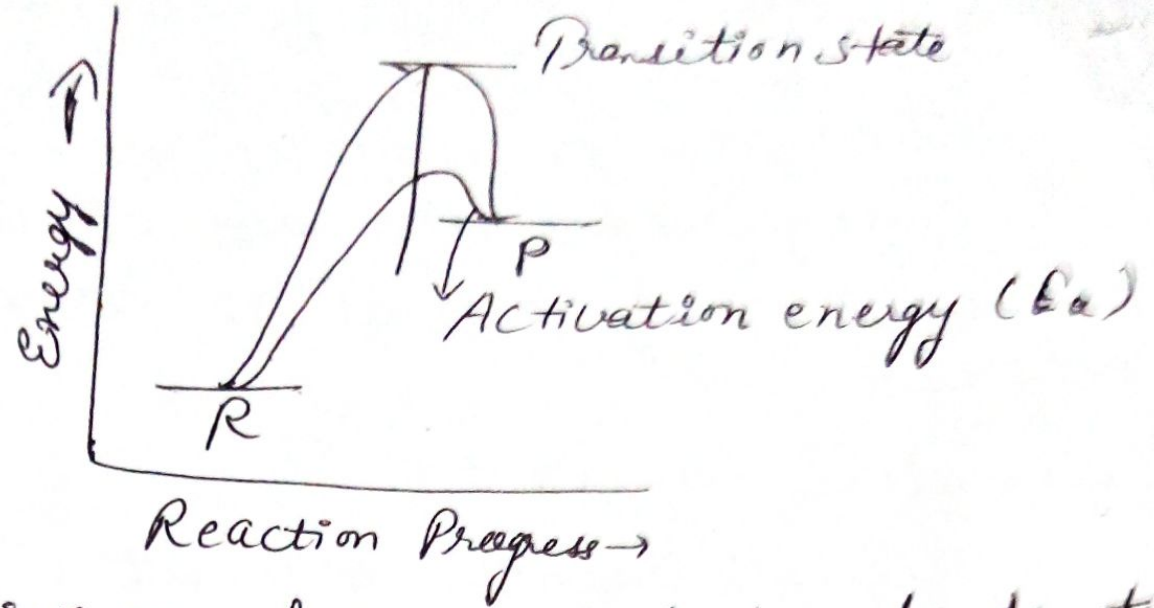
Temperature Coefficient

$$= \frac{\text{Specific reaction rate at } (T+10)K}{\text{Specific reaction rate at } TK}$$

There are certain cases when the reaction does not take place at room temperature but readily occurs at higher temperature. For example hydrogen and oxygen do not react at room temperature but react vicolently if an electric spark is passed through them.

4) Presence of a Catalyst :→

A catalyst is defined as a substance which increases the speed of the reaction without itself undergoing any chemical change.



The presence of a catalyst leads to the formation of an activated complex lower energy than that required for uncatalysed process. Thus, a catalyst lowers the activation energy of a rxn through an alternate path with lower energy. Due to lowering of energy barrier, greater number of molecules can cross over the energy barrier & form product and the rate of reaction increases.

(5) Presence of radiations :→

There are certain reactions e.g combinat of H_2 & Cl_2 which do not take place in dark but take place

mainly in the presence of light radiations. This is because in the dark, the reactant molecules do not have sufficient energy to cross over the energy barrier. As soon as they are exposed to light radiations, they absorb energy and have sufficient energy to cross over the energy barrier and result into the formation of products.

5) Surface area of reactants :→

Larger the surface area of the reactants, faster is the rate of reaction. Eg- a log of wood burns slowly as compared to small size wooden chips. This is because with increase in surface area, more molecules of the reactants come into contact with each other & the rate of reaction becomes more.

* ORDER OF REACTION :→

It is defined as sum of the powers present in rate law is called by order of a reaction.

$$aA + bB \rightleftharpoons cC + dD$$

$$\text{Rate} \Rightarrow K[A]^a[B]^b$$

$$\text{Order} = a + b$$

Eg- $H_2 + I_2 \rightarrow 2HI$ / Order $= 1+1 = 2$

$$\text{Rate} = K[H_2][I_2]^1$$

* INTEGRATED RATE EQUATION FOR ZERO ORDER REACTION :→

A reaction is said to be a zero order reaction if the rate of reaction is independent of concentration of the reactant

$$A \rightarrow \text{Product}$$

For zero order rxn

$$\text{Rate} \propto [A]^0$$

$$r = K[A]^0 \qquad \{[A]^0 = 1\}$$

$$\boxed{r = K} \quad -(1)$$

$$r = -\frac{d[A]}{dt} \quad -(2) \qquad -\frac{d[A]}{dt} = K \quad -(3)$$

$$[\because r = K]$$

$$-d[A] = K\,dt \text{ or } d[A] = -K\,dt \quad (4)$$

Integrating eqn (4)

$$\int d[A] = -k\int dt$$

$$[A] = -kt + I \quad \text{— (5)}$$

When rxn is not started then $t = 0$ or intial concentration is $[A]_0$, then

$$[A] = [A]_0 \quad \text{— (6)}$$

Put eqn (6) in (5)

$$[A]_0 = -k \times 0 + I$$

$$[A]_0 = I \quad \text{— (7)}$$

Put eqn (7) in (5)

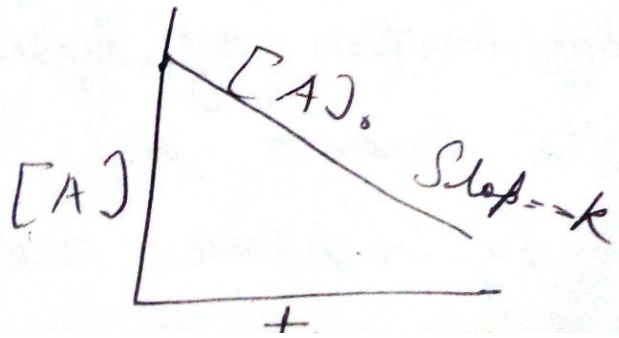
$$[A] = -kt + [A]_0 \quad \text{— (8)}$$

$$[A] = [A]_0 - kt$$

$$kt = [A]_0 - [A]$$

$$\boxed{k = \frac{[A]_0 - [A]}{t}} \quad \text{— (9)}$$

Compare eqn (8) by straight line eqn $y = mx + c$, then graph comes



Half life Period :→

The time taken for half of the reaction to be completed is called half life period.

$t = t_{1/2}$, $[A] = \frac{[A_0]}{2}$ — (A)

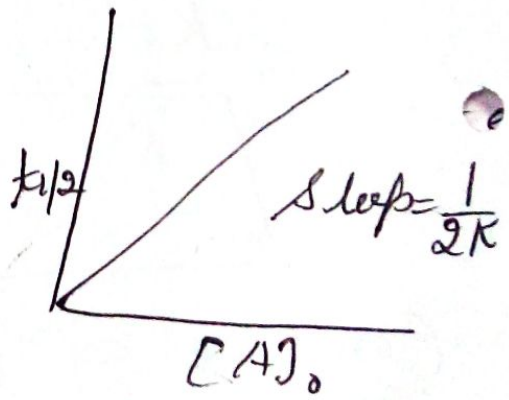
Put eqⁿ (A) in eqⁿ (9)

$$K = \frac{[A]_0 - \frac{[A]_0}{2}}{t_{1/2}}$$

$$K = \frac{[A_0]\left[1 - \frac{1}{2}\right]}{t_{1/2}}$$ [A_0 is common]

$$K = \frac{1}{2}\frac{[A_0]}{t_{1/2}}$$

$$\boxed{t_{1/2} = \frac{[A_0]}{2K}}$$



Examples for zero Order Reaction :-

* Photochemical combination of hydrogen and chlorine in the presence of sunlight to form hydrochloric acid

(6)

* Decomposition of ammonia on finely divided platinum.

* FIRST ORDER REACTION :→

A reaction is said to be a first order reaction if the rate of the reaction depends only upon one of the concentration term.

$$A \rightarrow \text{Product}$$

Rate expression $= -\frac{dA}{dt}$ — (1)

Rate $= K[A]^1$ — (2)

Comparining eqn (1) & (2)

$$-\frac{dA}{dt} = K[A]^1$$

$$\frac{-dA}{[A]} = Kdt \quad \text{or} \quad \frac{dA}{[A]} = -Kdt \quad (3)$$

Integrating eqn (3)

$$\int_{A_0}^{A} \frac{dA}{A} = -K\int_{0}^{t} dt$$

$$\ln A \Big|_{A_0}^{A} = -K \, t \Big|_0^t$$

$$\ln A - \ln A_0 = -Kt$$

$$Kt = \ln A_0 - \ln A \qquad \left(\ln m - \ln n = \ln \frac{m}{n}\right)$$

$$Kt = \ln \frac{A_0}{A}$$

$$\boxed{Kt = 2.303 \log \frac{A_0}{A}} \quad \text{— (4)}$$

$$\boxed{t = \frac{2.303}{K} \log \frac{A_0}{A}} \quad \text{— (5)}$$

where A_0 is initial concentration

A is concentration left

Half life Period :—

Put $t = t_{1/2}$, $A = A_0/2$ — (A)

Put eqn (A) in (5)

$$t_{1/2} = \frac{2.303}{K} \log \frac{A_0}{A_0/2}$$

$$t_{1/2} = \frac{2.303}{K} \log 2$$

$$t_{1/2} = \frac{2.303}{K} \times 0.3010 \qquad (\log 2 = .3010)$$

$$\boxed{t_{1/2} = \frac{0.693}{K}}$$

Examples of first Order Rxn :→

① Decomposition of nitrogen pentoxide

$$2N_2O_5(g) \rightleftharpoons 4NO_2(g) + O_2(g)$$

② Decomposition of ammonium nitrite in aqueous solution

$$NH_4 \cdot NO_2 \rightarrow 2H_2O + N_2$$

* Second Order Rxn :→

$$\text{Rate} = K[A]^2$$

$$-\frac{d[A]}{dt} = K[A]^2$$

$$\frac{d[A]}{[A]^2} = -Kdt \quad \text{— ①}$$

Integrating eqn ①

$$\int \frac{d[A]}{[A]^2} = -K\int dt$$

$$\int \frac{1}{[A]^2} d[A] = -K\int dt$$

$$\left|-\frac{1}{[A]}\right|_0^t = -Kt\Big|_0^t$$

$$-\frac{1}{[A]_t} - \left(-\frac{1}{A_0}\right) = -K(t-0)$$

Taking -ve sign common

$$\frac{1}{[A]_t} - \frac{1}{[A]_0} = Kt$$

$$\boxed{\frac{1}{[A]_t} = Kt + \frac{1}{[A]_0}} \quad \text{— (2)}$$

Half life Period :→

$$A = \frac{[A]_0}{2} \quad \text{— (A)}$$

Put in eqⁿ (2) given eqⁿ (A)

$$\frac{1}{[A]_0/2} = Kt_{1/2} + \frac{1}{[A]_0}$$

$$\frac{2}{[A]_0} - \frac{1}{[A]_0} = Kt_{1/2}$$

$$\frac{1}{[A]_0} = Kt_{1/2}$$

$$\boxed{t_{1/2} = \frac{1}{[A]_0 K}}$$

* Third Order Rxⁿ :→

Rate $= K[A]^3$

$$-\frac{d[A]}{dt} = k[A]^3$$

$$-\frac{d[A]}{[A]^3} = k\,dt \quad \text{or} \quad \frac{d[A]}{[A]^3} = -k\,dt \quad \text{—(1)}$$

Integrating eqn (1)

$$\int_{[A]_0}^{[A]} \frac{d[A]}{[A]^3} = -k\int_0^t dt$$

$$-\frac{1}{2[A]^2} - \left(-\frac{1}{2[A]_0^2}\right) = -k(t-0)$$

$$-\frac{1}{2[A]^2} + \frac{1}{2[A]_0^2} = -kt$$

$$\frac{1}{[A^3]} = A^{-3+1} = \frac{A^{-2}}{-2} = -\frac{1}{2[A]^2}$$

Multiply by -ve on both sides

$$\frac{1}{2}\left[\frac{1}{[A]^2} - \frac{1}{[A_0]^2}\right] = kt = \frac{1}{[A]^2} - \frac{1}{[A]_0^2} = 2kt$$

$$\boxed{\frac{1}{[A]^2} = 2kt + \frac{1}{[A]_0^2}}$$

Half life Period—

$$\frac{1}{[A]^2} - \frac{1}{[A]_0^2} = 2kt \quad \text{Put} = \frac{1}{2}[A]_0$$

$$\frac{1}{\frac{1}{2}[A]_0^2} - \frac{1}{[A]_0^2} = 2kt_{1/2}$$

$$\frac{4}{[A]_0^2} - \frac{1}{[A]_0^2} = 2kt_{1/2}$$

$$\frac{3}{[A]_0^2} = 2kt_{1/2} \qquad \boxed{t_{1/2} = \frac{3}{2k[A]_0^2}}$$

* Methods of determination of order of reaction :→

(1) Use of Integrated Rate Equation :-

In this method the initial concentration of reactants and the concentration of one of the product is measured by some suitable method. Then any one of the following methods is used for determination of the order of the reaction.

i) Substitution Method :→

In this method, the initial concentration a or C_0 & the concentration of reactants $(a-x)$ or C_t is noted at different intervals of time. These values are substituted in the integrated rate eq^n of zero, first, second, third order. The integated rate equation which gives constant value of K decides the order of reaction

ii) Graphical Method :→

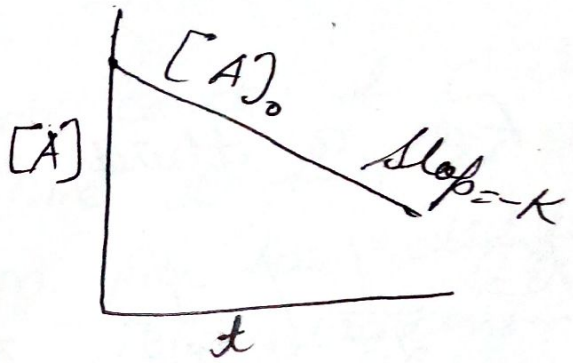
This method is used when there is only one reactant. In this method appropriate function of concentration is plotted against time. A straight line will be obtained only for the case in which appropriate integrated equation has been used.

i) For zero order reaction-

The rate eqn is-

$$K = \frac{[A]_0 - [A]}{t}$$

Plot of [A] vs t gives a straight line with slope k & intercept $[A]_0$



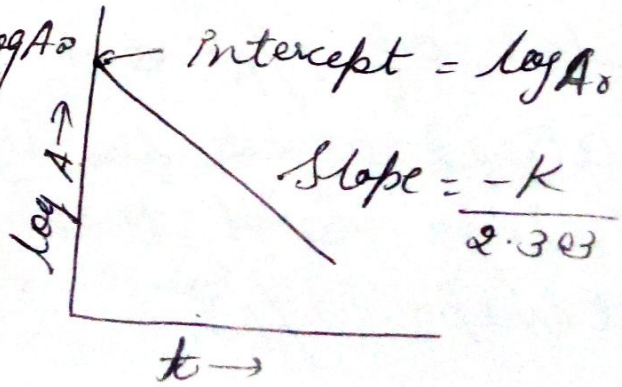
ii) For first order reaction -

The rate equation is-

$$t = \frac{2.303}{K} \log \frac{A_0}{A} \quad , K = \frac{2.303}{t} \log \frac{A_0}{A}$$

$$\log A_q = \frac{-Kt}{2.303} + \log A_0$$

Plot of log A vs t gives a straight line with slope $-K/2.303$ & intercept $\log A_0$



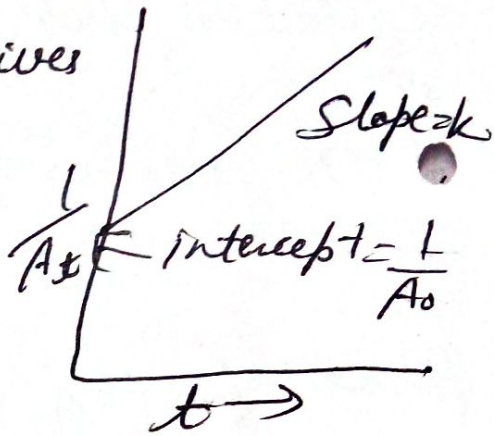
iii) For a second Order Rxn

The rate equation is-

$$K = \frac{1}{t}\left[\frac{1}{[A]_t} - \frac{1}{[A]_0}\right]$$

$$\frac{1}{[A]_t} = Kt + \frac{1}{[A]_0}$$

the plot of $1/A_t$ vs t gives a straight line having slope equal to K & intercept $1/A_0$



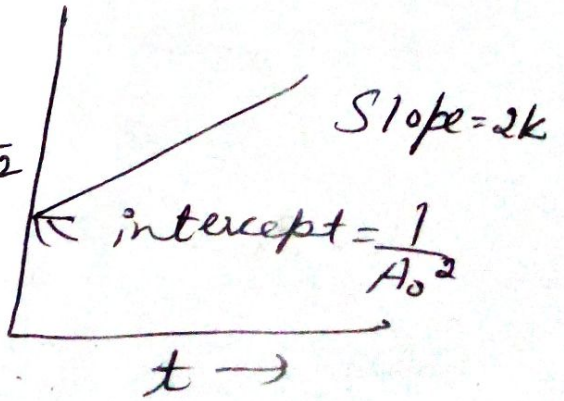
iv) For a third order reaction-

$$K = \frac{1}{2t}\left[\frac{1}{[A]^2} - \frac{1}{[A_0]^2}\right]$$

The eqn corresponding to $y = mx + c$ is

$$\frac{1}{[A]^2} = 2Kt + \frac{1}{A_0^2}$$

The plot of $1/A^2$ vs t gives a straight line with slope equal to $2k$ & intercept $1/[A_0]^2$



2) Differential Rate Equation Method (10)
(Van't Hoff's Differential Method)

We know that in first order reaction the rate is proportional to one concentration term, and in a second order reaction, the rate depends on two conc. terms. So, the rate of reaction of nth order is proportional to nth power of the concentration.

$$\text{Rate } (r) = -\frac{dC}{dt} = KC^n \quad \text{— (1)}$$

where K is the rate const. & C is the conc. at any time t & n is the order of the reaction. For two different concentrations—

$$r_1 = -\frac{dC_1}{dt} = KC_1^n \quad \text{— (2)}$$

$$r_2 = -\frac{dC_2}{dt} = KC_2^n \quad \text{— (3)}$$

Taking logarithms on both sides on eqn (2) & (3)

$$\log r_1 = \log K + n \log C_1 \quad \text{— (4)}$$

$$\log r_2 = \log K + n \log C_2 \quad \text{— (5)}$$

Substracting eqn (5) from (4)

$$\log r_1 - \log r_2 = n \log C_1 - n \log C_2$$

$$n = \frac{\log r_1 - \log r_2}{\log C_1 - \log C_2} \quad \text{—— (6)}$$

This the order of the reaction can be calculated using eqn (6)

The order of reaction n can be calculated if the values of rates r_1 & r_2 at two different concentrations C_1 & C_2 are known.

This can be done by any of the following methods

i) The small change in concentration ΔC of the reactant is measured in a small time interval Δt. The value of $\Delta C/\Delta t$ is assumed to be constant in a given time interval. Hence $\Delta C/\Delta t$ can be taken equal to dV/dt. Therefore, the values of r i.e dC_1/dt & r_2 i.e dC_2/dt at two different concentrations C_1 & C_2 can be calculated

3) Half life Period Method :→

This method is also known as fractional change method. Half life period of a reaction is the time during which the concentration of a reactant is reduced to half of its initial value. We also know -

i) Half life a initial concentration for a zero order reaction

i.e $t_{1/2} \propto a$ (for zero order reaction)

ii) Half life is independent of initial conc. for a first order reaction. $t_{1/2} = \frac{0.693}{K}$

iii) Half life is inversely proportional to initial concentration for a second order reaction i.e -

$$t_{1/2} \propto \frac{1}{a}$$

iv) Half life period is inversely proportional to square of initial concentration for a third order reaction

$$t_{1/2} \propto \frac{1}{a^2}$$ (for 3rd order reaction

For general for an nth order reaction

$$t_{1/2} \propto \frac{1}{a^{n-1}} \quad \text{— (1)}$$

For two initial concentration a_1 & a_2

$$(t_{1/2})_1 \propto \frac{1}{a_1^{\,n-1}} \quad \text{— (2)}$$

$$(t_{1/2})_2 \propto \frac{1}{a_2^{\,n-1}} \quad \text{— (3)}$$

Dividing eqn (2) by eqn (3) we get

$$\frac{(t_{1/2})_1}{(t_{1/2})_2} = \left(\frac{a_2}{a_1}\right)^{n-1}$$

Taking logarithms on both sides

$$\log (t_{1/2})_1 - \log (t_{1/2})_2 = (n-1)[\log a_2 - \log a_1]$$

$$n = 1 + \frac{\log (t_{1/2})_1 - \log (t_{1/2})_2}{\log a_2 - \log a_1}$$

Substituting the values of two initial concentrations a_1 & a_2 & half life periods from two experiments the value of n can be calculated

4) OSTWALD'S ISOLATION METHOD:

In this method the initial concentration of only one reactant is changed (keeping other concentrations constant) and the rate is determined. From this the order with respect to that reactant is calculated.

For example consider a reaction

$$A + B \longrightarrow \text{Products}$$

The concentration of A is doubled, tripled etc. and the effect on rate of reaction is observed. The order with respect to reactant A can be found. The same procedure is followed for reactant B while keeping the concentration of A is constant. The variation of rate w.r.t reactant B observed & the order of reaction w.r.t B is calculated

The overall order is the sum of individual orders.

Section- B

* Effect of Temperature on Rate of Reaction - Arhenius equation :→

In 1889, Arhenius gave the quantitative relationship between temperature and the rate constant and hence the rate of reaction The expression is called Arhenius equation & is written as

$$K = Ae^{-Ea/RT} \quad \text{— (1)}$$

where A is a constant called as frequency factor, Ea is the energy of activation, R is the gas constant and T is the absolute temperature. The factor $e^{-Ea/RT}$ gives the fraction of molecules having energy equal to or greater than activation energy, Ea. The activation energy Ea represents the minimum energy that the reacting molecules must possess before undergoing a reaction.

Activation energy E_a can not be measured directly but can be calculated using Arrhenius equation as follows—

Taking logarithms on both sides of eqⁿ (1),

$$\ln K = \ln A - \frac{E_a}{RT} \quad \text{— (2)}$$

If K_1 & K_2 are the rate constants for the reaction at two different temperatures T_1 & T_2 resp.

$$\ln K_1 = \ln A - \frac{E_a}{RT_1} \quad \text{— (3)}$$

$$\ln K_2 = \ln A - \frac{E_a}{RT_2} \quad \text{— (4)}$$

Subtracting eqⁿ (3) from (4), we get

$$\ln K_2 - \ln K_1 = -\frac{E_a}{RT_2} - \left(-\frac{E_a}{RT_1}\right)$$

$$= -\frac{E_a}{RT_2} + \frac{E_a}{RT_1} = \frac{E_a}{RT_1} - \frac{E_a}{RT_2}$$

$$\ln \frac{K_2}{K_1} = \frac{E_a}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

$$\log \frac{K_2}{K_1} = \frac{E_a}{2.303R}\left[\frac{T_2 - T_1}{T_1 T_2}\right] \quad \text{— (5)}$$

Thus, knowing the values of rate const. K_1 & K_2 at two different temperatures T_1 & T_2, the value of activation

Electrochemistry, with the

i) The inter-ionic attraction :- These are the attraction interactions between the ions formed by the electrolytes in solution & are known as solute-solute interaction. Larger the interionic attraction lesser is the freedom of movement of ions & smaller will be the electrical conductivity

ii) The salvation of ions :- These are the attractive interactions between the ions of the electrolyte & molecules of the solvent & are known as solute-solvent interactions. Larger the solute-solvent interactions, larger will be the salvation lesser will be the movement of ions & hence lower will be the electrical conductivity

iii) Viscosity of solvent :- This factor depends upon the attractive interaction between the solvent-molecules which is referred to as solvent-solvent interaction. Larger the solvent interaction, larger will be the viscosity and more will be the hindrance to the movement of ions. Hence, lower will be the electrical conductivity

with increase in

Alternatively, we can say that conductivity of electrolytic solution depends upon the following factor -

i) Nature of electrolyte - The conductance of an electrolyte depends upon the number of ions present in the solution. The number of ions produced by an electrolyte depends upon its nature. The strong electrolytes dissociate almost completely into ions in solution & therefore their solution have high conductance. Whereas, weak electrolytes dissociate to only small extent hence, their solutions have low conductance.

ii) Nature of solvent :- Electrolytes ionise to greater extent in polar solvents Therefore, greater the polarity of the solvent, larger is the ionisation & hence greater is the conductance

iii) Concentration of the solution :-
On increasing the concentration the electrolytic conductance decrease in case of both weak as well as strong electrolytes Because

Electrochemistry :→ The branch of

With increase in concentration in case of weak electrolytes the ionization decreases & in case of strong electrolytes the inter ionic attraction increase.

iv) Temperature :- The conductivity of an electrolyte depends upon the temperature. With increase in temperature the conductivity of an electrolyte increases due to increase in dissociation.

* Electrical Resistance & Conductance :-

According to ohm's law, the current I flowing through a metallic conductor is directly proportional to the potential difference -

$$I \propto V$$

$$I = V/R \qquad V = IR$$

Unit of R (Ω) - $\frac{kg\, m^2}{s^3 A^2}$

Conductance is the reciprocal of resistance

$$C = \frac{1}{R}$$

$$K = \frac{1}{R} \times \frac{l}{A}$$

$$K = C \times \frac{l}{A}$$

If $l = 1$ cm & $A = 1$ sq. cm, then $K = C$

* Relation between specific conductance (K) & equivalent conductance (Λ_{eq}) :-

The equivalent conductance Λ is equal to the product of specific conductance (K) & the Volume V in cm^3 which contain 1 gm equivalent the electrolyte.

$$\Lambda_{eq} = K \times V$$

In terms of concentration if a solution contains C g equivalents of electrolyte in 1000cc of the solution, then the volume of the solution containing 1g equivalent will be 1000/C.

$$\Lambda_{eq} = \frac{K \times 1000}{C_{eq}} = \frac{K \times 1000}{\text{Normality}}$$

* Molar Conductance :-

Molar conductance of a solution at dilution V is defined as the conductance of all the ions produced from one mole of the electrolyte dissolved in Vcc of solution such that the whole of the solution is placed between two parallel electrodes one centimeter apart. It is denoted by Λ_m.

Relationship between molar conductance & Specific Conductance :-

Molar conductance of a solution is obtained by multiplying the specific conductance by the volume V in cc which contains 1 mole of the electrolyte

$$\Lambda_m = K \times V$$

$$\boxed{\Lambda_m = \frac{K \times 1000}{C} = K \times \frac{1000}{\text{molarity}}}$$

Arhenius Theory of Ionisation:→

Arhenius put forward his theory of ionisation in 1884. Arhenius theory of ionisation is summarized as follows-

(1) An electrolyte when dissolved in water splits up into charged particles called ions. The positively charged particles are called cations + the negatively charged particles are called anions.

$$AB \rightarrow A^+ + B^-$$ (old form)

$$A^+B^- \rightarrow A^+ + B^-$$ (Modern form)

For this reason this theory is called as theory of electrolytic dissociation

(2) The charge carried by cations is equal to the charge carried by anions. As a result the electrolyte solution is electrically neutral.

(3) The charged ions move through the solution towards the oppositely charged electrodes. This migration of ions causes

the passage electric current through the electrolyte solution. This explains the conductance of electrolytes & the phenomenon of electrolysis.

(4) The electrolyte may not be completely ionized. The ratio of dissociated molecules to the total number of molecules is called the degree of dissociation

$$\alpha = \frac{\text{No. of molecules dissociated}}{\text{Total no of molecules}}$$

(5) The ions formed in the solution to form undissociated molecules.

$$AB \rightleftharpoons A^+B^-$$

The equilibrium const —

$$K = [A^+][B^-]/[AB]$$

where K is dissociation constant

(6) The degree of dissociation increases on dilution & becomes maximum at infinite dilution

(7) The electrical conductance of an electrolyte solution depends upon the no. of ions present in solution so greater the degree of dissociation

* Transference Number or Transport Number :→

During the passage of electric current through an electrolyte, the ions migrate towards electrodes. Thus, the current is carried by the anions & the cations. The current carried by an ion is directly proportional to the speed of the ion. The higher the speed of the ion, the more the current it carries & hence greater its transport number. The fraction of the total current carried by an ion is called its transport number, transference number or Hittorf's number.

If U_c represent the speed of the cation & U_a is that for anion,

The current carried by the cation $\propto U_c$
$= KU_c$

The current carried by the anion $\propto U_a = KU_a$

Total amount of current carried $= KU_c + KU_a$
$= K(U_c + U_a)$

Transport number of cation $n_c = \frac{K U_c}{K(U_c + U_a)}$ — (1)

$$\boxed{t_c = \frac{u_c}{u_c + u_a}} \quad \text{— (2)}$$

Transport number of anion $n_a = \frac{K u_a}{K(u_c + u_a)}$ — (3)

$$\boxed{t_a = \frac{u_a}{u_c + u_a}} \quad \text{— (4)}$$

Divide eq^n (2) & (4)

$$\frac{t_c}{t_a} = \frac{u_c}{u_c + u_a} \times \frac{u_c + u_a}{u_a}$$

$$\boxed{\frac{t_c}{t_a} = \frac{u_c}{u_a}}$$

By adding eq^n (3) & (4)

$$t_c + t_a = \frac{u_c}{u_c + u_a} + \frac{u_a}{u_c + u_a} = \frac{u_c + u_a}{u_c + u_a} = 1$$

$$\boxed{t_c + t_a = 1}$$

i.e the sum of transport number of cation & anion of an electrolyte is always unity. Hence, whole the of the current is carried by ions

...ed by r.

$$t_c = \frac{u_c}{u_c+u_a} = \frac{u_c/u_a}{1+u_c/u_a} = \frac{r}{1+r}$$

$$t_a = \frac{u_a}{u_c+u_a} = \frac{1}{1+\frac{u_c}{u_a}} = \frac{1}{1+r}$$

* Determination of Transport number by Hittorf's Method :-

Principle :→ This method is based on Hittorf's rule. According to this rule, the fall in concentration around any electrode is proportional to the speed of the ion moving away from that electrode

$$\frac{\text{Fall in conc around cathode}}{\text{Fall in conc around anode}} = \frac{\text{Speed of anion}}{\text{Speed of Cation}} = \frac{u_a}{u_c}$$

$$1+\frac{\text{Fall in conc around cathode}}{\text{Fall in conc around anode}} = 1+\frac{u_a}{u_c}$$

$$\frac{\text{Fall in conc around Cathode + Fall in conc around anode}}{\text{Fall in conc. around anode}} = \frac{u_a+u_c}{u_c}$$

$$\frac{\text{Total fall in conc. around both electrodes}}{\text{fall in conc around anode}} = \frac{u_a + u_c}{u_c}$$

Inverting both sides.

$$\frac{\text{Fall in conc. around anode}}{\text{Total fall in conc. around both electrodes}} = \frac{u_c}{u_a + u_c} = t_c$$

Expressing the concentration in terms of gram equivalent,

$$t_c = \frac{\text{No of gm equivalents lost around anodic compartment}}{\text{No of gm equivalent lost around both the compartment}}$$

This can be measured by placing a silver or a copper coulometer in series. According to Faraday's second law, when the same quantity of electricity flows through the silver or copper coulometer, the same number of gram equivalents of Ag or Cu will be deposited

$$t_c = \frac{\text{No of gm equivalent lost from anodic compartment}}{\text{No of gm equivalents deposited in the coulometer}}$$

... in this chapter.

Measurement of Transport Number by Hittorf's Method

For the measurement of transport number, the apparatus should be such that

(i) There should be three separate compartments *i.e.* anodic, cathodic and a middle compartment.

(ii) During electrolysis, there should be no intermixing of solutions of these compartments.

(iii) The solution from any compartment can be withdrawn without disturbing the solutions in other compartments.

This is achieved by using a suitable apparatus in which the anode and cathode compartments are separated by a *middle* compartment as shown in Fig. 13.

It consists of two vertical glass tubes joined together through a U-tube in the middle. All the three tubes are provided with stop-cocks at the bottom. By closing these stop-cocks, the mixing of solutions in the cathode and anode limbs can be stopped. The cathode and anode is made of platinum (non-attackable electrodes). The cathode and anode may be made of Ag or Cu if the transport number of Ag^+ or Cu^{2+} ions is to be determined.

A silver or copper voltameter is placed in series with the solution so that same quantity of electric current passes through them.

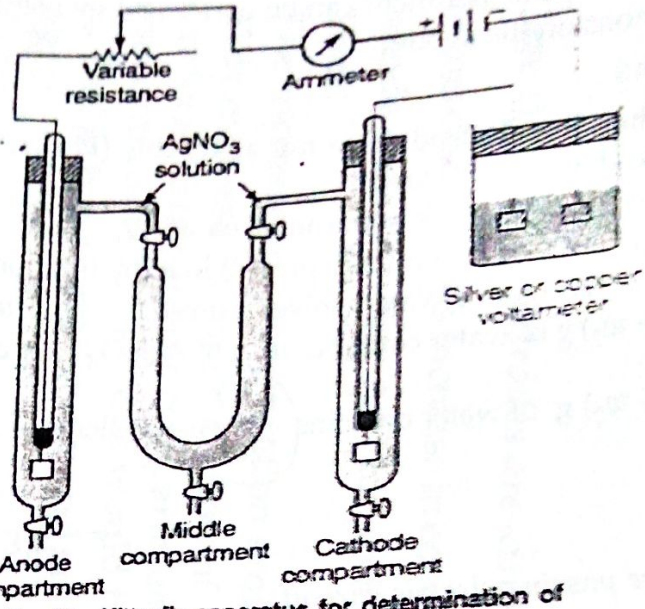


Fig. 13. Hittorf's apparatus for determination of transport numbers.

Procedure

(i) The apparatus is filled with the electrolyte solution of the ions whose transport number is to be determined.

(ii) The electrodes are inserted and the cell is connected in series with a silver or copper coulometer.

(iii) The concentration of the electrolyte is found by titrating the solution with a suitable reagent.

(iv) A steady current of 0.01 to 0.02 ampere is passed for two to three hours so as to produce appreciable change in concentration.

(v) After electrolysis the stopcocks of the U-tube are closed.

(vi) The whole liquid in the anode compartment is carefully drained into a weighed flask and its weight is determined. It is titrated to determine the weight of electrolyte present.

(vii) The weight of silver deposited in the silver coulometer (or copper in the copper coulometer) is determined.

(viii) There should be no change in the concentration of solution in U-tube. The solution from the central compartment is taken out and titrated to know if there is any change in the concentration of the electrolyte. In case the concentration change is there, the experiment is repeated.

If the above experiment is performed using silver electrodes, in this case nitrate ions attack the silver anode. Consequently, there is an increase in concentration of Ag^+ ions rather than decrease. The same experiment can be performed by using platinum electrodes to avoid the attack of anions on the anode.

Calculations

Case I : When the electrodes are not attackable (*Pt electrodes are used*)

After passing electric current

Let the weight of anodic solution taken = w_1 g

Weight of $AgNO_3$ found to be present in it (by titration) = w_2 g

$\therefore$ Weight of Water (solvent) present = $(w_1 - w_2)$ g

$\therefore$ $(w_1 - w_2)$ g of water contains w_2 g of $AgNO_3$ after electrolysis

or $(w_1 - w_2)$ g of water contains $\frac{w_2}{170}$ g equivalents of $AgNO_3$

$$= \frac{w_2}{170} \text{ g equivalent of A g} = x \text{ (say)}$$

Before passing electric current

Let w_3 g of solution contain Ag NO_3 = w_4 g

$\therefore$ Weight of water in the solution = $(w_3 - w_4)$ g

Hence before electrolysis $(w_3 - w_4)$ g of water contains Ag NO_3 = w_4 g

The weight of water remains unchanged after electrolysis,

$$\therefore (w_1 - w_2) \text{ g of water will contain} = \frac{w_4}{(w_3 - w_4)} \times (w_1 - w_2) \text{ g of Ag } NO_3$$

$$= \frac{w_4}{(w_3 - w_4)} \times \frac{(w_1 - w_2)}{170} \text{ g eq. of } AgNO_3$$

$$= \frac{w_4}{(w_3 - w_4)} \times \frac{(w_1 - w_2)}{170} \text{ g eq. of Ag} = y \text{ g eq. of Ag.}$$

When *electrodes are not attackable*, the amount of Ag or Cu deposited in the coulometer (x) is less than the actual increase in conc. of Ag^+ in the anodic compartment (y) so $x < y$

$\therefore$ Fall in conc. in the anodic compartment = $(y - x)$ g equivalents of Ag

Let the weight of Ag deposited in the silver coulometer

$$= w \text{ g} = \frac{w}{108} \text{ g eq. of Ag} = z \text{ g eqvt of Ag}$$

Then,

$$\text{Transport number of } Ag^+ \left(t_{Ag^+}\right) = \frac{\text{Fall in concentration around anode in g eqvt.}}{\text{Amount of Ag deposited in voltameter in g eqvt.}}$$

$$= \frac{y - x}{z}$$

$$\therefore \text{ Transport number of } NO_3^- \left(t_{NO_3^-}\right) = 1 - t_{Ag^+}$$

Case II : *When electrodes are attackable (Ag electrodes are used)*

In this case, there is increase in concentration around the anode. Because every NO_3^- reaching the anode dissolves one Ag^+ ion to form $Ag\,NO_3$.

Thus $$x > y$$

The increase in concentration around the anode = $(x - y)$ g equivalents of Ag

This increase in concentration of Ag^+ ions around the anode takes place even when Ag^+ ions migrate from anodic compartment. If no Ag^+ ions had migrated from the anode, the increase in concentration of Ag^+ ions would have been equal to z g equivalents.

∴ Fall in concentration around anode due to migration of Ag^+ ions = $z - (x - y)$ g equivalents of Ag

Hence, transport number of Ag^+ ion $\left(t_{Ag^+}\right) = \dfrac{z-(x-y)}{z}$

and transport number of NO_3^- ion $\left(t_{NO_3^-}\right) = 1 - t_{Ag^+} = 1 - \dfrac{z-(x-y)}{z}$

When copper coulometer is used in the experiment, the number of g equivalents of copper deposited in the coulometer is obtained by dividing the weight of copper deposited (*w g* say) by the equivalent mass of copper *i.e.* 31.75.

Section – C

Debye - Huckel - Onsager equation for Strong Electrolytes :→

Debye & Huckel (1923) derived an equation to show the variation of equivalent conductance with concentration.

Later on Onsager (1926-27) further extended the theory & derived the equation known as Debye - Huckel - Onsager equation or simply Onsager equation for uni-univalent electrolytes the equation is written -

$$\Lambda_c = \Lambda^\circ - \left[\frac{82.4}{\eta(DT)^{1/2}} + \frac{8.20\times10^5}{(DT)^{3/2}}\Lambda^\circ\right]\sqrt{C} \quad (1)$$

Λ_c - Equivalent conductance of electrolyte at concentration c

Λ° = Equivalent conductance of electrolyte at infinite dilution

D = Dielectric constant of the solvent

η = Coefficient of viscosity of the solvent

T = Temp. (K) of the solution

C = Concentration of the solution (moles/ltr)

which leads

Since the dielectric constant ε & the coefficient of viscosity η are const for a particular solvent, then at const temp (T) the eqn (1) can be written as

$$\Lambda_c = \Lambda^\circ - (A + B\Lambda^\circ)\sqrt{C}$$

where A & B are const for a given solvent & temperature

The constants A & B involve $\sqrt{\varepsilon T}$ in the denominator. Thus when ε & T increases the inter ionic attraction would decrease. Thus decrease in equivalent conductance will be less when dielectric const or temp high.

The first term $A\sqrt{C}$ is the measure of decrease of equivalent conductance due to electrophoretic effect. The const A in this term involves η the viscosity of the solvent in the denominator showing that in a more viscous solvent the decrease in equivalent conductance will be less because the speed of both the ions & the ionic atmosphere is slowed down in a more viscous solvent. The term $B\Lambda^\circ\sqrt{C}$ in the eqn gives the decrease of equivalent conductance due to asymmetry effect

Section – C

Electrochemistry :→ The branch of chemistry which deals with the study of relationship between electrical energy & chemical energy & interconversion of one form to another is called Electrochemistry.

* Electrical Transport :- A substance which allows an electric current to pass through it is called a conductor, while the substance which does not allow electric current to flow through it is called an insulator.

The conductors are of two types :-

i) Electronic Conductor - are the substances which do not undergo any chemical change as the electric current flows through them.

Eg- metal, graphite

ii) Electrolytic Conductor - are the substances which conduct electricity in their molten state or through their aqueous solution and which are decomposed by the

passage of electric current

* Electrolytes are further classified as strong electrolytes & weak electrolytes

Strong electrolytes - are substances which are almost completely dissociated into ions in their aqueous solution or in the molten state. Eg- strong acids like HCl, H_2SO_4 etc. strong bases like NaOH, KOH etc. & salts like NaCl, NH_4Cl etc.

Weak electrolytes :- are substances which dissociate in aqueous solution to a smaller extent. Eg- weak acids like HCN, H_3PO_4, weak bases like NH_4OH.

Non electrolytes :- substances like urea, glucose etc which do not conduct electricity in molten state or through their aqueous solutions are called non-electrolytes.

* Factors Affecting Electrolytic Conduction :-

Some of factors on which electrical conductivity of the solution of electrolyte depend are -

energy can be calculated. Eqn (5) can also be used to calculate the rate constant at any temperature if the rate constant at another temperature & the value of E_a is known for a particular reaction.

* Theories of Reaction Rates :→

Two main theories to explain the rates of chemical reactions are -

1. Collision theory
2. Transition state theory or the theory of absolute reaction rates.

(1) Collision Theory :-

This theory was put forward by Max Trautz and William Lewis in 1916-18. It is based Kinetic theory of gases. According to this theory, the reactant molecules are assumed to be hard spheres and the reaction occurs when molecules collide with each other.

For a collision to occur at least two molecules must collide therefore we consider bimolecular reactions.

Collision theory of bimolecular reaction

Collision theory of bimolecular gaseous reactions used for calculation of rate of reactions. It is based on the following postulates :-

i) The products are formed only when the reactant molecules collide with each other

ii) Only those collisions are effective in which the molecules possess sufficient energy of activation as well as proper orientation.

Each collision is not effective to bring about the reaction. Only a fraction of total number of molecules is effective in bringing about the chemical reaction.

If f is the fraction of the molecules having activation energy and Z is the number of bimolecular collisions per unit volume per second (ie collision frequency) between the reactant molecules, then the rate of a bimolecular reaction is given by —

$$\text{Rate} = Z \times f \quad \text{—} (1)$$

From Maxwell - Boltzmann law of distribution of energy, the fraction

of total molecules which possess (3)
energy equal to or more than activation
energy Ea is given by.

$$f = \frac{\Delta n}{N} = e^{-Ea/RT} \quad \text{— (2)}$$

where Δn is the number of activated molecules & N is the total number of molecules. The factor $e^{-Ea/RT}$ is called Boltzmann factor

Put eqn. (2) in (1)

$$\text{Rate} = -\frac{dn_A}{dt} = 2Xe^{-Ea/RT} \quad \text{— (3)}$$

The rate equations from collision theory are derived for two different cases-

Case 1. When bimolecular collisions occur between similar molecules

Consider a bimolecular gaseous reaction-

$$A + A \rightarrow \text{Product}$$

The molecules are considered to be rigid and hard spheres. It is assumed that there are no forces of attraction or repulsion between them. From Kinetic theory of gases, the collision per unit volume

per unit time is given by

$$Z_{AA} = \frac{1}{\sqrt{2}} \pi v \sigma_A^2 n_A^2 \quad \text{—(4)}$$

where σ_A is the diameter of molecule A, n_A is the number of molecules of A per unit volume of the container.

From Kinetic theory of gases, the value of average velocity v is given as -

$$v = \sqrt{\frac{8KT}{\pi m_A}} \quad \text{—(5)}$$

m_A = Mass of a single molecule A

K = Boltzmann constant

T = Absolute temperature

Put eqn (5) in (4)

$$Z_{AA} = \frac{1}{\sqrt{2}} \pi \sigma_A^2 n_A^2 \sqrt{\frac{8KT}{\pi m_A}}$$

$$= 2\sigma_A^2 n_A^2 \sqrt{\frac{\pi KT}{m_A}} \quad \text{—(6)}$$

In terms of molar mass-

$K = R/N$ & $m_A = \frac{M_A}{N}$ where M_A is the molar mass of A, N is the Avogadro's number & R is the gas cons

$$Z_{AA} = 2\sigma_A^2 n_A^2 \sqrt{\frac{\pi (R/N) T}{M_A/N}} = 2\sigma_A^2 n_A^2 \sqrt{\frac{\pi RT}{M_A}} \quad (7)$$

Put eqn (7) in (3)

$$\text{Rate} = \frac{-dn_A}{dt} = 2\sigma_A^2 n_A^2 \sqrt{\frac{\pi RT}{M_A}} \times e^{-E_a/RT} \quad (8)$$

Collisions $cm^{-3} s^{-1}$

Since each collision involves two similar molecules, the rate of reaction in terms of molecules of A reacting per cm^3 per second is given as-

$$\text{Rate} = -dn_A/dt = 2 \times \left(2\sigma_A^2 n_A^2 \sqrt{\frac{\pi RT}{M_A}} e^{-E_a/RT}\right)$$

molecules $cm^{-3} s^{-1}$

$$\boxed{\text{Rate} = 4\sigma_A^2 n_A^2 \sqrt{\frac{\pi RT}{M_A}} e^{-E_a/RT} \quad (9)}$$

molecules $cm^{-3} s^{-1}$

In general, for a bimolecular reaction $A + A \rightarrow$ Products, the reaction rate.

$$\text{Rate} = k n_A^2 \quad (10)$$

where k is the rate constant

Compairing eqn (9) & (10)

$$k = 4\sigma_A^2 \sqrt{\frac{\pi RT}{M_A}} e^{-E_a/RT} \quad (11)$$

molecules $cm^{-3} s^{-1}$

Using the value of K, we can determine the frequency factor A in Arrhenius eqn.

Compare eqn (11) with Arrhenius eqn

$$K = Ae^{-E_a/RT}$$

$$A = 4\sigma_A^2\sqrt{\frac{\pi RT}{M_A}} \text{ cm}^3 \text{ molecule}^{-1}\text{s}^{-1} \quad \text{—— (12)}$$

Eqn (9), (11) & (12) can be expressed in terms of molar concentrations –

The concentration of A is expressed in moles per litre as –

$$[A] = \frac{n_A \times 10^3}{N} \text{ moles } L^{-1}$$

where N is Avogadro's number

$$n_A = \frac{[A] \times N}{10^3}$$

$$dn_A = \frac{N}{10^3} \times d[A]$$

$$d[A] = \frac{10^3}{N} \times dn_A$$

Therefore, the reaction rate is –

$$-\frac{d[A]}{dt} = -\frac{10^3}{N}\left(\frac{dN_A}{dt}\right) = \frac{10^3}{N} - \frac{dn_A}{dt} \quad \text{—— (13)}$$

Put eqn (9) in (13)

$$-\frac{d[A]}{dt} = \frac{10^3}{N}\left[4\sigma_A^2 n_A^2 \sqrt{\frac{\pi RT}{M_A}} \times e^{-E_a/RT}\right]$$

Put value $n_A = \frac{[A]N}{10^3}$ in above eqn

$$-\frac{d[A]}{dt} = \frac{10^3}{N}\left[4\sigma_A^2 \frac{[A]^2N^2}{10^3 \times 10^3} \sqrt{\frac{\pi RT}{M_A}} \times e^{-E_a/RT}\right]$$

$$\boxed{\text{Rate} = 4\sigma_A^2 \frac{[A]^2 N}{10^3} \sqrt{\frac{\pi RT}{M_A}}\, e^{-E_a/RT} \text{ moles } L^{-1}s^{-1}} \quad (14)$$

Comparing eqn (14) with general rate law equation-

$$\text{Rate} = K[A]^2$$

$$\boxed{K = 4\sigma_A^2 \frac{N}{10^3} \sqrt{\frac{\pi RT}{M_A}} \times e^{-E_a/RT} \; L\,mol^{-1}s^{-1}} \quad (15)$$

Comparing eqn (15) with Arrhenius eqn

$$K = Ae^{-E_a/RT}$$

$$\boxed{A = 4\sigma_A^2 \frac{N}{10^3} \sqrt{\frac{\pi RT}{M_A}} \; L\,mol^{-1}s^{-1}} \quad (16)$$

Case 2 When the bimolecular collision occur between dissimilar molecules

Consider a bimolecular reaction

$$A + B \rightarrow \text{Products}$$

The no. of binary collisions Z_{AB} per unit volume per unit time between molecules A & B are given by –

$$Z_{AB} = \sigma_{AB}^2 \sqrt{\frac{8\pi kT}{\mu}}\, n_A n_B \quad \text{—— (17)}$$

where σ_{AB} is the distance of closest approach or the effective diameter for collision b/w molecules A & B. It is equal to the mean of the molecular diameter $\left(\frac{\sigma_A + \sigma_B}{2}\right)$, n_A & n_B are the no. of molecules of A & B per unit volume & μ is the reduced mass –

$$\frac{1}{\mu} = \frac{1}{m_A} + \frac{1}{m_B}$$

$$\frac{1}{\mu} = \frac{m_A + m_B}{m_A m_B}$$

$$\mu = \frac{m_A m_B}{m_A + m_B} \quad \text{—— (18)}$$

Put eqn (8) in (17)

$$Z_{AB} = \sigma_{AB}^2 \sqrt{8\pi KT\left(\frac{m_A + m_B}{m_A m_B}\right)}\, n_A n_B \quad (18)$$

In terms of molar mass –

$$m_A = \frac{M_A}{N}, \quad m_B = \frac{M_B}{N} \quad \& \quad K = \frac{R}{N}$$

Put value of m_A, m_B & K in eqn (18)

$$Z_{AB} = \sigma_{AB}^2 \sqrt{\frac{8\pi\left(\frac{R}{N}\right)T\left(\frac{M_A}{N} + \frac{M_B}{N}\right)}{\frac{M_A}{N} \times \frac{M_B}{N}}}\, n_A n_B$$

$$Z_{AB} = \sigma_{AB}^2 \sqrt{\frac{8\pi RT(M_A + M_B)}{M_A M_B}}\, n_A n_B$$

$$\text{Rate} = -\frac{dn_A}{dt} = -\frac{dn_B}{dt} = Z_{AB} \times e^{-E_a/RT}$$

Put eqn Z_{AB} in above equation –

$$\text{Rate} = -\frac{dn_A}{dt} = -dn_B/dt = \sigma_{AB}^2 \sqrt{8\pi RT\left(\frac{M_A + M_B}{M_A M_B}\right)}\, n_A n_B e^{-E_a}$$

Unit – molecules $cm^{-3} s^{-1}$ (19)

Also the rate is given by

$$\text{Rate} = K n_A n_B \quad \text{— (20)}$$

Comparing eqn (19) & (20)

$$K = \sigma_{AB}^2 \sqrt{8\pi RT\left(\frac{M_A + M_B}{M_A M_B}\right)}\, e^{-E_a/RT} \quad \text{(21)}$$

molecules $cm^3 s^{-1}$

Comparing eqn (21) with Arhenius eqn

$$K = Ae^{-E_a/RT}$$

$$\boxed{A = \sigma_{AB}^2 \sqrt{8\pi RT\left(\frac{M_A + M_B}{M_A M_B}\right)}\ cm^3\ molecule^{-1} s^{-1}} \quad \text{(22)}$$

Eqn (20), (21) & (22) in terms of molar concentrations of A & B -

$$[A] = \frac{n_A}{N} \times 10^3 \text{ moles } L^{-1} \text{ or } n_A = \frac{N \times [A]}{10^3} \quad \text{(23)}$$

$$dn_A = \frac{N}{10^3} d[A] \text{ or } d[A] = \frac{10^3}{N} dn_A$$

$$\frac{d[A]}{dt} = \frac{10^3}{N} \times \frac{dn_A}{dt}$$

Similarly, $[B] = \frac{n_B}{N} 10^3$ moles L^{-1}

or $n_B = \frac{N}{10^3} \times [B]$ (24)

$$dn_B = \frac{N}{10^3} d[B] \quad \text{or} \quad d[B] = \frac{10^3}{N} dn_B$$

$$\frac{d[B]}{dt} = \frac{10^3}{N} \frac{dn_B}{dt}$$

The reaction rate is

$$\text{Rate} = -\frac{d[A]}{dt} = -\frac{d[B]}{dt} = -\frac{10^3}{N} \times \frac{dn_A}{dt}$$

$$= \frac{10^3}{N} \times \left(-\frac{dn_A}{dt}\right) \quad \text{— (25)}$$

Put eqn (19) in (25)

$$\text{Rate} = \frac{10^3}{N} \sigma_{AB}^2 \sqrt{8\pi RT\left(\frac{M_A + M_B}{M_A M_B}\right)} n_A n_B e^{-E_a/RT}$$

Put eqn (23) & (24) in above eqn

$$\text{Rate} = \frac{10^3}{N} \sigma_{AB}^2 \sqrt{8\pi RT\left(\frac{M_A + M_B}{M_A M_B}\right)} \frac{N}{10^3} [A] \times \frac{N[B]}{10^3} \times e^{-E_a/RT}$$

$$\boxed{\text{Rate} = \frac{N}{10^3} \sigma_{AB}^2 \sqrt{8\pi RT\left(\frac{M_A + M_B}{M_A M_B}\right)} [A][B] e^{-E_a/RT} \; mol^{-1}s^{-1}} \quad \text{(26)}$$

Comparing eqn (26) with general rate eqn

$$\text{Rate} = K[A][B]$$

$$\boxed{K = \frac{N}{10^3} \sigma_{AB}^2 \sqrt{8\pi RT\left(\frac{M_A + M_B}{M_A M_B}\right)} e^{-E_a/RT} \; (mol^{-1}s^{-1})}$$

Comparing eqn (21) with Arrhenius eqn

$$K = Ae^{-E_a/RT}$$

$$\boxed{A = \frac{N}{10^3}\,\sigma_{AB}^{2}\sqrt{8\pi RT\left(\frac{M_A+M_B}{M_A M_B}\right)}\ L\,mol^{-1}s^{-1}}$$

Collision theory for Unimolecular Reaction :→

Collision theory proposes that the products are formed only when bimolecular collisions take place. This leads to a feeling that all gaseous reactions should be bimolecular and of second order. However, it is found experimentally that the decomposition reactions in gaseous phase follow first order kinetics

$$A \rightarrow \text{Products}$$

This can not be explained by the collision theory. Lindemann in 1922 explained how a bimolecular collision can give rise to first order kinetics.

According to Lindemann, the molecules of a reactant (say A) are continuously colliding with each other and as a result some molecules get activated. The activated molecules remain in the activated form for a finite period. During this time, the activated molecule may react or may get deactivated by colliding with another molecule.

$$A + A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} A + A^* \text{ (activated molecule)}$$

$$A^* \xrightarrow{k_3} \text{Products}$$

where A is normal & A^* is activated molecule & k_1, k_2, k_3 are the rate constant.

Rate of disappearance of $A = -\frac{d[A]}{dt}$

Rate of disappearance of $A^* = k_3[A^*]$

Hence Reaction rate $= -\frac{d[A]}{dt} = k_3[A^*]$ —— (1)

Since the concentration of A^* can not be measured directly, we make use of steady state principle. According to this principle, it is assumed that soon

after the start of the reaction, the concentration of A^* does not change

i.e. $\frac{d[A^*]}{dt} = 0$

Rate of formation of A^* = Rate of disappearance of A^*

Rate of formation of $A^* = k_1[A]^2$

Rate of disappearance of A^* = Rate of deactivation of A^* into reactant molecule + Rate of conversion of A^* into products

$$= k_2[A^*][A] + k_3[A^*]$$

$$= [A^*](k_2[A] + k_3)$$

$$k_1[A]^2 = [A^*](k_2[A] + k_3)$$

$$[A^*] = \frac{k_1[A]^2}{k_2[A] + k_3} \quad \text{—(2)}$$

Put eqn (2) in (1)

$$-\frac{d[A]}{dt} = \frac{k_1 k_3 [A]^2}{k_2[A] + k_3} \quad \text{—(3)}$$

Case 1. If the concentration of A is very high

In this case the rate of deactivation

of A^* is much faster than its rate of decomposition.

$$k_2[A] >> k_3$$

Then eq^n (2) becomes

$$-\frac{d[A]}{dt} = \frac{k_1 k_3 [A]^2}{k_2[A]} = \frac{k_1 k_3}{k_2}[A] \quad (3)$$

where $k = k_1 k_3 / k_2$ is a const then eq^n (3) becomes

$$-\frac{d[A]}{dt} = k[A]$$

This reaction follow first order kinetics

Case-2 If the concentration of A is very low.

Rate of decomposition of A^* is much greater than its rate of deactivation

$$k_3 >> k_2[A]$$

Eq^n (3) becomes

$$-\frac{d[A]}{dt} = \frac{k_1 k_2 [A]^2}{k_3}$$

Reaction rate = $k_1[A]^2$

This reaction follow a second order kinetics.

* Transition State Theory or the Theory of Absolute reaction rates :

The transition state theory explain that the reacting molecules approach each and a series of changes occur in the bond distances. The reacting molecules forms an intermediate before getting converted into products. This intermediate is called the transition state or activated complex

Consider a reaction :-

$$A + B \rightleftharpoons X^* \longrightarrow \text{Product}$$

(Activated complex)

Erying shows the rate constant for any reaction -

$$K = \frac{RT}{Nh} K^* \quad \text{—— (1)}$$

This equation is called by Erying eqn where R is the gas constant
K^* is the equilibrium constant

Now, $$K^* = \frac{[X^*]}{[A][B]} \quad \text{—— (2)}$$

The equilibrium constant K^* is related to free energy change ΔG^*

$$\Delta G^* = -RT \ln K^*$$

$$\ln K^* = \frac{-\Delta G^*}{RT}$$

$$K^* = e^{-\Delta G^*/RT} \quad \text{— (3)}$$

ΔG^* is the free energy

Put eqn (3) in (1)

$$K = \frac{RT}{Nh} e^{-\Delta G^*/RT} \quad \text{— (4)}$$

We know that

$$\Delta G^* = \Delta H^* - T\Delta S^* \quad \text{— (5)}$$

ΔH^* is the enthalpy of activation &

ΔS^* is the entropy of activation

Put eqn (5) in (4)

$$K = \frac{RT}{Nh} e^{-(\Delta H^* - T\Delta S^*)/RT}$$

$$K = \frac{RT}{Nh} e^{\Delta S^*/R} \cdot e^{-\Delta H^*/RT} \quad \text{— (6)}$$

Transition state Theory & Arhenius equation

Arhenius equation is -

$$K = Ae^{-Ea/RT} \quad \text{— (7)}$$

Comparing eqⁿ ⑥ + ⑦

$$A = \frac{RT}{Nh} e^{\Delta S^*/R}$$

$$e^{-E_a/RT} = e^{-\Delta H^*/RT}$$

$$E_a = \Delta H^*$$

Exact relationship between E_a + ΔH^* is derived as follows –

Eqⁿ ⑥ can be rewritten as –

$$K = \left(\frac{R}{Nh} \times e^{\Delta S^*/R}\right) \times T \times e^{-\Delta H^*/RT}$$

$$K = K' \times T \times e^{-\Delta H^*/RT} \quad \text{— (8)}$$

where $k' = \frac{R}{Nh} \times e^{\Delta S^*/RT}$ is a constant

Taking logarithms on both sides of eqⁿ ⑧, we get

$$\ln k = \ln k' + \ln T - \frac{\Delta H^*}{RT}$$

Differentiating above eqⁿ w.r.t temp.

$$\frac{d \ln k}{dt} = \frac{1}{T} + \frac{\Delta H^*}{RT^2} = \frac{\Delta H^* + RT}{RT^2} \quad \text{— (9)}$$

According to Arrhenius eqn-

$$k = Ae^{-E_a/RT}$$

Taking logarithm on both sides

$$\ln k = \ln A - \frac{E_a}{RT}$$

Differentiating above eqn w.r.t temp

$$\frac{d \ln k}{dT} = \frac{E_a}{RT^2} \quad \text{— (10)}$$

Compairing eqn (9) & (10)

$$E_a = \Delta H^* + RT$$

$$\Delta H^* = E_a - RT \quad \text{— (11)}$$

Comparision of Transition state Theory and Collision Theory-

Collision theory rate eqn is

$$k = pAe^{-E_a/RT} \quad \text{— (12)}$$

The activated complex theory rate eqn is

$$k = \frac{RT}{Nh} e^{\Delta S^*/R} \cdot e^{-\Delta H^*/RT} \quad \text{— (13)}$$

Compairison eqn (12) & (13)

$$pA = \frac{RT}{Nh} \times e^{\Delta S^*/R}$$

Advantages of Transition state theory:

i) Transition state theory offers an appropriate concept of formation of activated complex rather than the instantaneous formation of products by collision of reactant molecules.

ii) Transition state theory is thermodynamic in nature, it justifies the steric factor p of collision theory in terms of entropy of activation ΔS^*.

Section - D

Kohlrausch's law :→ At infinite dilution, where the dissociation of the electrolyte is complete, the molar conductivity of the electrolyte is the sum of limiting ionic conductivities of the cations & anions each multiplied by the number of ions composing one formula unit of the electrolyte.

$$\Lambda_m^\circ (A_xB_y) = x\lambda^\circ(A^+) + y\lambda^\circ(B^-)$$

where x & y rep. the number of positive & negative ions, $\Lambda_m^\circ (A_xB_y)$ is the limiting molar conductance of the electrolyte A_xB_y & $\lambda^\circ(A^+)$ & $\lambda^\circ(B^-)$ are the limiting molar conductivies of the cation A^+ & anion B^-.

Eg- For NaCl

$$\Lambda_m^\circ (NaCl) = \lambda^\circ(Na^+) + \lambda^\circ(Cl^-)$$

For KNO_3 $\Lambda_m^\circ (KNO_3) = \lambda^\circ(K^+) + \lambda^\circ(NO_3^-)$

* Effect of Viscosity on molar ionic Conductance – Walden's Rule :–

The frictional force f acting on the ion is given by stoke's law as

$$f = 6\pi\eta r u_i \quad —(1)$$

$r \rightarrow$ radius of the ion

$u_i \rightarrow$ ionic mobility of ion at infinite dilution

Under the potential difference E the driving force of an ion having charge z, moving between the electrodes l cm apart-

$$f = zeE/l \quad —(2)$$

from eqn (1) + (2)

$$6\pi\eta r u_i^\circ = zeE/l$$

$$\eta u_i^\circ = \frac{zeE}{6\pi r l} \quad —(3)$$

$$u_i^\circ = \frac{\lambda_i^\circ}{96500} \quad —(4)$$

Put eqn (4) in (3)

$$\eta \frac{\lambda_i^\circ}{96500} = \frac{zeE}{6\pi r l} \quad \text{or} \quad \eta\lambda_i^\circ = \frac{zeE \times 96500}{6\pi r l}$$

$$\eta \lambda_i^\circ = \text{Const} \quad -(6)$$

From Kohlrausch's law

$$\Lambda^\circ = (\lambda_+^\circ + \lambda_-^\circ)$$

Eqn (6) can be written as

$$\eta \lambda_+^\circ + \eta \lambda_-^\circ = \eta \Lambda^\circ = \text{Constant} \quad -(7)$$

That is the product of viscosity coefficient of a solvent & the equivalent conductance of an electrolyte at infinite dilution is constant. This is known as Walden's rule

* Effect of Temperature & Pressure on the Molar ionic Conductance :-

The molar ionic conductance is found to increase with increase in temperature. From eqn (7) molar ionic conductance is inversely proportional to the coefficient of viscosity η of the solvent. The viscosity of solvent decrease with increase in temperature, thus molar ionic conductance of an ion & increases as the temperature

increases. For example, for ions other than H^+ & OH^-, the increase in ionic conductance is about 2% for one degree rise in temperature in the temperature range of 0-100°C, whereas for H^+ & OH^- ions, the increase in ionic conductance is about 14% & 16% resp. per degree rise in temp.

Molar ionic conductance decreases on increasing pressure. This is because the viscosity of the medium increases on increase of pressure.

* Application of Conductance Measurements / Application of Kohlrausch's law :→

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① Degree of dissociation of a weak electrolyte :-

Arhenius theory assumes that in case of weak electrolytes the increase in equivalent conductance on dilution is due to increase in the degree of

of dissociation of the electrolyte.
The degree of dissociation (α) is given by

$$\alpha = \Lambda_c / \Lambda^\circ$$

where Λ_c is the equivalent conductance at any concentration & Λ° is the equivalent conductance at infinite dilution. The value of Λ° for strong electrolytes can be calculation using Kohlrausch's law.

(2) Dissociation constant (K_a) of weak acids :—

Consider the dissociation of a weak acid HA having initial concentration as c moles per litre. Let α be its degree of dissociation

$$HA \rightleftharpoons H^+ + A^-$$

Initial conc	$c\,mol^{-1}$	0	0
Equilibrium conc	$c(1-\alpha)$	$c\alpha$	$c\alpha$

Applying the law of chemical equilibrium the dissociation const K_a of a weak acid HA can be written as

$$K_a = \frac{[H^+][A^-]}{[HA]} = \frac{c\alpha \cdot c\alpha}{c(1-\alpha)} = \frac{c\alpha^2}{1-\alpha}$$

③ Solubility of sparingly soluble salts :-

Salts such as $AgCl$, $PbSO_4$, $BaSO_4$ etc dissolve to a very small extent in water & therefore are called sparingly soluble salts. Since they are very slightly soluble their solutions may be taken as infinite dilute. Moreover because their solutions are saturated, their concentration may be taken equal to their solubility. Thus, by determining the specific conductance (K) & equivalent conductance of such solutions, we can easily calculate solubility as Equivalent conductance (Λ) & specific conductance (K) of such solution

$$\Lambda = K \times 1000 \times S$$

$$\Lambda^\circ = K \times 1000 \times S$$

$$S = K \times 1000 \times \Lambda^\circ$$

(4) Determination of solubility product of a sparingly soluble salt :-

$$AB \underset{}{\overset{\text{Water}}{\rightleftharpoons}} A^+ + B^-$$

$$K_c = \frac{[A^+][B^-]}{[AB]}$$

- Molar conc. of solid is taken to be const. (k).

$$K_c \times k = [A^+][B^-] \quad \text{or}$$

$$K_{sp} = [A^+][B^-]$$

where $K_c \times k = K_{sp}$ is known as solubility product

- For any sparingly soluble salt A_xB_y,

$$A_xB_y \rightleftharpoons xA^{y+} + yB^{x-}$$

Solubility product -

$$K_{sp} = [A^{y+}]^x [B^{x-}]^y$$

$$[A^{y+}] = xS \quad [B^{x-}] = yS$$

$$K_{sp} = [xS]^x [yS]^y$$

For Calcium phosphate $Ca_3(PO_4)_2$

$x = 3,\ y = 2$

$K_{sp} = (3S)^3\ (2S)^2 = 9S^3 \cdot 4S^2 = 36S^5$

* Conductometric Titration :-

The basic principle of conductometric titration is the conductance of a solution serves as means of determining the end point of titration involving acid - base neutralisation or precipitation reactions.

These titrations are based on the fact that the conductance of a solution at a constant temperature depends on the number of ions present in it and their mobility. For this purpose, the titrant is added from the burette into a known volume of solution taken in a conductivity cell. As a result the number of ions in the solution changes and there is change in conductance. The small volumes of titrant are added and corresponding change in conductance is noted. The values of measured conductance are plotted against the volume of the titrant added.

In this graph two linear curves are obtained. The *point of intersection of these curves indicates the end point*. Some typical conductometric titrations are discussed ahead :

(i) Titration of a strong acid against a strong base

Consider a titration in which a strong acid (HCl) is titrated with a strong base (NaOH). The HCl solution is taken in a conductivity cell and the NaOH solution is taken in a burette. The conductance of HCl solution is noted. Then NaOH solution from the burette is added in small instalments. After each addition, the conductance of solution is noted. *Initially the conductance of HCl solution is high due to presence of highly mobile H^+ ions.* As NaOH solution is added the H^+ ions are removed by combination with OH^- ions forming weakly ionised H_2O

$$(H^+ + Cl^-) + (Na^+ + OH^-) \longrightarrow (Na^+ + Cl^-) + H_2O \text{ (weakly ionised)}$$

Thus, H^+ ions are replaced by slow moving Na^+ ions.

As a result the conductance of the solution decreases the keeps on falling till the end-point is reached. After the end point, the further addition of NaOH causes an increase in conductance due to increase in number of OH^- ions because the OH^- ions are no longer removed to form H_2O.

On plotting a graph between conductance and the volume of NaOH used, we get two straight lines AB and BC. The point of intersection of these lines is the end point of the titration as shown in Fig. 15. The point of minimum conductance gives the end point of titration. The end point B gives the volume of NaOH used for the titration.

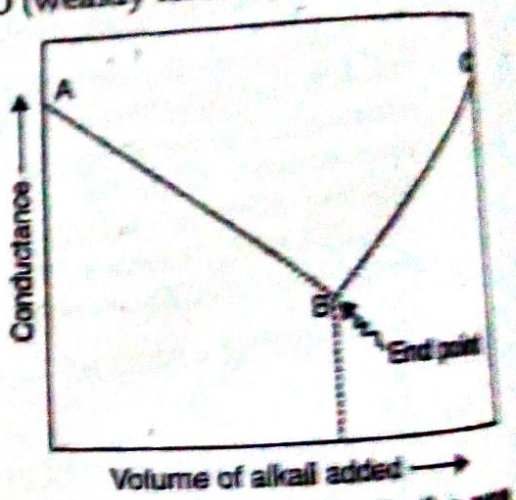

Fig. 15. Conductometric titration curve for strong acid and strong base.

(ii) Titration of weak acid with a strong base

When a weak acid like CH_3COOH is titrated with a strong base like NaOH, we get a curve the initial as shown in Fig. 16.

Conductance of acetic acid solution is very low as acetic acid is weakly dissociated. On adding NaOH solution, a highly ionised salt CH_3COONa is formed and the conductance of the solution increases along the curve AB (Fig. 16). The neutralization reaction is

$$CH_3COOH + (Na^+ + OH^-) \longrightarrow (CH_3COO^- + Na^+) + H_2O \text{ (Weakly ionised)}$$

Immediately after the neutralization of whole of CH_3COOH, *i.e.* after the end point, further addition of NaOH causes sharp increase in conductance along the curve BC. This is because addition of NaOH introduces excess of fast moving OH^- ions. The point of intersection of curves AB and BC gives the end point at B. The same titration curve is obtained when a weak acid like oxalic acid is titrated with strong base like NaOH.

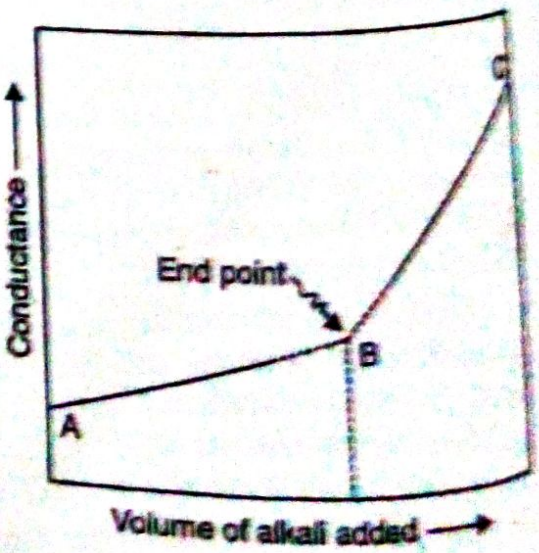

Fig. 16. Conductometric titration curve for titration of a weak acid against a strong base.

(iii) Titration of a strong acid with a weak base

When a strong acid like HCl is titrated with a weak base like NH_4OH, the curve obtained is shown in Fig. 17. In this case the initial conductance of HCl solution is high due to presence of fast moving H^+ ions. As NH_4OH solution is added, the H^+ ions are removed by combination with OH^- ions to form weakly dissociated H_2O.

$$(H^+ + Cl^-) + NH_4OH \longrightarrow (NH_4^+ + Cl^-) + H_2O$$

Thus the fast moving H^+ ions are replaced by slow moving NH_4^+ ions. Hence the conductance of the solution falls along the curve AB (fig. 17). After the end point, the conductance remains almost constant on addition of NH_4OH as is it weakly ionised. Thus the curve BC is almost horizontal.

The point of intersection of curve, AB and BC gives the end point.

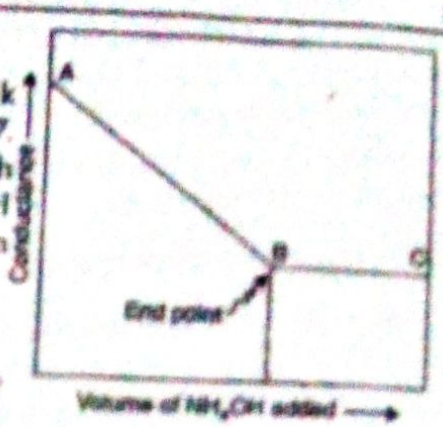

Fig. 17. Curve for titration of a strong acid against a weak base.

(iv) Titration of weak acid with a weak base

When a weak acid (CH_3COOH) is titrated with a weak base (NH_4OH), the curve as shown in Fig. 18 is obtained. The initial solution of CH_3COOH has low conductance as acetic acid is weakly ionised. On adding NH_4OH solution, highly ionised salt CH_3COONH_4 is formed. The conductance increases along curve AB. The neutralisation reaction is

$$CH_3COOH + NH_4OH \longrightarrow (CH_3COO^- + NH_4^+) + H_2O \text{ (weakly ionised)}$$

Further addition of NH_4OH after end point causes no change in conductance because NH_4OH is poorly ionised base. The curve BC is almost horizontal. The end point is the intersection point of curves AB and BC.

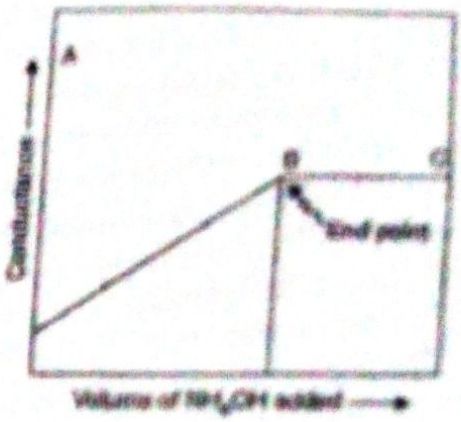

Fig. 18. Curve for titration of acetic acid against ammonium hydroxide.

(v) Titration of a mixture of weak and strong acids against a strong base

Suppose a mixture of weak acid like CH_3COOH and a strong acid like HCl is titrated with a strong base NaOH. The curve of the type as shown in Fig. 19 is obtained. In the beginning the ionisation of weak acid CH_3COOH remains suppressed due to common ion effect of a strong acid HCl.

Thus the initial decrease in conductance is due to the neutralisation of strong acid HCl. The equivalent point B represents the neutralisation of strong acid. Then the neutralisation of weak acid CH_3COOH takes place, the conductance increases along BC due to formation of highly ionised salt CH_3COONa. The point C represents the end point of neutralization of weak acid CH_3COOH.

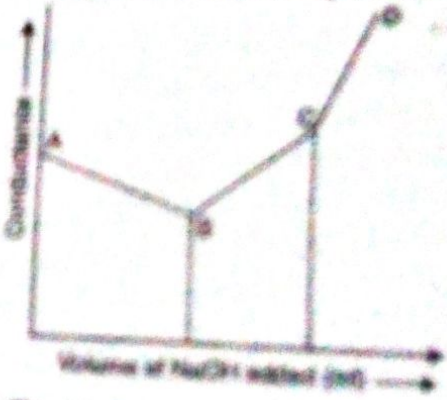

Fig. 19. Conductometric titration of a mixture of a weak and a strong acid against a strong base

The rise in conductance after the end point C is due to addition of strong base NaOH.

(vi) Titration of a salt of weak acid with a strong acid (Displacement reactions)

Consider the titration of sodium acetate solution with a strong acid HCl. In this titration reaction a weak acid is displaced by a strong acid i.e.,

$$(CH_3COO^- + Na^+) + (H^+ + Cl^-) \longrightarrow CH_3COOH + Na^+ + Cl^-$$

In this reaction highly ionised CH_3COONa is replaced by highly ionised NaCl. In other words CH_3COO^- ions are replaced by Cl^- ions. Since both these ions have almost same ionic conductance, so the conductance of the solution remains nearly constant until the end point is reached. Further addition of HCl after the end point causes increase in conductance due to fast moving H^+ ions as shown in Fig. 20.

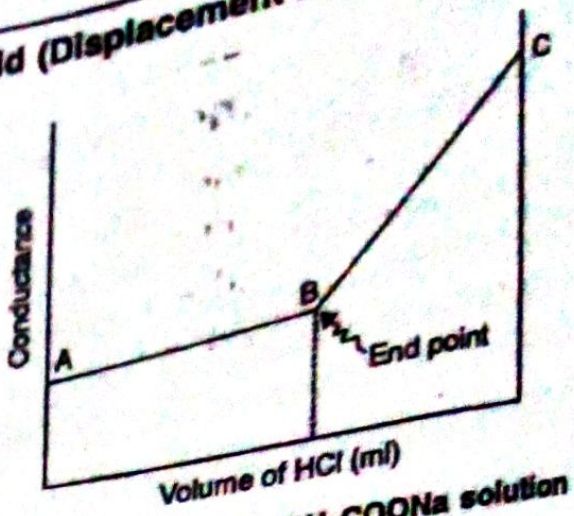

Fig. 20. Titration of CH_3COONa solution with strong acid HCl

(vii) Precipitation Reactions

The conductometric titration curve of a titration involving precipitation is shown in Fig. 21. Consider the titration of $AgNO_3$ with KCl solution. The reaction taking place is

$$(Ag^+ + NO_3^-) + (K^+ + Cl^-) \longrightarrow (K^+ + NO_3^-) + AgCl\downarrow (ppt).$$

Initially $AgNO_3$ has some conductance value depending upon its concentration. When KCl solution is added to it, a precipitate of AgCl is formed and the Ag^+ ions are replaced by K^+ ions. *Since the ionic mobilities of Ag^+ and K^+ ions are nearly equal, the conductance remains almost constant until the end point is reached.* The conductance starts increasing only after the end point. This is due to addition of excess of KCl which ionises to give K^+ and Cl^- ions. The increase in conductance takes place along curve BC. The point of intersection of curves AB and BC gives the end point of the titration.

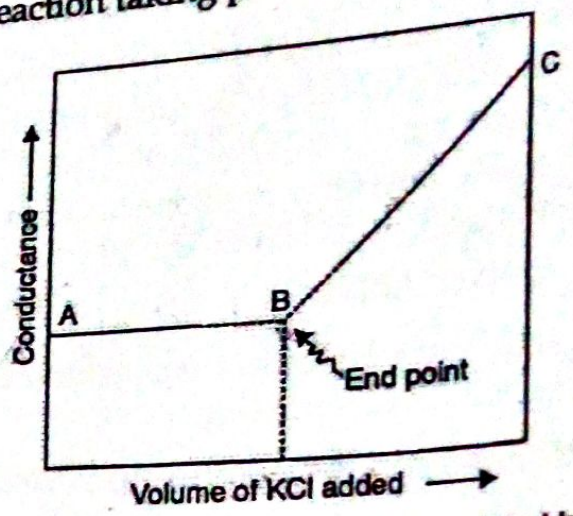

Fig. 21. Titration of potassium chloride against silver nitrate.

3.32.1 Advantages of conductometric titrations

(*i*) These titrations can be performed for coloured liquids where the end point can not be detected by ordinary indicators.

(*ii*) Conductometric titrations can be successfully performed in very dilute solutions.

(*iii*) These titrations can be used for the titrations of weak acids against weak bases which do not give sharp end point with indicators in volumetric analysis. These titrations can be successfully carried out with a mixture of weak and strong acids which is not possible in volumetric titrations.

(*iv*) The end point obtained graphically is more accurate.

(*v*) As the end point is indicated by the intersection of two curves so no extra precaution like dropwise addition of titrant is needed near the end point.

3.35 BUFFER SOLUTION

It is often necessary to maintain a definite pH of a solution in laboratory and in many industrial processes. This can be achieved with the help of **buffer solutions.**

A **buffer solution** *is defined as the solution whose pH remains practically constant by the addition of small amounts of either an acid (H_3O^+ ions) or a base (OH^- ions).*

3.35.1 Types of Buffer Solutions

Buffer solutions are of two types

1. *Buffer solutions containing single salt*

Such buffer solutions are the aqueous solutions of single salts. For example the aqueous solution of salt of weak acid and weak base *e.g.* ammonium acetate (CH_3COONH_4) acts as a buffer.

2. *Buffer solutions containing mixtures*

These solutions are one of the following two types :

(*i*) **Acidic Buffer :** It is the solution of mixture of a weak acid and its salt with a strong base, *e.g.* $CH_3COOH + CH_3COONa$. The pH of these buffer solutions is less than 7.

(*ii*) **Basic Buffer :** It is the solution of weak base and its salt with a strong acid, *e.g.*, $NH_4OH + NH_4Cl$. The pH value of basic buffer solutions is more than 7.

3.35.2 Buffer Action

The ability of a buffer solution to resist the change in pH even on addition of small amounts of acid or base is called **buffer action.**

1. Buffer Action of Ammonium Acetate Solution

The buffer action of solution of ammonium acetate can be explained as follows :

Ammonium acetate is completely dissociated in aqueous solution as under

$$CH_3COONH_4\ (aq) \rightleftharpoons CH_3COO^-\ (aq) + \overset{+}{N}H_4\ (aq)$$

Due to complete dissociation the salt provides excess of CH_3COO^- and $\overset{+}{N}H_4$ ions.

When a small amount of an acid is added to it, the additional H_3O^+ ions given by the acid combine with CH_3COO^- present in the buffer to form poorly dissociated CH_3COOH.

$$\underset{\text{from buffer}}{CH_3COO^-\ (aq)} + \underset{\text{from acid}}{H_3O^+} \rightleftharpoons CH_3COOH\ (aq)$$

Thus the increase of H^+ ions is counter balanced due to formation of undissociated CH_3COOH. Hence the added H^+ ions are neutralised and the pH of the solution remains unchanged. Similarly on addition of small amount of base the additional OH^- ions combine with NH_4^+ ions of the buffer to form poorly dissociated NH_4OH molecules.

$$\underset{\text{(From buffer)}}{NH_4^+ (aq)} + \underset{\text{(from base)}}{OH^- (aq)} \rightleftharpoons NH_4OH (aq)$$

Thus the excess OH^- ions are neutralised and the pH of the buffer solution remains unaltered.

On the other hand, *the aqueous solution of a salt of strong acid and a strong base e.g. sodium chloride* cannot act as a buffer because NaCl remains completely dissociated in aqueous solution as

$$NaCl (aq) \rightleftharpoons Na^+ (aq) + Cl^- (aq)$$

When a small amount of acid is added, Cl^- ions combine with H^+ to form HCl and when a base is added, Na^+ ions combine with OH^- ions to form NaOH. Both the HCl and NaOH are again completely dissociated to give back H^+ and OH^- ions. Hence the pH of the aqueous solution of NaCl changes on addition of small amounts of acid or base.

2. Buffer Action of Acidic Buffer

Consider an acidic buffer solution containing CH_3COOH and CH_3COONa. In aqueous solution CH_3COOH is weakly dissociated while CH_3COONa is completely dissociated as follows :

$$CH_3COOH (aq) \rightleftharpoons CH_3COO^- (aq) + H_3O^+ (aq) \quad ...(1)$$

$$CH_3COONa (aq) \longrightarrow CH_3COO^- (aq) + Na^+ (aq) \quad ...(2)$$

Due to common ion effect, the dissociation of acetic acid is further suppressed. As a result the solution contains excess of CH_3COO^- ions and small amount of H_3O^+ ions.

On addition of small amount of acid, the H_3O^+ ions provided by the acid combine with excess of CH_3COO^- ions to form poorly ionised CH_3COOH. Thus the added H_3O^+ ions are neutralised and hence the H_3O^+ ions concentration does not change. As a result the *p*H of buffer remains unchanged. Similarly, when a small amount of base is added to the buffer, the OH^- ions given by the base combine with H_3O^+ ions to form undissociated water.

$$\underset{\text{(From buffer)}}{H_3O^+ (aq)} + \underset{\text{(From base)}}{OH^- (aq)} \rightleftharpoons 2H_2O (l)$$

As a result the equilibrium (1) shifts to the right to produce more H_3O^+ ions to compensate the loss of H_3O^+ ions. Hence the concentration of H_3O^+ ions is maintained and original *p*H of the buffer solution remains unchanged.

3. Buffer Action of Basic Buffer

The buffer action of basic buffer solution *e.g.* a mixture of NH_4OH and NH_4Cl may be explained as follows :

Due to common ion effect, the dissociation of NH_4OH is depressed thus, the solution contains large concentration of NH_4^+ ions and small amount of OH^- ions.

When *a small amount of an acid is added* the H_3O^+ ions from the acid are neutralised by OH^- ions present in the buffer.

$$\underset{\text{(from buffer)}}{OH^- (aq)} + \underset{\text{(from acid)}}{H_3O^+ (aq)} \rightleftharpoons 2H_2O (l)$$

As the OH^- ions from NH_4OH combine with H_3O^+ ions from the acid, it would result in the greater ionization of NH_4OH to restore the OH^- ion concentration. Hence the *p*H of the solution remains unaltered.

On the other hand, *when a small amount of base is added* to the buffer solution, it would give OH^- ions. The additional OH^- ions will combine with NH_4^+ ions from the buffer to form poorly ionised NH_4OH.

$$NH_4^+ (aq) + OH^- (aq) \rightleftharpoons NH_4OH (aq)$$

(From buffer) (From base)

Thus the H_3O^+ ion concentration and hence the pH of the solution remains unaltered.

3.36 IMPORTANCE OF BUFFER SOLUTIONS

1. In biological processes

Many biological fluids such as blood, urine, etc. have a definite pH which is maintained by buffer action of many substances. The pH of human blood is maintained between 7.35 and 7.45 by buffer action of carbonic acid (H_2CO_3), bicarbonate ions (HCO_3^-) and carbon dioxide.

2. In industrial process

Buffer solutions play an important role in many industrial processes, *e.g.*

(i) Electroplating

(ii) Manufacture of alcohol by fermentation of molasses, medicines, dyes, photographic materials, in tanning of leather etc.

(iii) In investigation of many biochemical and physiochemical processes.

(iv) In analytical chemistry.

3.37 pH OF A BUFFER SOLUTION (HANDERSON-HASSEL EQUATION)

pH of buffer solution is calculated by applying **Handerson Hasselbalch equation.** This equation is derived as follows :

3.37.1 Expression for the pH of an Acidic Buffer

Consider an acidic buffer containing a weak acid (HA) and its salt (BA). The ionisation of weak acid can be written as :

$$HA\ (aq) \rightleftharpoons H_3O^+\ (aq) + A^-\ (aq) \text{ (Weakly dissociated)} \quad ...(1)$$

$$BA\ (aq) \longrightarrow B^+\ (aq) + A^-\ (aq) \text{ (Strongly dissociated)}$$

Applying law of chemical equilibrium, the dissociation constant K_a for equilibrium (1) can be written as

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

or

$$[H^+] = K_a \times \frac{[HA]}{[A^-]} \quad ...(2)$$

HA is a weak acid, its dissociation is further depressed by the common ion effect due to presence of the salt BA which provides A^- ions. As a result at equilibrium the concentration of unionised acid HA is nearly equal to the initial concentration of the acid HA. Since BA is completely dissociated, at equilibrium then concentration of A^- can be taken equal to the initial concentration of BA (salt)

Thus $[A^-] = [salt]$

Equation (2) can be written as

$$[H^+] = K_a \times \frac{[acid]}{[salt]}$$

Taking logarithm of both the sides we get

$$\log [H_3O^+] = \log K_a + \log \frac{[acid]}{[salt]}$$