Chemical Kinetics

Prof. (Dr.) Radha Tomar
Professor
School of Studies in Chemistry,
Jiwaji University, Gwalior-India

Outline

- **Introduction**
- **Collision Theory of reaction Rate**
- **Factors affecting rate of reaction**
- **Arrhenius Equation**
- **Kinetic Salt effects**
- **Kinetics of Chain reactions**

- **Homogeneous Catalysis**

- **Enzyme Kinetics**

- **Study of fast reactions by Nuclear Magnetic resonance Method, Flow Method, Relaxation Method, Flash Photolysis Method**

- **Theories of Unimolecular Reaction Rates**

Introduction

- Chemical kinetics is that branch of chemistry which deals with the study of rate of chemical reactions and the mechanism by which they occur. In other words, it deals with how fast and through what mechanism a particular chemical reaction occurs.

  The chemical reactions can be classified into the following categories on the basis of their speeds :

(a) ***Instantaneous or fast reactions*** *which proceed at a very fast speed and* it is practically impossible to measure the speed of such reactions. Typical examples of fast reactions include (i) several ionic reactions, i.e., neutralisation of acids and bases, (ii) organic substitution reactions, (iii) reactions of biological importance and (iv) explosive reactions of oxygen with hydrogen and hydrocarbons. The rates of such reactions can be measured by using special methods.

(b) ***Extremely slow reactions*** which proceed at a very slow speed and the speed is so slow that it is again not possible to measure the speed of such reactions.

(c) ***Reactions which proceed at a measurable speed.*** Reactions involving organic substances belong to this category, e.g., inversion of cane sugar, saponification of ethyl acetate etc.

Reactions belonging to the above third category, *viz.*, *(c) are utilized in the study* of chemical kinetics.

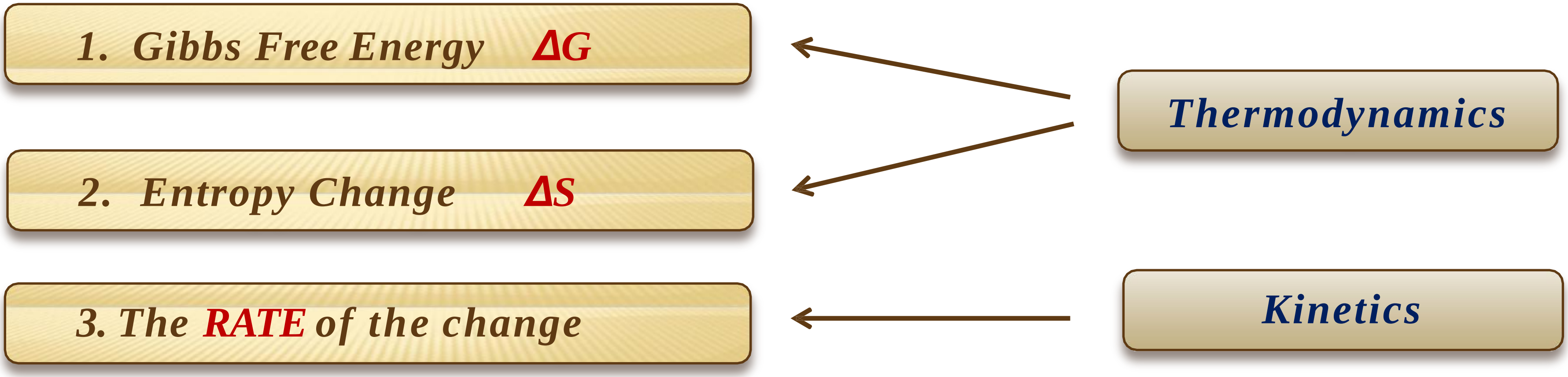
KINETICS -BACKGROUND

- *To understand & predict behaviour of a chemical system one must consider both Thermodynamics & Kinetics*

***Thermodynamics** : does a reaction takes place ???*

***Kinetics** : how fast does a reaction proceed ???*

- *Factors to be considered when predicting whether or not a change will take place*



1. Gibbs Free Energy ΔG

2. Entropy Change ΔS

*3. The **RATE** of the change*

Thermodynamics

Kinetics

RATE OF REACTION

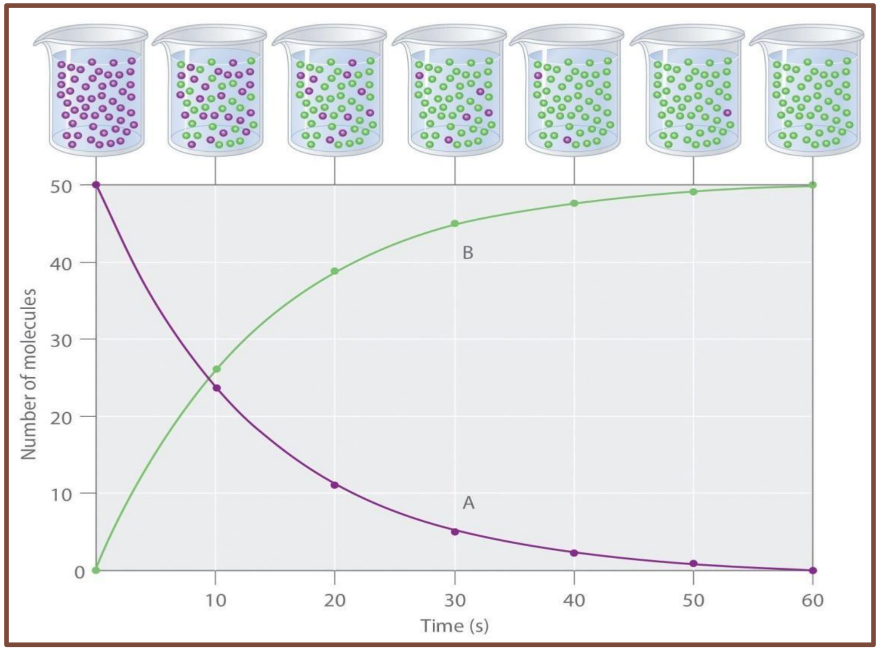
Rate Of Reaction

Change in the concentrations of reactants or products per unit time

Progress of a simple reaction,

Reactant A → Product B

- *Concentration of Reactant A (purple) decreases with time*
- *Concentration of Product B (Green) increases with time*
- *Concentrations of A & B are measured at time t_1 & t_2 respectively A_1, A_2 & B_1, B_2*



The graph shows the change in the number of A and B molecules in the reaction as a function of time over a 1min period (bottom)

Cont.

Rate with respect to A

$$Rate = \frac{\text{Change in concentration of } A}{\text{change in time}} = - \frac{\text{Conc. } A_2 - \text{Conc. } A_1}{t_2 - t_1} = - \frac{\Delta[A]}{\Delta t}$$

Rate with respect to B

$$Rate = \frac{\text{Change in concentration of } B}{\text{change in time}} = \frac{\text{Conc. } B_2 - \text{Conc. } B_1}{t_2 - t_1} = \frac{\Delta[B]}{\Delta t}$$

$$Rate = \frac{\Delta[A]}{\Delta t} = \frac{\Delta[B]}{\Delta t}$$ ………………………………… *for simpler reactions*

The (- ve) sign is used because the concentration of A is decreasing.

Cont.

For complex Reactions

$$aA + bB + cC + \ldots\ldots\ldots \longrightarrow eE + fF + gG + \ldots\ldots\ldots$$

where a, b, c,.....e, f, g,.... are ***stoichiometric coefficients*** *in the balanced Chemical equation & A, B, C ,..... E, F, G, ... are* ***Chemical Species***

At const. V .....

$$Rate = -\frac{1}{a}\frac{\Delta[A]}{\Delta t} = -\frac{1}{b}\frac{\Delta[B]}{\Delta t} = \frac{1}{e}\frac{\Delta[E]}{\Delta t} = \frac{1}{f}\frac{\Delta[F]}{\Delta t}$$

Unit Of Rate

$mol\ L^{-1}\ s^{-1}$ for gaseous reactants & products , conc. is usually expressed as partial pressures , so R is atm s^{-1}

Cont.

Average Rate Of **Reaction decreases with time as concentration of reactants decreases**

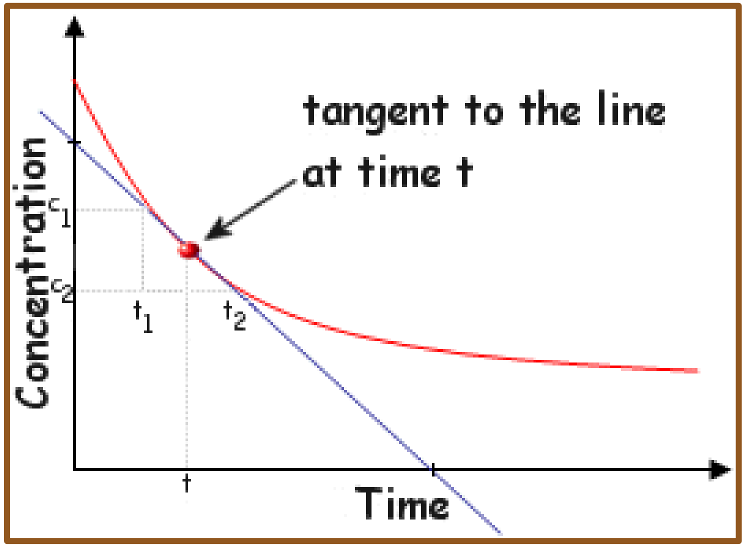
Instantaneous Rate

Change in the concentration of reactants or products at a given instant of time

slope of a tangent line to the curve of a conc. versus time plot

$$\text{Slope} = \frac{C_2 - C_1}{t_2 - t_1}$$

$$\text{Instantaneous Rate} = \lim_{t \to 0} = \Delta x/\Delta t = dx/dt$$



Concentration Versus Time Plot

Collision Theory of Reaction Rates

- For most reactions, for a reaction to take place, the reacting molecules must collide with each other.

  (On average, there are about 10^9 collisions per second!)

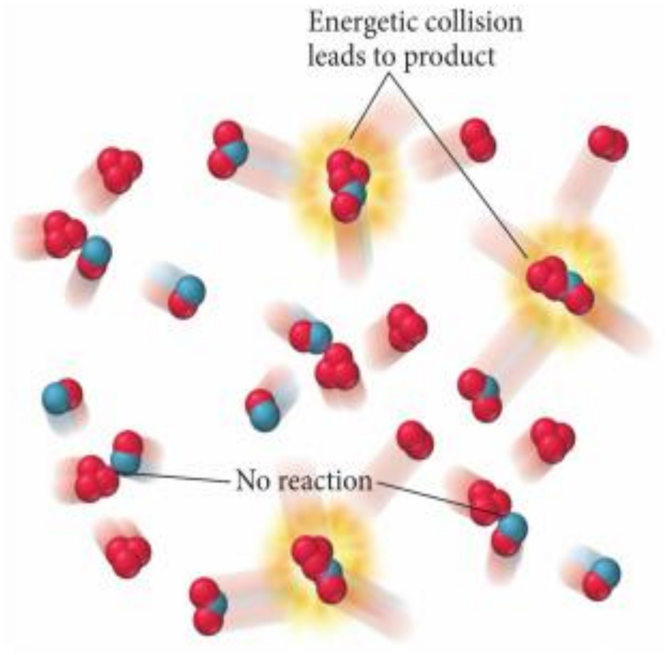
- Once molecules collide they may react together or they may not, depending on two factors:

– Whether the collision has enough kinetic energy to "break the bonds holding reactant molecules together“

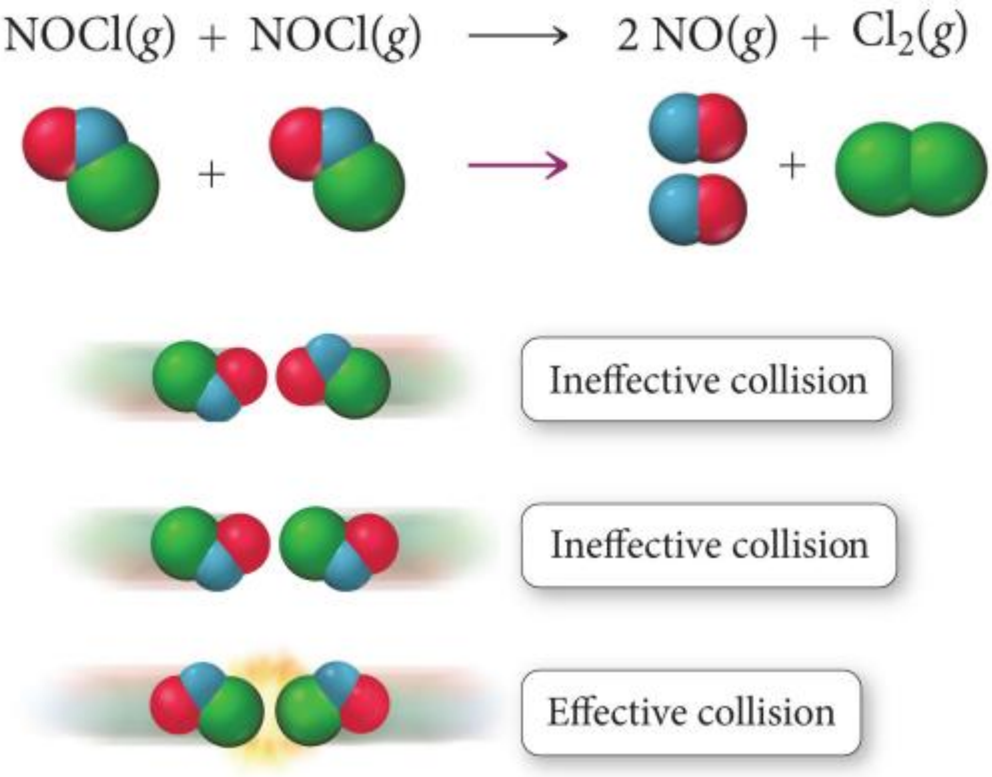
– Whether the reacting molecules collide in the proper orientation for new bonds to form

Effective Collisions: Kinetic Energy Factor

For a collision to lead to overcoming the energy barrier, the reacting molecules must have sufficient kinetic energy so that when they collide the activated complex can form.



Effective Collisions: Orientation Effect



$$NOCl(g) + NOCl(g) \longrightarrow 2\,NO(g) + Cl_2(g)$$

Effective Collisions

- Collisions in which these two conditions are met (and therefore lead to reaction) are called effective collisions.

❖ The higher the frequency of effective collisions, the faster the reaction rate.

❖ When two molecules have an effective collision, a temporary, high energy (unstable) chemical species is formed— the activated complex.

Factors Affecting Reaction Rate:

1. Reactant Concentration

- Generally, the larger the concentration of reactant molecules, the faster the reaction.

– This increases the frequency of reactant molecule contact.

– Concentration of gases depends on the partial pressure of the gas.

Higher Pressure = Higher Concentration

- Concentrations of solutions depend on the solute-to-solution ratio (molarity).

2. Nature of the Reactants

- Nature of the reactants means what kind of reactant molecules and what physical condition they are in.
  - Small molecules tend to react faster than large molecules.
  - Gases tend to react faster than liquids, which react faster than solids.
  - Powdered solids are more reactive than “blocks.”
    - **More surface area for contact with other reactants**
  - Certain types of chemicals are more reactive than others.
    - **For example, potassium metal is more reactive than sodium.**
  - Ions react faster than molecules.
    - **No bonds need to be broken**

3. Catalysts

- Catalysts are substances that affect the speed of a reaction without being consumed.
- Most catalysts are used to speed up a reaction; these are called positive catalysts. – Catalysts used to slow a reaction are called negative catalysts.
- Homogeneous = present in same phase
- Heterogeneous = present in different phase
- How catalysts work will be examined later.

4. Temperature

- Increasing temperature increases the reaction rate. This should make sense to us:

  Temperature is kinetic energy – higher KE means more forceful collisions, and a higher percentage of effective collisions.

  - Chemist’s rule—for each 10 °C rise in temperature, the speed of the reaction doubles.

- There is a mathematical relationship between the absolute temperature and the speed of a reaction discovered by Svante Arrhenius.

The Effect of Temperature on Rate

- Changing the temperature changes the rate constant of the rate law.
- Svante Arrhenius investigated this relationship and showed the following-

$$k = A\left(e^{\frac{-E_a}{RT}}\right)$$

where T is the temperature in kelvins.

R is the gas constant in energy units, 8.314 J/(mol · K).

A is called the frequency factor, the rate the reactant energy approaches the activation energy.

E_a is the activation energy, the extra energy needed to start the molecules reacting.

Arrhenius Equation

Vat't hoff showed that the value of equilibrium constant changes with temperature. On this basis he suggested that the logarithm of the specific reaction rate must be a linear function of the reciprocal of absolute temperature. Arrhenius extended this suggestion and gave his own hypothesis. According to this,

(i) All molecules of a system can not take part in a chemical reaction.

(ii) It is only a certain number of molecules which react. These reacting molecules are known as **active molecules**.

(iii) The molecules which do not take part in the chemical reaction are known as **Passive molecules**.

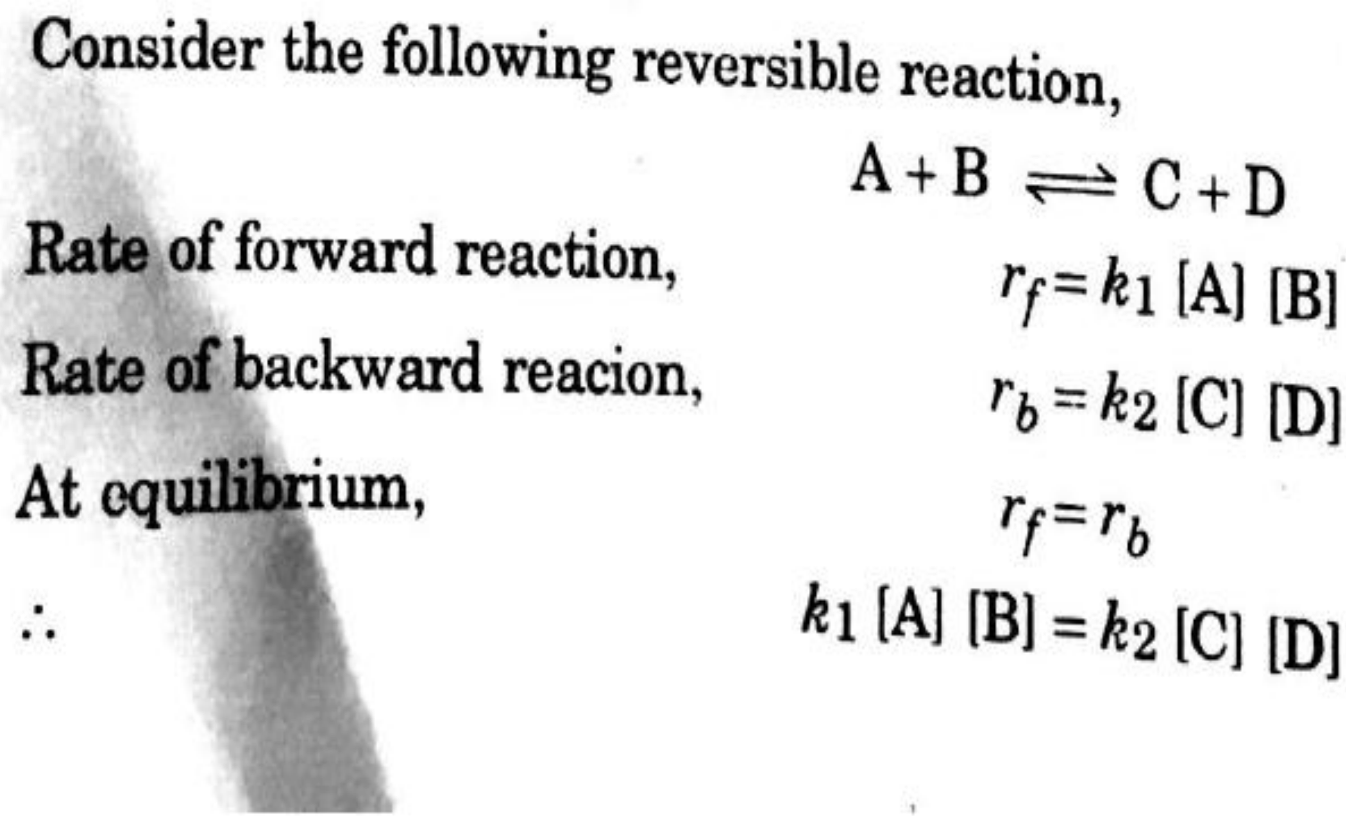
(iv) An equilibrium exists between active and passive molecules.

M (active) ==== M (Passive)

(v) When temperature is raised, the above equilibrium shifts to the left. This increases the number of active molecules which are ready to take part in a reaction. Thus the increase in reaction rate with increase in temperature is due to an increase in the number of active molecules not due to the number of collisions.

So, the basic concept of Arrhenius theory is that **the passive molecules become active due to the absorption of heat energy**

Derivation of Arrhenius Equation



Consider the following reversible reaction,

$$A + B \rightleftharpoons C + D$$

Rate of forward reaction,

$$r_f = k_1 [A] [B]$$

Rate of backward reacion,

$$r_b = k_2 [C] [D]$$

At equilibrium,

$$r_f = r_b$$

$$\therefore \quad k_1 [A] [B] = k_2 [C] [D]$$

$$K_C = \frac{k_1}{k_2} = \frac{[\mathrm{C}]\,[\mathrm{D}]}{[\mathrm{A}]\,[\mathrm{B}]} \qquad \ldots (1)$$

From thermodynamics, van't Hoff equation is,

$$\frac{d \ln K_c}{d T} = \frac{\Delta E}{R T^2}$$

where ΔE is the heat of reaction, K_c is the equilibrium constant. As $K_c = k_1 / k_2$, where k_1 and k_2 are the rate constants of the forward and the backward reactions, respectively. Equation (1) becomes

$$\frac{d \ln k_1 - d \ln k_2}{d T} = \frac{\Delta E}{R T^2} \quad \text{or} \quad \frac{d \ln k_1}{d T} - \frac{d \log k_2}{d T} = \frac{\Delta E}{R T^2}$$

The heat of reaction ΔH may be written as $E_1 - E_2$ and then

$$\frac{d \ln k_1}{d T} - \frac{d \ln k_2}{d T} = \frac{E_1}{R T^2} - \frac{E_2}{R T^2}$$

If E_1 and E_2 are assumed to be characteristic of the forward and backward reactions only, then

$$\frac{d \ln k_1}{d T} = \frac{E_1}{R T^2} + I$$

$$\frac{d \ln k_2}{d T} = \frac{E_2}{R T^2} + I$$

It has been found that I is independent of temperature and is equal to zero. So, we can write

$$\frac{d \ln k_1}{d T} = \frac{E_1}{R T^2} \qquad \text{...(2)}$$

and

$$\frac{d\, n\, k_2}{d T} = \frac{E_2}{R T^2} \qquad \text{... (3)}$$

known as ***Arrhenius***

Equations (2) and (3) were proposed by Arrhenius and are known as ***Arrhenius equations.*** The term E is called the energy of activation, which may be defined as the ***energy in excess to the average energy of the molecules at a given temperature which a molecule must have to enter into a chemical reaction.***

Integrating equations (2) and (3), we get

$$\ln k_1 = -\frac{E_1}{RT} + \text{constant } (A)$$

$$\ln k_2 = -\frac{E_2}{RT} + \text{constant } (A)$$

The above equations can be put as $k_1 = Ae^{-E_1/RT}$ and $k_2 = Ae^{-E_2/RT}$.

These equations are the alternative forms of Arrhenius equation.

In general,

$$k = A\,e^{-E/RT} \qquad \text{...(4)}$$

In equation (4), A is constant. The factor $e^{-E/RT}$ is responsible for the marked influence of temperature on the reaction rate. The equation (4) shows that the rate constant increases exponentially with temperature. The factor A is known as ***frequency factor*** of the reaction or ***collision number***. It is also called ***pre-exponential factor.***

Integrating equation (4) between proper limits, we get,

$$\int_{k_1}^{k_2} d \ln k = \int_{T_1}^{T_2} \frac{E}{R\,T^2} \,.\, d\,T$$

or

$$\ln \frac{k_2}{k_1} = -\frac{E}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right] \qquad \text{...(5)}$$

or

$$\log \frac{k_2}{k_1} = -\frac{E}{2.303\,R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right]$$

or

$$\ln \frac{k_2}{k_1} = -\frac{E}{RT} + \text{constant} \qquad \text{...(6)}$$

Kinetic Salt Effects

- An important features of reaction between ions is the way in which the addition of an inert electrolyte i.e., one whose ions do not enter in the chemical reaction taking place, can alter the rate of the reaction proceeding in the system. This phenomenon is known as Kinetic Salt effect.

  The effect of electrolytes is of two types, viz., Primary salt effect and secondary salt effect. The former effect refers to the effect of the electrolytic concentration of the activity coefficients, whereas the later is concerned with actual changes in the concentration of the reacting substances or ions resulting from the addition of electrolytes.

Primary Salt Effect

- The effect of the neutral salt on ion-ion interactions has been most satisfactorily explained by Bronsted, using the theory of strong electrolytes, introducing the idea of the activity of ions. The addition of an inert electrolytes serves to increase the ionic strength which is turn is related to the activity coefficients of all ions present, by the Debye-Huckel limiting Law.

The variation of activity coefficient with the concentration in dilute solutions can be expressed by the Debye-Huckel limiting law, Which is given as follows at 250 C, is given as follows at 25°C,

$$-\log f = 0{\cdot}51 z^2 \sqrt{\mu}, \qquad \dots (1)$$

where z = valency of the ion and μ = ionic strength of the solution.

Consider the reaction

$$A^{\pm} + B^{\pm} = X^{\circ} = \text{Products.} \qquad \dots (2)$$

where $A^{\pm}$ = neutral molecule or ion

$B^{\pm}$ = univalent positive or negative ion

X° = activated complex, which in turn dissociates into products.

If z_A, z_B and $z_{X^{\circ}}$ are the charges carried by A, B and X°, respectively and f_A, f_B and $f_{X^{\circ}}$ are the respective activity coefficients, then from equation (1), we can write

$$\log \left| \frac{f_A f_B}{f_{X^{\circ}}} \right| = -0.51 \sqrt{\mu} \, (z_A^2 + z_B^2 - z_{X^{\circ}}^2) \qquad \dots (3)$$

Since the activated complex will be equal to the algebraic sum of the charges of A and B, *i.e.*, $z_{X^\circ} = z_A + z_B$. So, from equation (3),

$$\log \frac{f_A f_B}{f_{X^\circ}} = -0.51 \sqrt{\mu}\ [z_A^2 + z_B^2 - (z_A + z_B)^2]$$

$$= +0.51 \sqrt{\mu}\ .\ 2z_A z_B = 1.02\, z_A z_B \sqrt{\mu} \qquad \ldots (4)$$

Applying the law of mass action to equation (2), we get

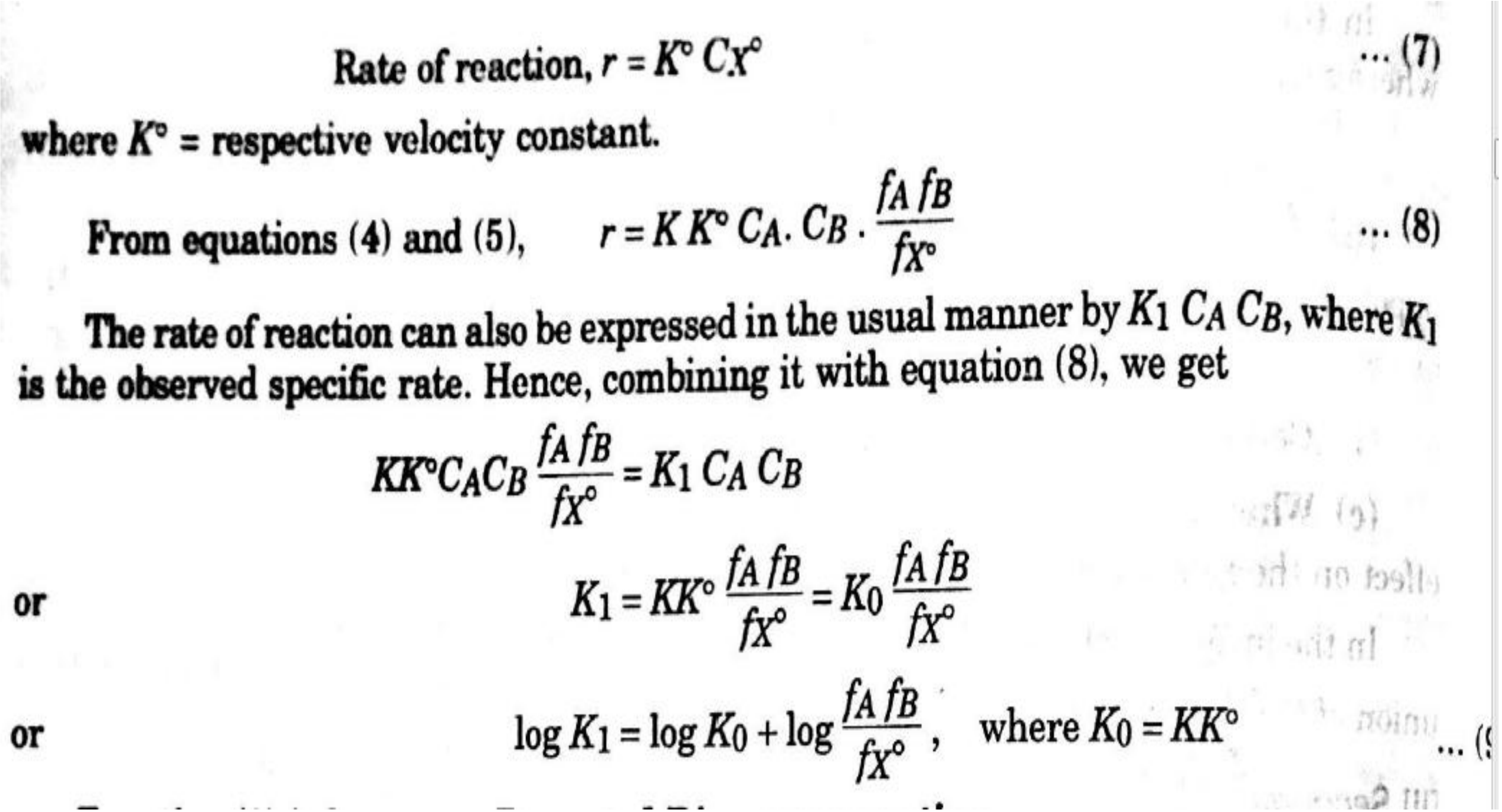
$$K = \frac{a_{X^\circ}}{a_A\, a_B} \qquad \ldots (5)$$

Replacing the activities in equation (5) by concentration and activity coefficient terms, we get

$$K = \frac{f_{X^\circ}\, C_{X^\circ}}{f_A\, C_A\, f_B\, C_B}$$

$$C_{X^\circ} = \frac{K\, f_A\, C_A\, f_B\, C_B}{f_{X^\circ}} \qquad \ldots (6)$$

The rate of reaction given by equation (2) is proportional to the concentration of the activated complex, *i.e.*, X°. Hence,



$$\text{Rate of reaction, } r = K^\circ C_{X^\circ} \qquad \ldots (7)$$

where K° = respective velocity constant.

From equations (4) and (5), $$r = K K^\circ C_A . C_B . \frac{f_A f_B}{f_{X^\circ}} \qquad \ldots (8)$$

The rate of reaction can also be expressed in the usual manner by $K_1 C_A C_B$, where K_1 is the observed specific rate. Hence, combining it with equation (8), we get

$$KK^\circ C_A C_B \frac{f_A f_B}{f_{X^\circ}} = K_1 C_A C_B$$

or $$K_1 = KK^\circ \frac{f_A f_B}{f_{X^\circ}} = K_0 \frac{f_A f_B}{f_{X^\circ}}$$

or $$\log K_1 = \log K_0 + \log \frac{f_A f_B}{f_{X^\circ}}, \quad \text{where } K_0 = KK^\circ \qquad \ldots ($$

Equation (9) is known as Bronsted – Bjerrum equation.

From equations (4) and (a),

$$\log K_1 = \log K_0 + 1.02\, z_A z_B \sqrt{\mu}$$

or

$$\log K_1 - \log K_0 = 1.02\, z_A z_B \sqrt{\mu} \qquad \dots (10)$$

If the values of $\log K_1 - \log K_0$ are plotted against $\sqrt{\mu}$, then it should be a straight line with a slope $1.02\, z_A z_B$ (Fig. 6). The reactions represented in the figure are :

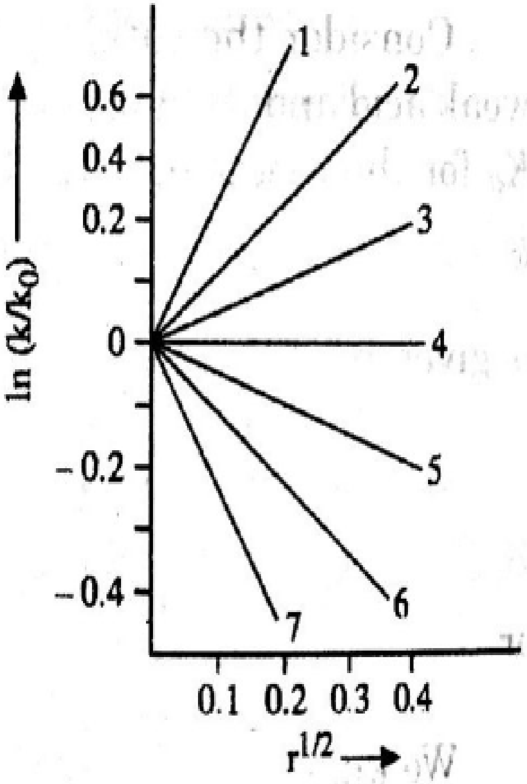


Fig. 6. Effect of ionic strength on the rate constant of a reaction. The product $z_A z_B$ gives the slope of the line.

(1) $[Co(NH_3)_5Br]^{2+} + Hg^{2+}$ $(z_A z_B = 4)$

(2) $S_2O_3^{2-} + I^-$ $(z_A z_B = 2)$

(3) $[Co(OC_2H_5)N : NO_2]^- + OH^-$ $(z_A z_B = 1)$

(4) $CH_3COOC_2H_5 + OH^-$ $(z_A z_B = 0)$

(5) $H^+ + Br + H_2O_2$ $(z_A z_B = -1)$

(6) $[Co(NH_3)_5Br]^{2+} + OH^-$ $(z_A z_B = -2)$

(7) $Fe^{2+} + [Co(C_2O_4)_3]^{3-}$ $(z_A z_B = -6)$

Thus, we see that it is the activity coefficients which are affected strongly by the addition of neutral salts. In the above treatment, f_X° cannot be measured directly by any method, but it has to be presumed that it will be affected by neutral salts in the same manner as f_A and f_B.

The variation of the specific rate, K_1 with ionic strength should depend on the magnitude and sign of the poduct $z_A z_B$. So, three cases can be observed and studied.

(a). When $z_A z_B$ is positive : In such a case, the reacting ions must have the same charge either positive or negative. So the reaction velocity will increase with increasing ionic strength. This type of phenomenon is called ***positive salt catalysis.***

(*t*) $2Co[(NH_3)_5Br]^{2+} + Hg^{2+} + 2H_2O = 2CO\ [(NH_3)_5H_2O]^{3+} + HgBr_2$

In this reaction, the rate determining stage is the following bimolecular process, where $z_A z_B = 4$

$$Co[NH_3)_5Br]^{2+} + Hg^{2+} \rightarrow \text{Products.}$$

(b) When $z_A z_B$ is negative : In such a case, the reacting ions must have the opposite charges. The reaction velocity will then decrease with increasing ionic strength or vice versa. This type of phenomenon is called ***negative salt catalysis.***

(1) $Co[(NH_3)_5Br]^{2+} + OH^- = Co[(NH_3)_5(OH)]^{2+} + Br^-$ where $z_A z_B = -2$.

(c) When $z_A z_B$ is zero : In dilute solutions, the ionic concentration has little or no effect on the rate of reaction or velocity constant.

In the inversion of cane sugar by acids, it is assumed that the complex is formed by a union of $C_{12}H_{22}O_{11}$ and H^+ (or H_3O^+). We find that $z_A = 0$, $z_B = 1$, so that $z_A z_B = 0$.

Secondary Salt Effect

- This effect is involved in catalytic reactions, so it can be studied by changing the actual concentrations of the catalytically active ions. If these are roduced by strong acid or strong base, the secondary salt effect is negligible. This effect becomes important, if the ions are produced by the dissociation of a weak electrolyte.

Consider the catalytic effect of hydrogen ions which are produced by a mixture of a weak acid and its salt at a definite concentration. The equilibrium (or hydrolysis) Constant Ka for the reaction.

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

is given by,

$$K_a = \frac{(a_{H_3O^+})(a_{A^-})}{(a_{HA})}$$

or

$$K_a = \frac{(c_{H_3O^+})(c_{A^-})}{(c_{HA})} \times \frac{(f_{H_3O^+})(f_{A^-})}{(f_{HA})} \quad (\because \ a = fc) \qquad \ldots (11)$$

We know that the pH of a mixture of a weak acid and its salt of constant composition is given by

$$pH = K_a \times \left[\frac{c_{HA}}{c_{A^-}} \right] = \text{constant} = K$$

So, equation (11) can be written as

$$c_{H_3O^+} = \frac{K \, . \, (f_{HA})}{(f_{H_3O^+})\,(f_{A^-})} \quad \ldots (12)$$

As the activity term varies with the ionic strength of the medium, it follows that hydrogen ion concentration and its catalytic activity will also change with ionic strength of the medium. This is known as ***secondary salt effect.***

The velocity of a reaction involving H^+ ions as catalyst is proportional to $[H^+]$, so, we can write,

$$k_r = k_0 \frac{(f_{HA})}{(f_{A^-})\,(f_{H_3O^+})} \qquad \text{... (13)}$$

where k_0 is a constant and becomes equal to experimental rate constant provided the activity coefficients of H_A, H_3O^+ and A^- are all unity. Using Debye-Huckel limiting law, equation (13) can be written as,

$$\log k_r = \log k_0 + 1.02\sqrt{\mu}$$

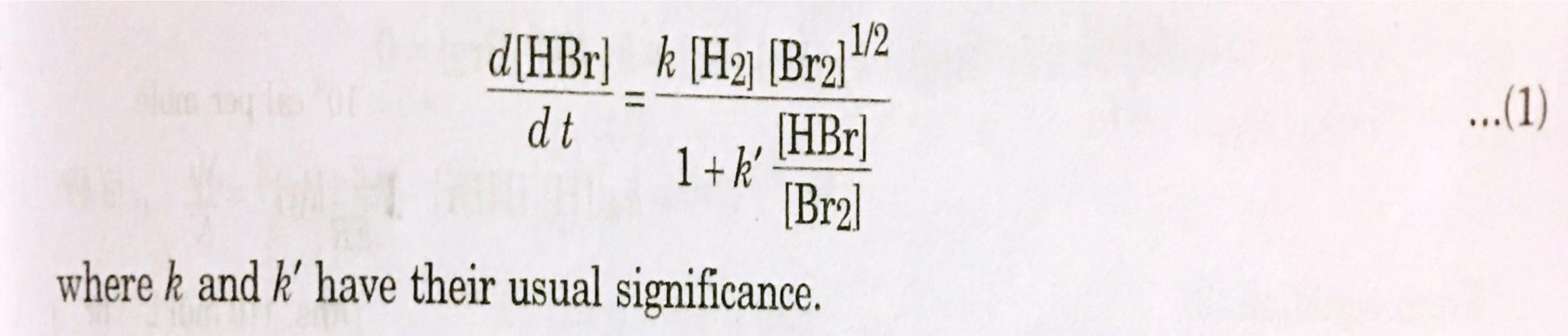
So, the rate constant will increase with the increasing concentration of the electrolyte. This secondary salt effect has been seen to exist in a number of cases.

Kinetics of Chain reactions

Defination:-A chemical or nuclear reaction which proceed through a sequence (chain) of self repeating steps initiated by a suitable primary process is called a chain reaction.

Reaction Kinetics of thermal hydrogen-Bromine Reaction

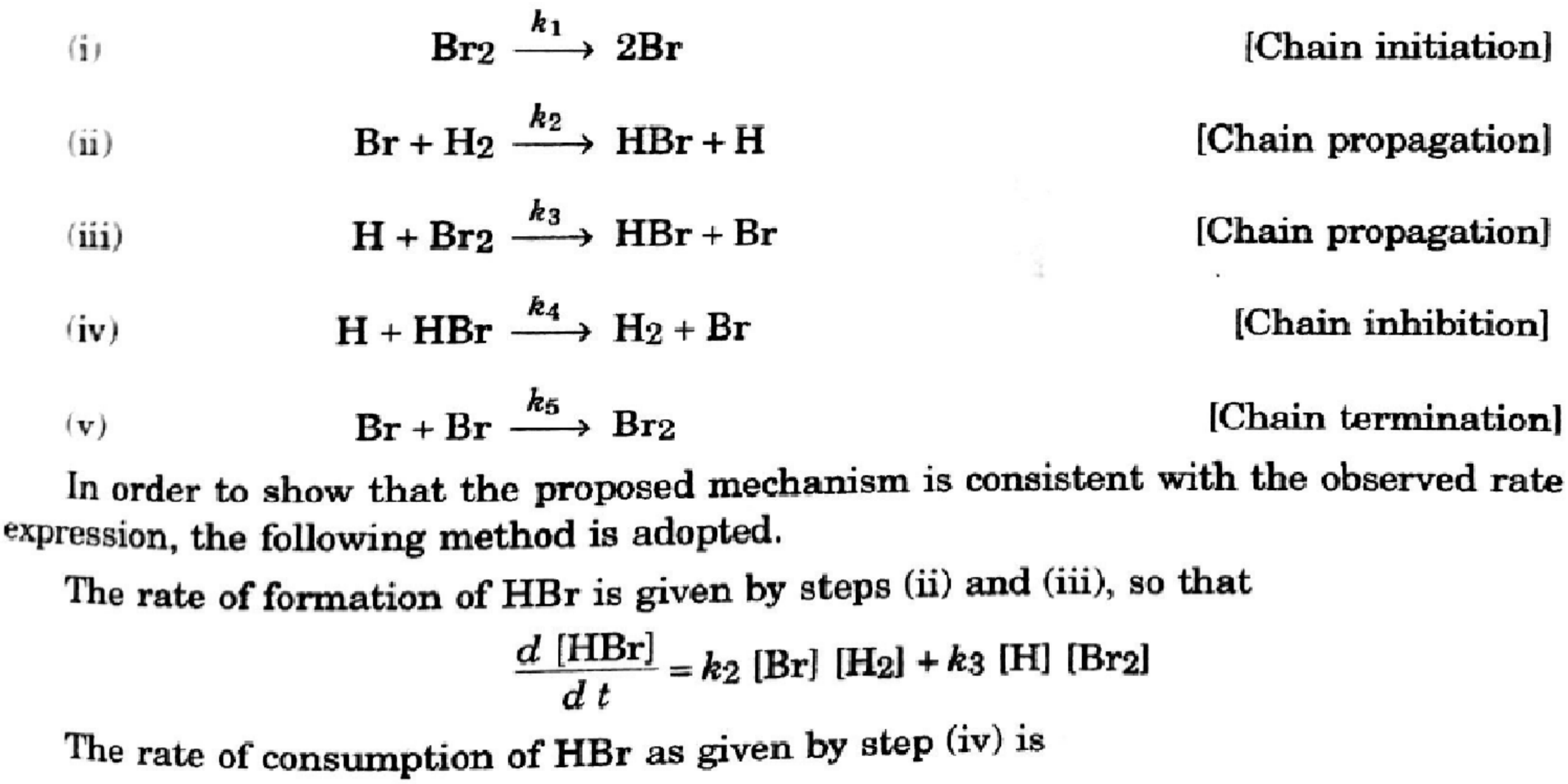
- Bodenstein (1870) after finding the reaction H_2 and I_2 to be bimolecular, also hoped the same for the reaction between H_2 and Br_2. but he found that in contrast to H_2-I_2 reaction, the rate of the latter reaction is given by the empirical equation:



$$\frac{d[\mathrm{HBr}]}{dt} = \frac{k\,[\mathrm{H_2}]\,[\mathrm{Br_2}]^{1/2}}{1 + k'\dfrac{[\mathrm{HBr}]}{[\mathrm{Br_2}]}} \qquad \text{...(1)}$$

where k and k' have their usual significance.

- Christiansen, Herzfeld and Polanyi (1920) proposed the following complex mechanism. The essence of the Mechanism is the proposal that reaction is initiated by the dissociation of molecular bromine.



(i) $$Br_2 \xrightarrow{k_1} 2Br$$ [Chain initiation]

(ii) $$Br + H_2 \xrightarrow{k_2} HBr + H$$ [Chain propagation]

(iii) $$H + Br_2 \xrightarrow{k_3} HBr + Br$$ [Chain propagation]

(iv) $$H + HBr \xrightarrow{k_4} H_2 + Br$$ [Chain inhibition]

(v) $$Br + Br \xrightarrow{k_5} Br_2$$ [Chain termination]

In order to show that the proposed mechanism is consistent with the observed rate expression, the following method is adopted.

The rate of formation of HBr is given by steps (ii) and (iii), so that

$$\frac{d\,[HBr]}{d\,t} = k_2\,[Br]\,[H_2] + k_3\,[H]\,[Br_2]$$

The rate of consumption of HBr as given by step (iv) is

$$\frac{-d\,[\mathrm{HBr}]}{d\,t} = k_4\,[\mathrm{H}]\,[\mathrm{HBr}]$$

The net rate is given by

$$\frac{d\,[\mathrm{HBr}]}{d\,t} = k_2\,[\mathrm{Br}]\,[\mathrm{H_2}] + k_3\,[\mathrm{H}]\,[\mathrm{Br_2}] - k_4\,[\mathrm{H}]\,[\mathrm{HBr}] \qquad \ldots(2)$$

As the above expression involves concentration of bromine atoms and hydrogen atoms i.e., transitory intermediates, which are present in too small quantities, direct measurements are not possible. This implies that atoms or free radicals are consumed as soon as they are produced. This is known as steady state principle. According to it, the time derivative of atom or ion concentration is taken to be zero. So , for hydrogen and bromine atoms, we get,

$$\frac{d\,[\mathrm{H}]}{d\,t} = k_2\,[\mathrm{H_2}]\,[\mathrm{Br}] - k_3\,[\mathrm{H}]\,[\mathrm{Br_2}] - k_4\,[\mathrm{H}]\,[\mathrm{HBr}] = 0 \qquad \ldots(3)$$

$$\frac{d\,[\mathrm{Br}]}{d\,t} = k_1\,[\mathrm{Br_2}] - k_2\,[\mathrm{H_2}]\,[\mathrm{Br}] + k_3\,[\mathrm{H}]\,[\mathrm{Br_2}] = 0$$

$$+\,k_4\,[\mathrm{H}]\,[\mathrm{HBr}] - 2k_5\,[\mathrm{Br}]^2 = 0 \qquad \ldots(4)$$

From equation (3)

$$k_2\,[\mathrm{H_2}]\,[\mathrm{Br}] = k_3\,[\mathrm{H}]\,[\mathrm{Br_2}] + k_4\,[\mathrm{H}]\,[\mathrm{HBr}] \qquad \ldots(5)$$

From equation (4), we also have,

$$k_2\,[\mathrm{H_2}]\,[\mathrm{Br}] = k_1\,[\mathrm{Br_2}] + k_3\,[\mathrm{H}]\,[\mathrm{Br_2}] + k_4\,[\mathrm{H}]\,[\mathrm{HBr}] - 2k_5\,[\mathrm{Br}]^2 \qquad \ldots(6)$$

From equations (5) and (6), we have

$$k_3\,[\mathrm{H}]\,[\mathrm{Br_2}] + k_4\,[\mathrm{H}]\,[\mathrm{HBr}] = k_1\,[\mathrm{Br_2}] + k_3\,[\mathrm{H}]\,[\mathrm{Br_2}] + k_4\,[\mathrm{H}]\,[\mathrm{HBr}] - 2k_5\,[\mathrm{Br}]^2$$

or

$$k_1\,[\mathrm{Br_2}] = k_5\,[\mathrm{Br}]^2$$

or

$$[\mathrm{Br}]^2 = \frac{k_1}{k_5}\,[\mathrm{Br_2}]$$

or

$$[\mathrm{Br}] = \left(\frac{k_1}{k_5}\right)^{1/2} [\mathrm{Br_2}]^{1/2} \qquad \ldots(7)$$

Substituting the value of [Br] from equation (7) in (3), we get

or $$k_2 \cdot \left(\frac{k_1}{k_5}\right)^{1/2} [Br_2]^{1/2}[H_2] - k_3 [H] [Br_2] - k_4 [H] [HBr] = 0$$

or $$\{k_3 [Br_2] + k_4 [HBr]\} [H] = k_2 \left(\frac{k_1}{k_5}\right)^{1/2} [Br_2]^{1/2} [H_2]$$

$$[H] = \frac{k_2 \left(\frac{k_1}{k_5}\right)^{1/2} [Br_2]^{1/2} [H_2]}{k_3 [Br_2] + k_4 [HBr]} \qquad \ldots(8)$$

Substituting the values of [H] and [Br] from equations (8) and (7) in equation (3), we get the rate expression for formation of hydrogen bromide. This is given by,

$$\frac{d\,[HBr]}{d\,t} = k_2 \cdot \left(\frac{k_1}{k_5}\right)^{1/2} [Br_2]^{1/2} [H_2] + k_3 \cdot \frac{k_2 \left(\frac{k_1}{k_5}\right)^{1/2} [Br_2]^{1/2} [H_2]}{k_3 [Br_2] + k_4 [HBr]} \cdot [Br_2]$$

$$- k_4 \cdot \frac{k_2 \left(\frac{k_1}{k_5}\right)^{1/2} [Br_2]^{1/2} [H_2]}{k_3 [Br_2] + k_4 [HBr]} \cdot [HBr]$$

$$= k_2 \left(\frac{k_1}{k_5}\right)^{1/2} [\mathrm{Br}_2]^{1/2} [\mathrm{H}_2] \left\{1 + \frac{k_3 \,.\, [\mathrm{Br}_2]}{k_3 [\mathrm{Br}_2] + k_4 [\mathrm{HBr}]} - \frac{k_4 \,.\, [\mathrm{HBr}]}{k_3 [\mathrm{Br}_2] + k_4 [\mathrm{HBr}]}\right\}$$

$$= k_2 \,.\, \left(\frac{k_1}{k_5}\right)^{1/2} .\, [\mathrm{Br}_2]^{1/2} [\mathrm{H}_2] \left\{\frac{k_3 \,.\, [\mathrm{Br}_2] + k_4 [\mathrm{HBr}] + k_3 \,.\, [\mathrm{Br}_2] - k_4 [\mathrm{HBr}]}{k_3 [\mathrm{Br}_2] + k_4 [\mathrm{HBr}]}\right\}$$

$$= k_2 \,.\, \left(\frac{k_1}{k_5}\right)^{1/2} .\, [\mathrm{Br}_2]^{1/2} [\mathrm{H}_2] \,.\, \left\{\frac{2k_3 \,.\, [\mathrm{Br}_2]}{k_3 [\mathrm{Br}_2] + k_4 [\mathrm{HBr}]}\right\}$$

$$\frac{d\,[\mathrm{HBr}]}{d\,t} = \frac{2k_2 \,.\, \left(\frac{k_1}{k_5}\right)^{1/2} [\mathrm{Br}_2]^{1/2} [\mathrm{H}_2]}{\frac{k_3 [\mathrm{Br}_2]}{k_3 [\mathrm{Br}_2]} + \frac{k_4 [\mathrm{HBr}]}{k_3 [\mathrm{Br}_2]}}$$

or
$$\frac{d\,[\mathrm{HBr}]}{d\,t} = \frac{2k_2 \,.\, \left(\frac{k_1}{k_5}\right)^{1/2} [\mathrm{Br}_2]^{1/2} [\mathrm{H}_2]}{1 + \frac{k_4}{k_3} \cdot \frac{[\mathrm{HBr}]}{[\mathrm{Br}_2]}}$$

or
$$\frac{d\,[\mathrm{HBr}]}{d\,t} = \frac{k\,[\mathrm{H}_2]\,[\mathrm{Br}_2]^{1/2}}{1 + k' \,.\, \frac{[\mathrm{HBr}]}{[\mathrm{Br}_2]}} \qquad \dots (9)$$

where $k = 2\,k_2\,(k_1/k_5)^{1/2}$ and $k' = k_4/k_3$.

Expression (9) is identical with the empirical equation (1) given by Bodenstein.

The chain length is defined as,

$$\text{Chain length} = \frac{\text{Rate of the overall reaction}}{\text{Rate of the initiation reaction}}$$

$$= \frac{2k_2 \cdot \left(\dfrac{k_1}{k_5}\right)^{1/2} [\mathrm{Br_2}]^{1/2}\,[\mathrm{H_2}]}{1 + \dfrac{k_4\,[\mathrm{HBr}]}{k_3\,[\mathrm{Br_2}]}} \times \frac{1}{k_1\,[\mathrm{Br_2}]}$$

$$= \frac{2k_2 \cdot \left(\frac{k_1}{k_5}\right)^{1/2} \cdot [\mathrm{H_2}]}{k_1 \left\{1 + \frac{k_4\,[\mathrm{HBr}]}{k_3\,[\mathrm{Br_2}]}\right\} [\mathrm{Br_2}]^{1/2}}$$

The equilibrium constant, K_{eq} for dissociation of bromine is given by k_1/k_5.

Also, $$\frac{d \log K_{eq}}{d\,T} = \frac{\Delta E}{RT^2} = \frac{d \log (k_1/k_5)}{d\,T} = \frac{E_a\,(i) - E_a\,(\mathrm{v})}{RT^2}$$

The activation energy difference is given by comparison with equation (9), as

$$E_a\,(i) - E_a\,(\mathrm{v}) = \Delta E = 45{,}200 \text{ cal/mole}$$

This value is known both from equilibrium and spectroscopic data.

Reaction Kinetics of Pyrolysis of Acetaldehyde

- In order for the overall kinetics to be of the three halves order, for a first order initiation reaction, the chain terminating step must be a second order reaction between two radicals that undergoes second order propagation reactions. As an example may be considered the mechanism originally proposed by Rice and Herzfeld for the thermal decomposition of Acetaldehyde.

$$CH_3CHO \xrightarrow{k_1} CH_3 + CHO$$

$$CH_3 + CH_3CHO \xrightarrow{k_2} CH_4 + CH_3CO$$

$$CH_3CO \xrightarrow{k_3} CH_3 + CO$$

$$2CH_3 \xrightarrow{k_4} C_2H_6$$

The radical CHO also undergoes further reactions, and for the sake of simplicity they will be ignored here.

The steady state equations are now, for the methyl radicals,

$$k_1 [CH_3CHO] - k_2 [CH_3] [CH_3CHO] + k_3 [CH_3CO] - k_4 [CH_3]^2 = 0 \qquad \ldots (1)$$

and, for the CH_3CO radicals,

$$k_2 [CH_3] [CH_3CHO] - k_3 [CH_3CO] = 0 \qquad \ldots (2)$$

Addition of these equations gives rise to

$$[CH_3] = \left(\frac{k_1}{k_4}\right)^{1/2} [CH_3CHO]^{1/2} \qquad \ldots (3)$$

The rate of formation of methane is

$$\frac{d\,[CH_4]}{dt} = k_2 [CH_3] [CH_3CHO] \qquad \ldots (4)$$

$$= k_2 \left(\frac{k_1}{k_4} \right)^{1/2} [\mathrm{CH_3CHO}]^{3/2} \quad \text{... (5)}$$

The mechanism thus correctly explains the three-halves order. The overall activation energy is now

$$E = E_2 + \frac{1}{2} (E_1 - E_4) \quad \text{... (6)}$$

and this is again usually much less than E_1, since E_2 is very small as compared to E_1. The chain length is now given by,

$$\text{Chain length} = k_2 \left(\frac{1}{k_1 k_4} \right)^{1/2} [\mathrm{CH_3CHO}]^{1/2} \quad \text{... (7)}$$

and depends on the concentration of reactant.

Reaction Kinetics of Decomposition of Ethane

- An example of reaction showing first order overall kinetics is the decomposition of ethane into ethylene and hydrogen. If the initiation reaction is taken to be first order it is necessary to assume, in order to explain the overall order of unity, that the chain ending step is a reaction between a hydrogen atom and an ethyl radical. The Complete scheme is then-

(i) $C_2H_6 \xrightarrow{k_1} 2CH_3$ (Chain initiation)

(ii) $CH_3 + C_2H_6 \xrightarrow{k_2} CH_4 + C_2H_5$ (Chain transfer)

(iii) $C_2H_5 \xrightarrow{k_3} C_2H_4 + H$ (Chain propagation)

(iv) $H + C_2H_6 \xrightarrow{k_4} H_2 + C_2H_5$ (Chain propagation)

(v) $H + C_2H_5 \xrightarrow{k_5} C_2H_6$ (Chain termination)

The steady state equations for this reaction scheme are, for the methyl radicals,

$$2k_1 [C_2H_6] - k_2 [CH_3] [C_2H_6] = 0 \qquad \dots (1)$$

for the ethyl radicals,

$$k_2 [CH_3] [C_2H_6] - k_3 [C_2H_5] + k_4 [H] [C_2H_6] - k_5 [H] [C_2H_5] = 0 \qquad \dots (2)$$

and for hydrogen atoms,

$$k_3 [C_2H_5] - k_4 [H] [C_2H_6] - k_5 [H] [C_2H_5] = 0 \qquad \dots (3)$$

Addition of equations (1), (2) and (3) leads to

$$[H] = \frac{k_1\,[C_2H_6]}{k_5\,[C_2H_5]} \qquad \ldots (4)$$

Insertion of this in equation (3) gives, after rearrangement,

$$k_3k_5\,[C_2H_5]^2 - k_1k_5\,[C_2H_6]\,[C_2H_5] - k_1k_4\,[C_2H_6]^2 = 0 \qquad \ldots (5)$$

The general solution of this quadratic equation is

$$\text{Rate} = \left\{ \frac{k_1}{2k_3} + \left[\left(\frac{k_1}{2k_3} \right)^2 + \frac{k_1k_4}{k_3k_5} \right]^{1/2} \right\} [C_2H_6] \qquad \ldots (6)$$

The constant k_1 is very small, since the initiating reaction has a very high activation energy; the terms involving $k_1/2k_3$ are, therefore, very small in comparison to k_1k_4/k_3k_5 (which appears as the square root), and, therefore,

$$[C_2H_5] = \left(\frac{k_1k_4}{k_3k_5}\right)^{1/2} [C_2H_6] \qquad \ldots (7)$$

The rate of production of ethylene is

$$\frac{d\,[C_2H_4]}{dt} = k_3\,[C_2H_5] \qquad \ldots (8)$$

$$= \left(\frac{k_1k_3k_4}{k_5}\right)^{1/2} [C_2H_6] \qquad \ldots (9)$$

The reaction is thus of the first order. If the activation energies for reactions (i), (iii), (iv) and (v) are E_1, E_3, E_4, and E_5, and the corresponding frequency factors are A_1, A_3, A_4, and A_5, equation (9) may be written as

$$\frac{d\,[C_2H_4]}{dt} = \left(\frac{A_1\,e^{-E_1/RT}\,A_3\,e^{-E_2/RT}\,A_4\,e^{-E_4/RT}}{A_5\,e^{-E_5/RT}}\right)^{1/2} [C_2H_6] \qquad \ldots (10)$$

$$\frac{d\,[C_2H_4]}{dt} = \left(\frac{A_1\,A_3\,A_4}{A_5}\right)^{1/2} \exp\left[-\frac{E_1 + E_3 + E_4 - E_5}{2RT}\right] [C_2H_6] \qquad \ldots (11)$$

The activation energy for the overall reaction is, therefore,

$$E = \frac{1}{2}(E_1 + E_3 + E_4 - E_5) \qquad \text{... (12)}$$

Since E_1 is usually very much larger than E_3 and E_4, the overall activation energy is usually appreciably smaller than E_1. The ***chain length*** of a reaction is defined as the rate of the overall reaction divided by the rate of the initiation reaction. In this case

$$\text{Chain length} = \frac{\left(\dfrac{k_1 k_3 k_4}{k_5}\right)^{1/2} [C_2H_6]}{k_1 [C_2H_6]} \qquad \text{... (13)}$$

$$= \left(\frac{k_3 k_4}{k_1 k_5}\right)^{1/2} \qquad \text{... (14)}$$

Since k_1 is very small, this quantity is frequently very large. It represents the average amount of reactant transformed each time the initiating step occurs.

Reaction Kinetics of Photochemical Hydrogen-Bromine Reaction

- The photochemical combination of H_2 and Br_2 resembles with the thermal reaction. It means that the secondary chemical stages obey the laws of kinetics. The first stage of the reaction is the dissociation of bromine, brought about by light in the continuous region of the bromine spectrum as:

(i) $$Br_2 + h\nu \xrightarrow{k_1} 2Br$$ [Chain initiation]

The other steps are the same as in thermal reaction *viz.*,

(ii) $$Br + H_2 \xrightarrow{k_2} HBr + H$$ [Chain propagation]

(iii) $$Br_2 + H \xrightarrow{k_3} HBr + Br$$ [Chain propagation]

(iv) $$H + HBr \xrightarrow{k_4} H_2 + Br$$ [Chain inhibition]

(v) $$Br + Br \xrightarrow{k_5} Br_2$$ [Chain breaking]

The net rate of formation HBr may be represented as,

$$\frac{d\,[HBr]}{d\,t} = k_2\,[Br]\,[H_2] + k_3\,[H]\,[Br_2] - k_4\,[H]\,[HBr] \qquad \ldots(1)$$

The net rate of formation of bromine atoms is given by,

$$\frac{d\,[Br]}{d\,t} = k_1\,I_{abs} + k_3\,[H]\,[Br_2] + k_4\,[H]\,[HBr] - k_2\,[Br]\,[H_2] - k_5\,[Br]^2$$

According to steady state principle, $\frac{d\,[\mathrm{Br}]}{d\,t} = 0$

$\therefore$ $$k_1 I_{abs} + k_3\,[\mathrm{H}]\,[\mathrm{Br_2}] + k_4\,[\mathrm{H}]\,[\mathrm{HBr}] = k_2\,[\mathrm{Br}]\,[\mathrm{H_2}] + k_5\,[\mathrm{Br}]^2 \quad \ldots(2)$$

The net rate of formation of hydrogen atoms is given by,

$$\frac{d\,[\mathrm{H}]}{d\,t} = k_2\,[\mathrm{Br}]\,[\mathrm{H_2}] - k_3\,[\mathrm{H}]\,[\mathrm{Br_2}] - k_4\,[\mathrm{H}]\,[\mathrm{HBr}]$$

According to steady state principle, $\frac{d\,[\mathrm{H}]}{d\,t} = 0$

$\therefore$ $$k_2\,[\mathrm{Br}]\,[\mathrm{H_2}] = k_3\,[\mathrm{H}]\,[\mathrm{Br_2}] + k_4\,[\mathrm{H}]\,[\mathrm{HBr}] \quad \ldots(3)$$

Combining equations (2) and (3),

$$k_1 I_{abs} = k_5\,[\mathrm{Br}]^2$$

or $$[\mathrm{Br}] = \left(\frac{k_1}{k_5}\right)^{1/2} .\, I_{abs}^{1/2} \quad \ldots(4)$$

Substituting the value of [Br] in equation (3),

$$k_2\left(\frac{k_1}{k_5}\right)^{1/2} . I_{abs}^{1/2} . [\mathrm{H_2}] = k_3\,[\mathrm{H}]\,[\mathrm{Br_2}] + k_4\,[\mathrm{H}]\,[\mathrm{HBr}]$$

$$= [\mathrm{H}]\,\{k_3\,[\mathrm{Br_2}] + k_4\,[\mathrm{HBr}]\}$$

$$[\mathrm{H}] = \frac{k_2\left(\dfrac{k_1}{k_5}\right)^{1/2} . I_{abs}^{1/2}\,[\mathrm{H_2}]}{k_3\,[\mathrm{Br_2}] + k_4\,[\mathrm{HBr}]} \qquad \ldots(5)$$

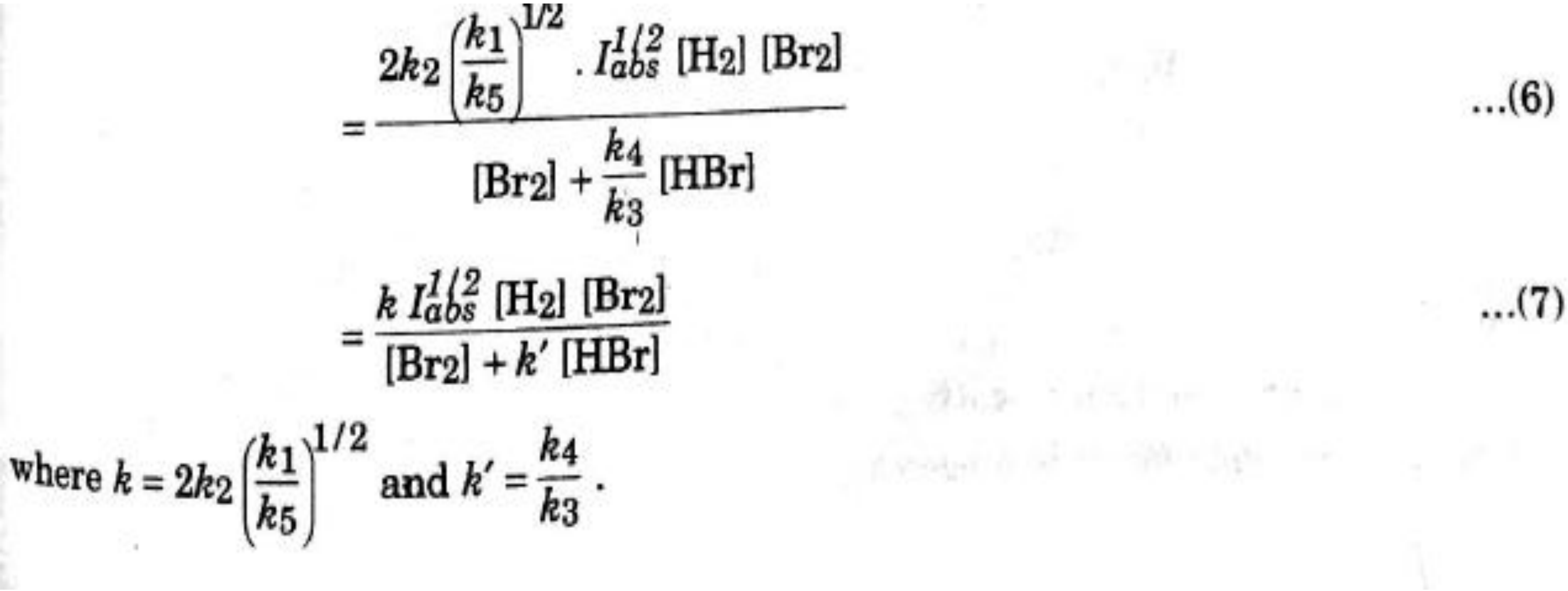
Substituting the values of [H] and [Br] in equation (1),

$$\frac{d\,[\mathrm{HBr}]}{d\,t} = k_2\left(\frac{k_1}{k_5}\right)^{1/2} . I_{abs}^{1/2} . [\mathrm{H_2}] + \frac{k_2\left(\dfrac{k_1}{k_5}\right)^{1/2} . I_{abs}^{1/2}\,[\mathrm{H_2}]}{k_3\,[\mathrm{Br_2}] + k_4\,[\mathrm{HBr}]}\,\{k_3\,[\mathrm{Br_2}] - k_4\,[\mathrm{HBr}]\}$$

$$= k_2\left(\frac{k_1}{k_5}\right)^{1/2} . I_{abs}^{1/2}\,[\mathrm{H_2}]\left\{1 + \frac{k_3\,[\mathrm{Br_2}] - k_4\,[\mathrm{HBr}]}{k_3\,[\mathrm{Br_2}] + k_4\,[\mathrm{HBr}]}\right\}$$

$$= k_2\left(\frac{k_1}{k_5}\right)^{1/2} . I_{abs}^{1/2}\,[\mathrm{H_2}]\left\{\frac{k_3\,[\mathrm{Br_2}] + k_4\,[\mathrm{HBr}] + k_3\,[\mathrm{Br_2}] - k_4\,[\mathrm{HBr}]}{k_3\,[\mathrm{Br_2}] + k_4\,[\mathrm{HBr}]}\right\}$$

$$= \frac{2k_2k_3\left(\dfrac{k_1}{k_5}\right)^{1/2} . I_{abs}^{1/2}\,[\mathrm{H_2}]\,[\mathrm{Br_2}]}{k_3\,[\mathrm{Br_2}] + k_4\,[\mathrm{HBr}]}$$



$$= \frac{2k_2 \left(\frac{k_1}{k_5}\right)^{1/2} . I_{abs}^{1/2} [H_2] [Br_2]}{[Br_2] + \frac{k_4}{k_3} [HBr]} \qquad \ldots(6)$$

$$= \frac{k\, I_{abs}^{1/2} [H_2] [Br_2]}{[Br_2] + k' [HBr]} \qquad \ldots(7)$$

where $k = 2k_2 \left(\frac{k_1}{k_5}\right)^{1/2}$ and $k' = \frac{k_4}{k_3}$.

Equations (6) and (7) agree well with the experimental data of bodenstein (1923). From equation (7), it is clear that the rate of reaction is directly proportional to the square root of light intensity. The mechanism assumed for Photochemical combination is tenable only at constant pressure. If the pressure is changed, then the denominator of equation (7) has to be multiplied by the square root of the total pressure.

Reaction Kinetics of Photochemical Hydrogen-Chlorine Reaction

- An interesting but perplexing photochemical process is afforded by the reaction between H_2 and Cl_2. It was observed by Cruickshank (1801) and studied in details by later workers such as Draper (1842), Bunsen and Roscoe (1857), Bodenstein (1916), but Nernst (1918) gave a mechanism for the reaction which is universally accepted.

  According to Nernst, when exposed to light in the continuous region of chlorine spectrum (λ= 4785 Å), chlorine molecule dissociate into atom as:

(i) $Cl_2 + h\nu \xrightarrow{k_1} 2Cl$ [Chain initiation]

The first step is followed by,

(ii) $Cl + H_2 \xrightarrow{k_2} HCl + H$ [Chain propagation]

(iii) $H + Cl_2 \xrightarrow{k_3} HCl + Cl_2$ [Chain propagation]

(iv) $Cl + Cl \xrightarrow[\text{Wall}]{k_4} Cl_2$ [Chain termination]

In the reaction mechanism of $H_2 - Cl_2$ reaction as represented by the above equations, it has been shown that the cycle initiated by formation of chlorine atoms in step (i) is kept going by subsequent steps. The chain may be broken either by the combination of hydrogen and chlorine atoms to form hydrogen and chlorine molecules, respectively or on the walls of the vessel or by the union with some impurity, *viz*, NH_3 or O_2 which act as inhibitors.

The total rate of formation of hydrogen chloride is given by steps (ii) and (iii), and so

$$\frac{d\,[\mathrm{HCl}]}{d\,t} = k_2\,[\mathrm{Cl}]\,[\mathrm{H_2}] + k_3\,[\mathrm{H}]\,[\mathrm{Cl_2}] \qquad \ldots(1)$$

The rate of formation of chlorine atoms is given by steps (i) and (iii), and so

$$\frac{d\,[\mathrm{Cl}]}{d\,t} = k_1\,I_{abs} + k_3\,[\mathrm{H}]\,[\mathrm{Cl_2}] \qquad \ldots(2)$$

where I_{abs} = intensity of radiation.

The rate of removal of chlorine atoms is given by steps (ii) and (iv), and so

$$\frac{-d\,[\mathrm{Cl}]}{d\,t} = k_2\,[\mathrm{Cl}]\,[\mathrm{H_2}] + k_4\,[\mathrm{Cl}]^2$$

The net rate is given by,

$$\frac{d\,[\mathrm{Cl}]}{d\,t} = k_1\,I_{abs} + k_3\,[\mathrm{H}]\,[\mathrm{Cl_2}] - k_2\,[\mathrm{Cl}]\,[\mathrm{H_2}] - k_4\,[\mathrm{Cl}]^2$$

In the stationary state :

$$\frac{d\,[\mathrm{Cl}]}{d\,t} = 0$$

∴
$$k_1 I_{abs} + k_3 [\mathrm{H}] [\mathrm{Cl_2}] - k_2 [\mathrm{Cl}] [\mathrm{H_2}] - k_4 [\mathrm{Cl}]^2 = 0$$

or
$$k_1 I_{abs} + k_3 [\mathrm{H}] [\mathrm{Cl_2}] = k_2 [\mathrm{Cl}] [\mathrm{H_2}] + k_4 [\mathrm{Cl}]^2 \qquad \ldots(3)$$

Similarly, for hydrogen atoms in the stationary state, we have

$$\frac{d [\mathrm{H}]}{d t} = 0 = k_2 [\mathrm{Cl}] [\mathrm{H_2}] - k_3 [\mathrm{H}] [\mathrm{Cl_2}]$$

or
$$k_2 [\mathrm{Cl}] [\mathrm{H_2}] = k_3 [\mathrm{H}] [\mathrm{Cl_2}] \qquad \ldots(4)$$

Substituting the value of $k_2 [\mathrm{Cl}] [\mathrm{H_2}]$ from equation (4) in (3), we get

$$k_1 I_{abs} + k_3 [\mathrm{H}] [\mathrm{Cl_2}] = k_3 [\mathrm{H}] [\mathrm{Cl_2}] + k_4 [\mathrm{Cl}]^2$$

or
$$k_1 I_{abs} = k_4 [\mathrm{Cl}]^2$$

or

$$[\mathrm{Cl}] = \sqrt{\frac{k_1}{k_4}} \, . \, I_{abs}{}^{1/2} \qquad \ldots(5)$$

From equations (1) and (4), we have

$$\frac{d\,[\mathrm{HCl}]}{d\,t} = k_2\,[\mathrm{Cl}]\,[\mathrm{H_2}] + k_2\,[\mathrm{Cl}]\,[\mathrm{H_2}]$$

$$= 2k_2\,[\mathrm{Cl}]\,[\mathrm{H_2}] \qquad \ldots(6)$$

Substituting the value of [Cl] from equation (5) in (6), we get

$$\frac{d\,[\mathrm{HCl}]}{d\,t} = 2k_2 \, . \sqrt{\frac{k_1}{k_4}} \, . \, I_{abs}{}^{1/2}\,[\mathrm{H_2}] \qquad \ldots(7)$$

Expression (7) is in perfect agreement with the experimental data.

The chain length is given by the expression,

$$\text{Chain length} = \frac{\text{Rate of the overall reaction}}{\text{Rate of the initiation reaction}}$$

$$= \frac{2k_2\sqrt{\frac{k_1}{k_4}} \, . \, I_{abs}{}^{1/2}\,[\mathrm{H_2}]}{k_1\,I_{abs}} = \frac{2k_2\,[\mathrm{H_2}]}{\sqrt{k_1 k_4} \, . \, I_{abs}{}^{1/2}}$$

In presence of high chlorine content, step (iv) is replaced by rather complicated steps, *viz.*,

(v) $$Cl + Cl_2 \rightleftharpoons Cl_3$$

(vi) $$2Cl_3 \rightleftharpoons 3Cl_2$$

From steps (v) and (vi) the rate expression as given by (7) becomes very complex.

In presence of oxygen as impurity, steps (i), (ii) and (iii) are followed by

(vii) $$H + O_2 \longrightarrow HO_2$$

which is a chain terminating step.

Some chains are terminated as :

(viii) $$Cl + O_2 + HCl = HO_2 + Cl_2$$

In presence of oxygen, it is assumed that removal of hydrogen atoms determines the kinetics of the reaction to a great extent, but in the absence of oxygen, the chains are supposed to be broken by the removal of chlorine atoms.

From steps (i), (ii), (iii) and (iv), we get

$$\frac{d\,[HCl]}{d\,t} = \frac{k_1 \,.\, I_{abs}\,[Cl_2]}{[O_2]} \qquad ...(8)$$

The rate of reaction in presence of oxygen is directly proportional to the intensity of light radiation. But the inhibiting action of oxygen is approximately proportional to its own concentration as given by equation (8).

Homogeneous Catalysis

- Homogeneous catalysis is catalysis in a solution by a soluble catalyst. Homogeneous catalysis refers to catalytic reactions where the catalyst is in the same phase as the reactants. Homogeneous catalysis applies to reactions in the gas phase and even in solids. Heterogeneous catalysis is the alternative to homogeneous catalysis, where the catalysis occurs at the interface of two phases, typically gas-solid. The term is used almost exclusively to describe solutions and often implies catalysis by organometallic compounds.

Contd.

- Homogeneous catalysis using transition metal complexes is an area of research that has grown enormously in recent years. Many remarkable catalytic discoveries have been reported by researchers both in industry and in academia. The area is one of intense research and many practical applications, e.g., the production of acetic acid.

Kinetics of Homogeneous Catalysis

Many Homogeneous catalysis reactions have been studied in the liquid phase as well as gas phase. The reaction rate in such catalysed reactions are found to be proportional to the concentration of the catalyst.

In the case of catalyst forming an intermediate compound with the reactant, we get the products, when this intermediate compound either gets decomposed or reacts with the remaining reactants. The reactant with which the catalyst combines is known as substrate. The catalyst provides, with lesser energy of activation, an alternative path for the reaction in which the rate is dependent on the concentration of the catalyst. Therefore-

(i) $A + X \underset{k_2}{\overset{k_1}{\rightleftharpoons}} AX;$ (ii) $AX + B \xrightarrow{k_3} P + X$

where, A is substrate, X is catalyst, P is product and AX is the intermediate compound B is another reactant molecule. The reaction (ii) is slow and is the rate determining step.

$$\therefore \qquad \text{Rate of reaction} = k_3\,[AX]\,[B] \qquad \ldots (1)$$

If we use the steady state concept for the intermediate compound AX, then

$$\frac{d\,[AX]}{dt} = k_1\,[A]\,[X] - k_2\,[AX] - k_3\,[AX]\,[B] = 0$$

or

$$k_1\,[A]\,[X] = k_2\,[AX] + k_3\,[AX]\,[B]$$

or

$$[AX] = \frac{k_1\,[A]\,[X]}{k_2 + k_3\,[B]}$$

Substituting this value of [AX] in equation (1), we get

$$\text{Rate of reaction} = \frac{k_1\,k_3\,[A]\,[X]\,[B]}{k_2 + k_3\,[B]} \qquad \ldots (2)$$

(i) If $k_2 << k_3$ [B], then equation (1) becomes

$$\text{Rate of reaction} = \frac{k_1 k_3 [A] [X] [B]}{k_3 [B]} = k_1 [A] [X] \qquad \dots (3)$$

(ii) If $k_2 >> k_3$ [B], then equation (1) becomes

$$\text{Rate of reaction} = k_1 k_3 \frac{[A] [X] [B]}{k_3} \qquad \dots (4)$$

From equations (2) and (3), it follows that the rate of reactions depends on the concentration of catalyst, although is neither consumed nor produced in the reaction.

We will now discuss the mechanisms of the two examples of homogeneous catalysis, viz, acid and base catalysis and the enzyme catalysis

Enzyme Kinetics

- Enzyme Kinetics – Quantitative measurement of the rates of enzyme catalyzed reactions

&

- The systematic study of factors that affect these rates

- Enzyme kinetics began in 1902 when Adrina Brown reported an investigation of the rate of hydrolysis of sucrose as catalyzed by the yeast enzyme inveratase.

- Brown demonstrated – when sucrose concentration is much higher than that of the enzyme, reaction rate becomes independent of sucrose concentration

- Brown proposal – overall reaction is composed of two elementary reactions in which the substrate forms a complex with the enzyme that subsequently decomposes to products and enzymes.

$$E + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ES \xrightarrow{k_2} P + E$$

- Here E, S, ES and P symbolize the enzyme, substrate, enzyme-substrate complex and products

- According to this model
  - When the substrate concentration becomes high enough to entirely convert the enzyme to the ES form, the second step of the reaction becomes rate limiting step.
  - The overall reaction rate becomes insensitive to further increase in substrate concentration.
- The general expression of the **velocity (rate)** of this reaction is

$$v = \frac{d[P]}{dt} = k_2[ES]$$

- The overall rate of production of [ES] – Difference between the rates of elementary reactions leading to its appearance and those resulting in its disappearance.

$$E+S \underset{K_{-1}}{\overset{K_1}{\rightleftarrows}} ES \xrightarrow{k\ 2} P+E$$

$$\frac{d[ES]}{dt} = k_1[E][S] - k_{-1}[ES] - k_2[ES]$$

- At this point, an assumption is required to achieve an analytical solution.
- The rapid equilibrium assumption
  •Michaelis - Menten Approach. The
- Steady-state assumption.
  - Briggs and Haldane Approach.

Michaelis - Menten Approach

The rapid equilibrium assumption:

- Assumes a rapid equilibrium between the enzyme and substrate to form an [ES] complex.

$$E+S \underset{K_{-1}}{\overset{K_1}{\rightleftarrows}} ES \xrightarrow{k_2} P+E$$

- $k_1[E][S] = k_{-1}[ES]$

- The equilibrium constant K_m can be expressed by the following equation in a dilute system.

$$K_m = \frac{k_{-1}}{k_1} = \frac{[E][S]}{[ES]}$$

Contd.

- Since the enzyme is not consumed, the conservation equation on the enzyme yields

$$[E] = [E_0] - [ES]$$

- Then rearrange the equilibrium constant equation

$$K_m = \frac{k_{-1}}{k_1} = \frac{[E][S]}{[ES]} \qquad [ES] == \frac{[E][S]}{K_m}$$

- Substituting [E] in the above equation with enzyme mass conservation equation

$$[ES] == \frac{([E_0] - [ES])[S]}{K_m}$$

Contd.

$$[ES] == \frac{([E_0]-[ES])[S]}{K_m}$$

$$[ES]K_m == [E_0][S]-[ES][S]$$

$$[ES]K_m+[ES][S] == [E_0][S]$$

$$[ES](K_m+[S]) == [E_0][S]$$

$$[ES] == \frac{[E_0][S]}{K_m+[S]}$$

Contd.

- Then the rate of production formation v can be expressed in terms of [S]

$$v = \frac{d[P]}{dt} = k_2[ES] = \frac{k_2[E_0][S]}{K_m + [S]} = \frac{V_{max}[S]}{K_m + [S]}$$

- Where $V_{max} = k_2[E_0]$

kinetics of fast reaction

Fast Reaction

- Reaction which go to equilibrium in a few seconds are known as fast reactions.
- This reaction even proceed in less time can not be kinetically studied by conventional methods.
- The reasons for inability are as follows-

A] The time it takes to make a measurement of concentration may be significant as compared to its half-life.

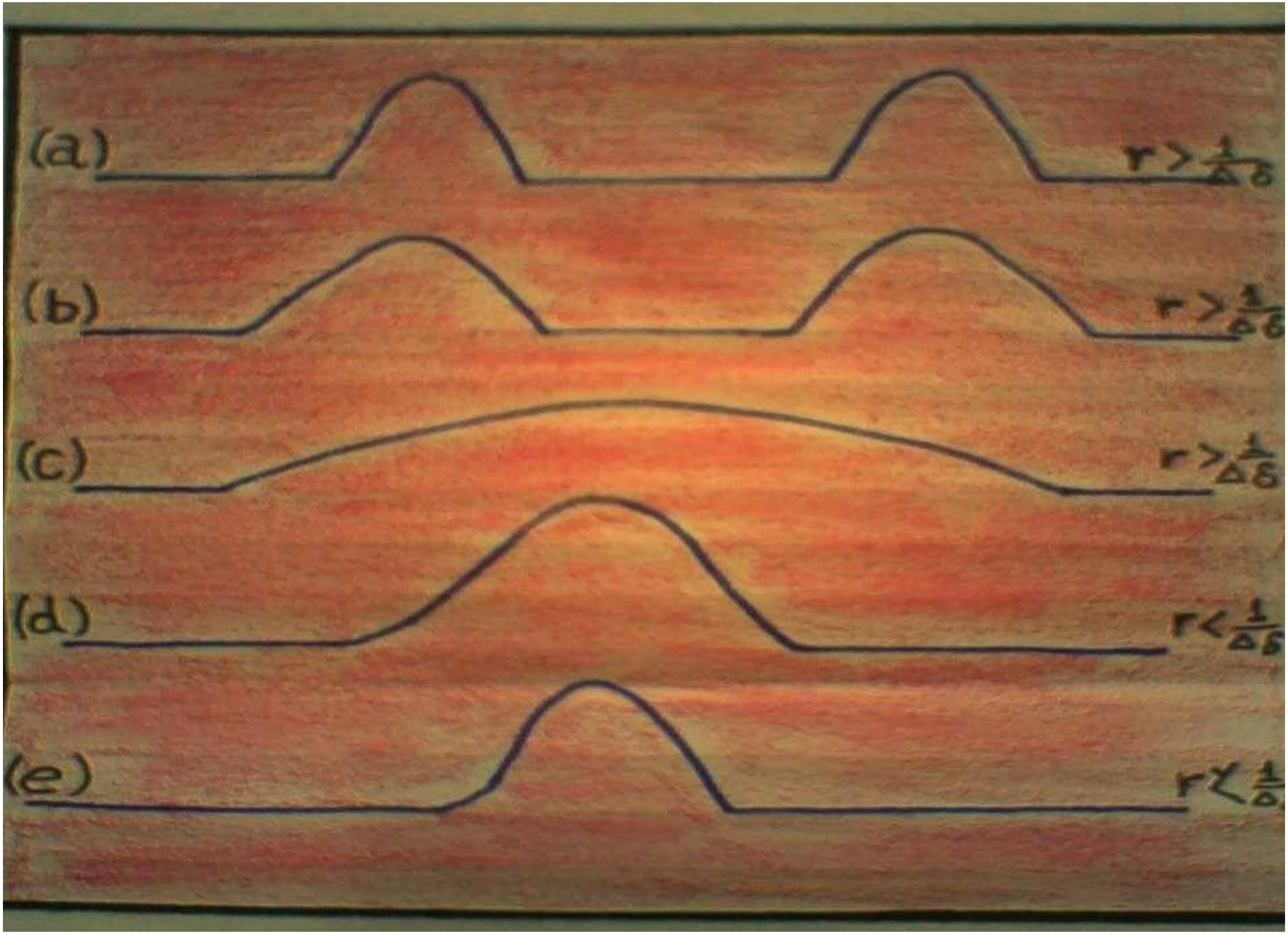
Contd.

B] The time it takes to mix reactants or to bring them to a desired temp may be significant as compared to the half-life of the reaction. An appreciable error creeps in because the initial time cannot be accurately determined.

Nuclear Magnetic Resonance

- Kinetic data on reactions in solution are obtained by NMR methods.

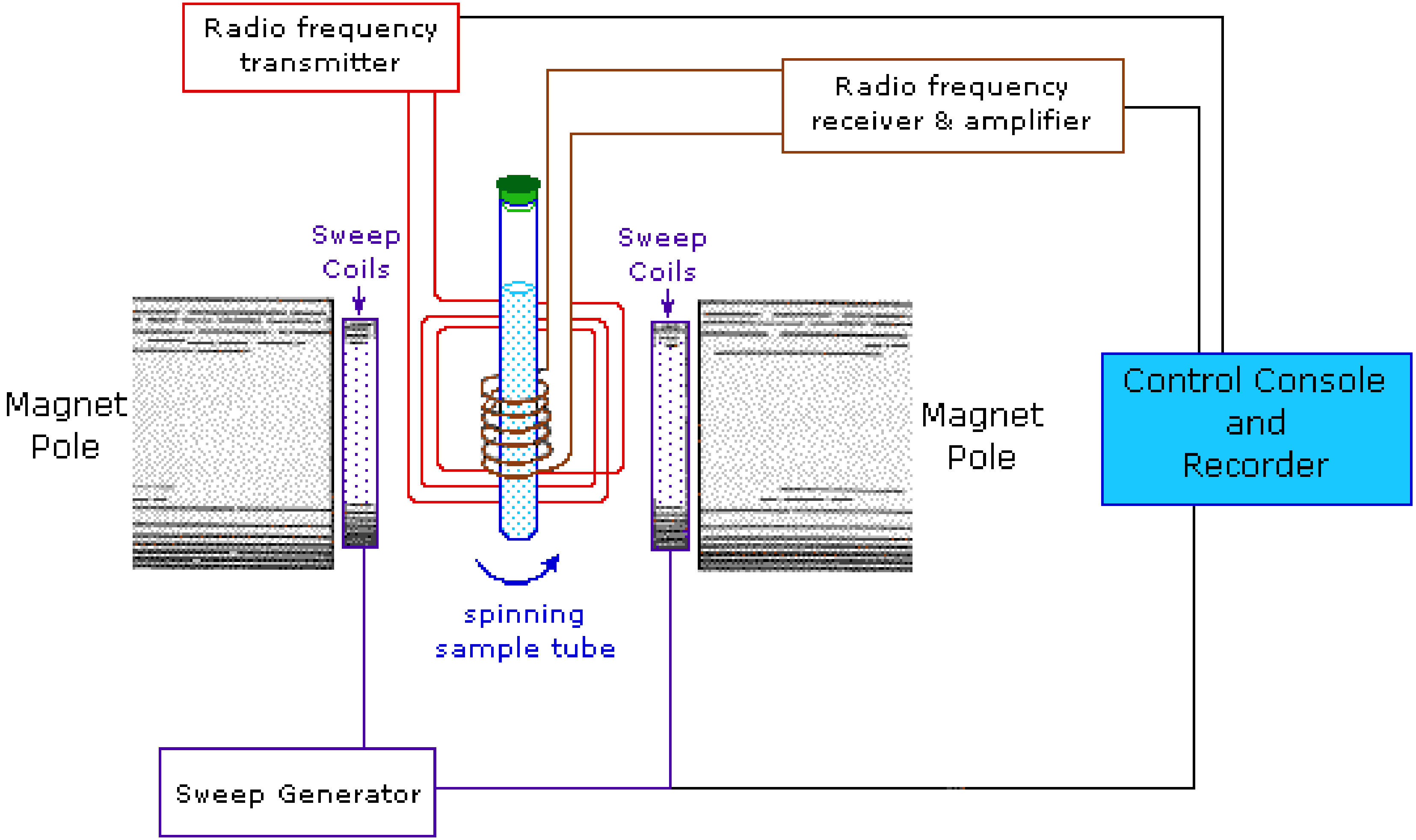
  This method is based on the fact that when two compounds with different NMR chemical shifts change rapidly from one to another, their two NMR peaks merge into one.


(a)
$r > \frac{1}{\Delta\delta}$
(b)
$r > \frac{1}{\Delta\delta}$
(c)
$r > \frac{1}{\Delta\delta}$
(d)
$r < \frac{1}{\Delta\delta}$
(e)
$r < \frac{1}{\Delta}$

- The NMR method is a relaxation method in which the systems studied are usually close to equilibrium, and those molecules which are excited by the absorption of radiation lose their excess energy rather quickly due to collisions.

- With relaxation methods, the rate constants of second order reactions with numerical values appreciably above $\Delta\delta$ may be studied when the concentrations of reactants are substantially below 1 M.

NMR spectrophotometer



Flow Method

- Flow method is also known as “mix and shake” method in which the reactants are mixed within a fraction of a second.

- It was first developed by “ROUGHTON and HASTRIDGE” ,are used to measure the reaction half-time in the range from 1/10 sec to 1/1000 sec.

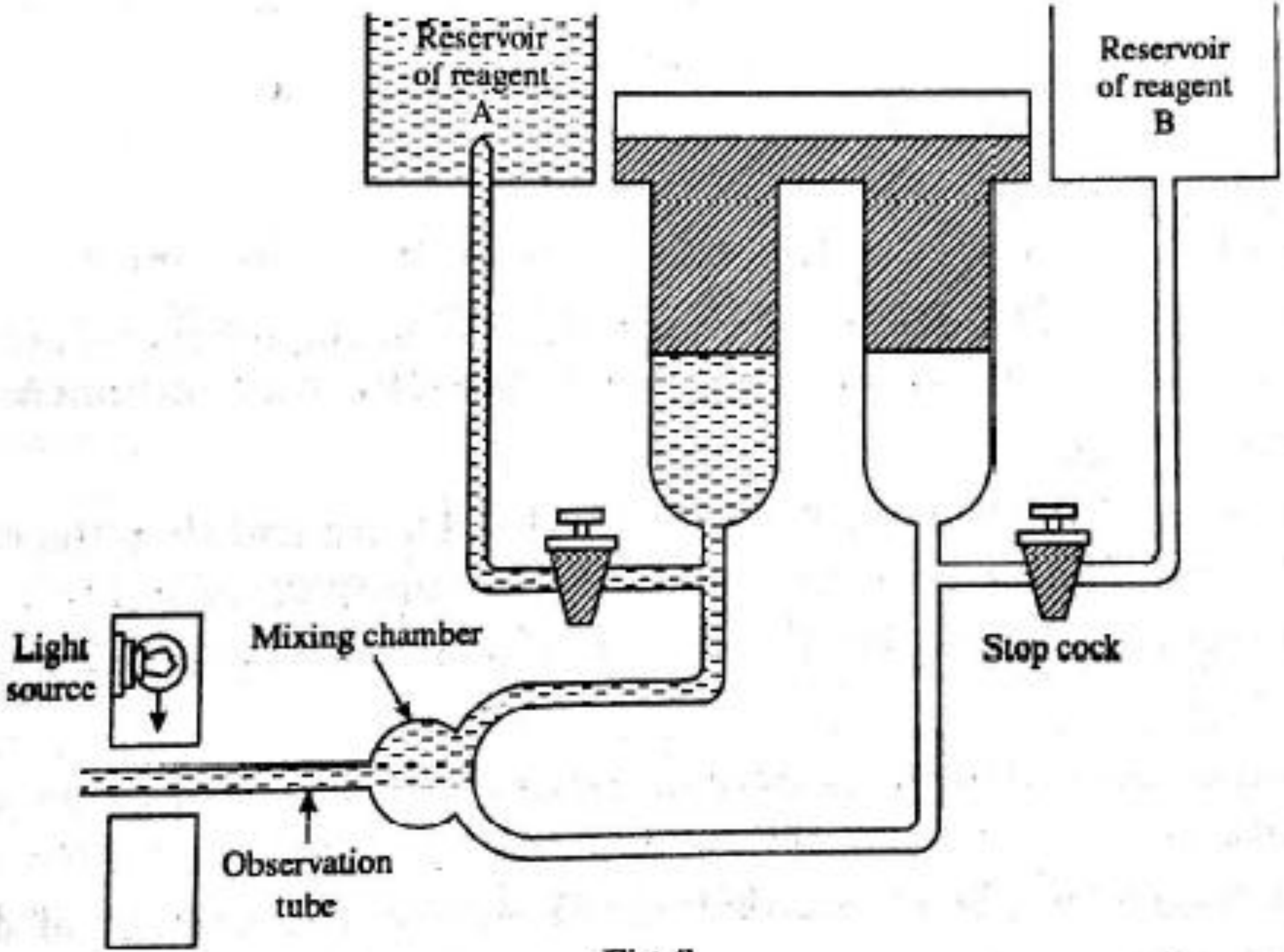

Reservoir of reagent A
Reservoir of reagent B
Light source
Mixing chamber
Stop cock
Observation tube

Fig. 2

- With flow of completely mixed solution at a constant rate , reaction occurs at a certain extent at a position along the observation tube.

This condition exist because each position along the observation tube corresponds for a particular flow rate to the lapse of some definite time interval after mixing.

- Measurement of light absorption may be used conveniently in this type of experiment to determine the extent of reaction if the absorption spectrum of the product differs from that of the reactant.

If experiments are done with different rate of flow , value of light absorption at anyone particular point will give results from which a plot of extent of reaction against time can be prepared.

- The first reaction studied by this method was the reaction between Fe^{3+} and CNS^{-1} in aqueous solution. It rate law may be expressed as:

- $\text{RATE} = k\,[Fe^{3+}][CNS^{-]}]\,[\,\mathbf{1+a/H^{+]}]}$

where k denotes the order rate constant, and a is an empirical constant which gets related to the dependence of reaction rate on pH.

Flash Photolysis Method

- It was first used by “PORTER”.
- This method has been used for the study of reactions in solution as well as those in gaseous phase.
- PHOTOCHEMICAL DISSOSIATION OF IODINE-If iodine vapour is illuminated with light of suitable wavelength , the dissociation occurs .

$$I_2 + hv \rightarrow 2\ I$$

- Non-photochemical Recombination of Iodine Atom-

$$2I \rightarrow I_2$$

- Under steady illumination with light of moderate intensity , steady state is reached with only a very small fraction of iodine dissociated into atoms.

- This steady state is obtained when the rate of photochemical dissociation of iodine molecules and non-photochemical recombination of iodine atoms equals each other.

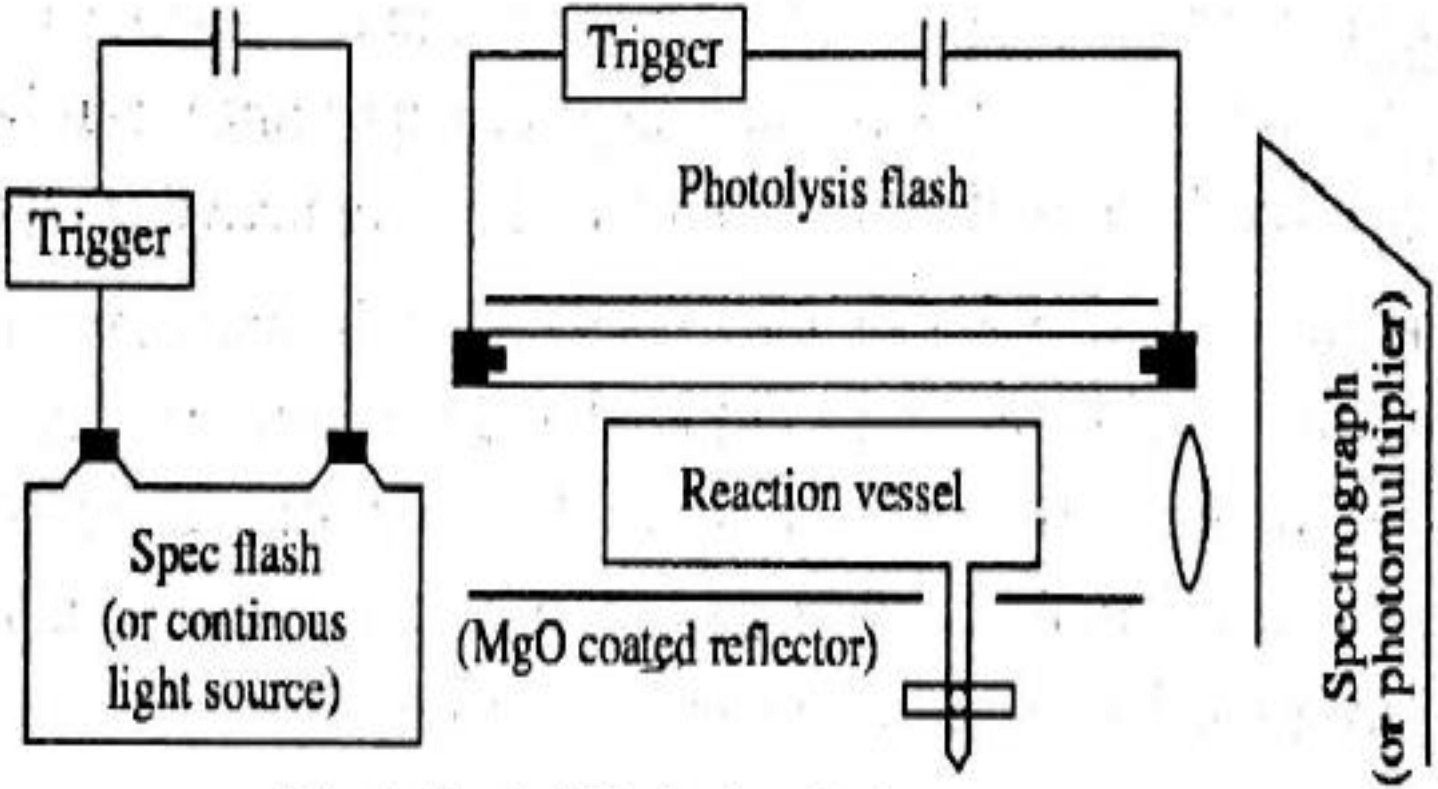


Fig. 5. Typical flash photolysis apparatus.

- In actual experiments , the peak intensity of a flash may build up in 10^{-5}sec and their decay over a period of 4×10^{-4} sec or even less.

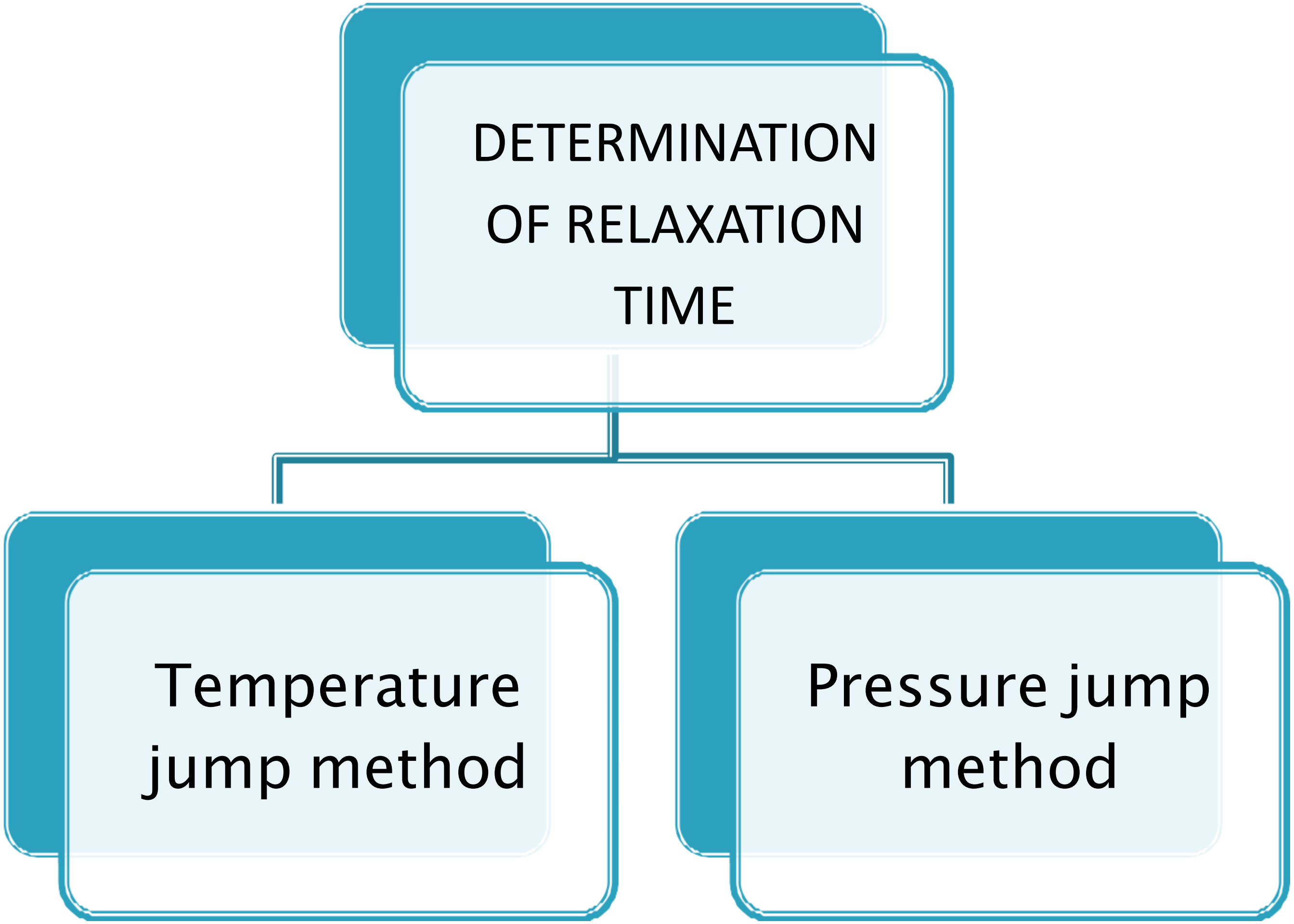
- After the decay of light intensity from the flash , light of law intensity can be used in a spectrophotometric arrangement to follow the increase in concentration of molecular iodine.

Chemical Relaxation Method

- In all relaxation method, a chemical equilibrium is perturbed by a rapid change in one of several possible external parameters, like electric field intensity , temperature and pressure.

- The equilibrium process is then followed by spectrophotometric or conductophotometric method.

Determination of Relaxation Time



DETERMINATION OF RELAXATION TIME

Temperature jump method

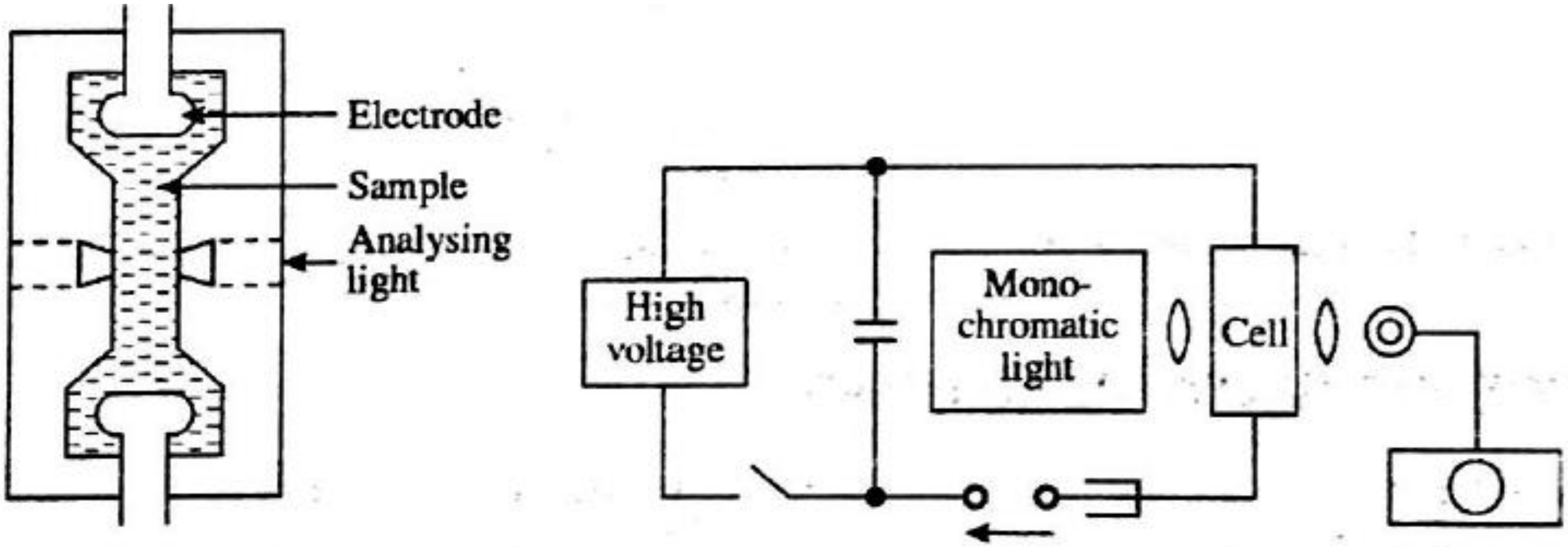
Pressure jump method

Temperature Jump Method

- A temperature change of several degrees [10^0c] in [10^{-5}s] ,is created by a discharge of high voltage condenser through a small quantity of solution . Then the time dependence of concentrations is followed by the adsorption spectroscopy.

- A temperature range of 1degree centigrade has been found to change the equilibrium concentration by about 3%.

Apparatus



(a) Temperature-jump cell.

(b) Schematic diagram of temperature-jump method which uses electrical discharge for heating solution.

Fig. 8

Pressure Jump Method

- It involves a sudden and rapid change of pressure to displace the equilibrium.
- The sensitivity of a reaction to pressure depends on the change in volume ΔV and is represented quantitatively by the equation

$$[\partial \ln K/\partial P]_T = -\Delta v/RT$$

Apparatus

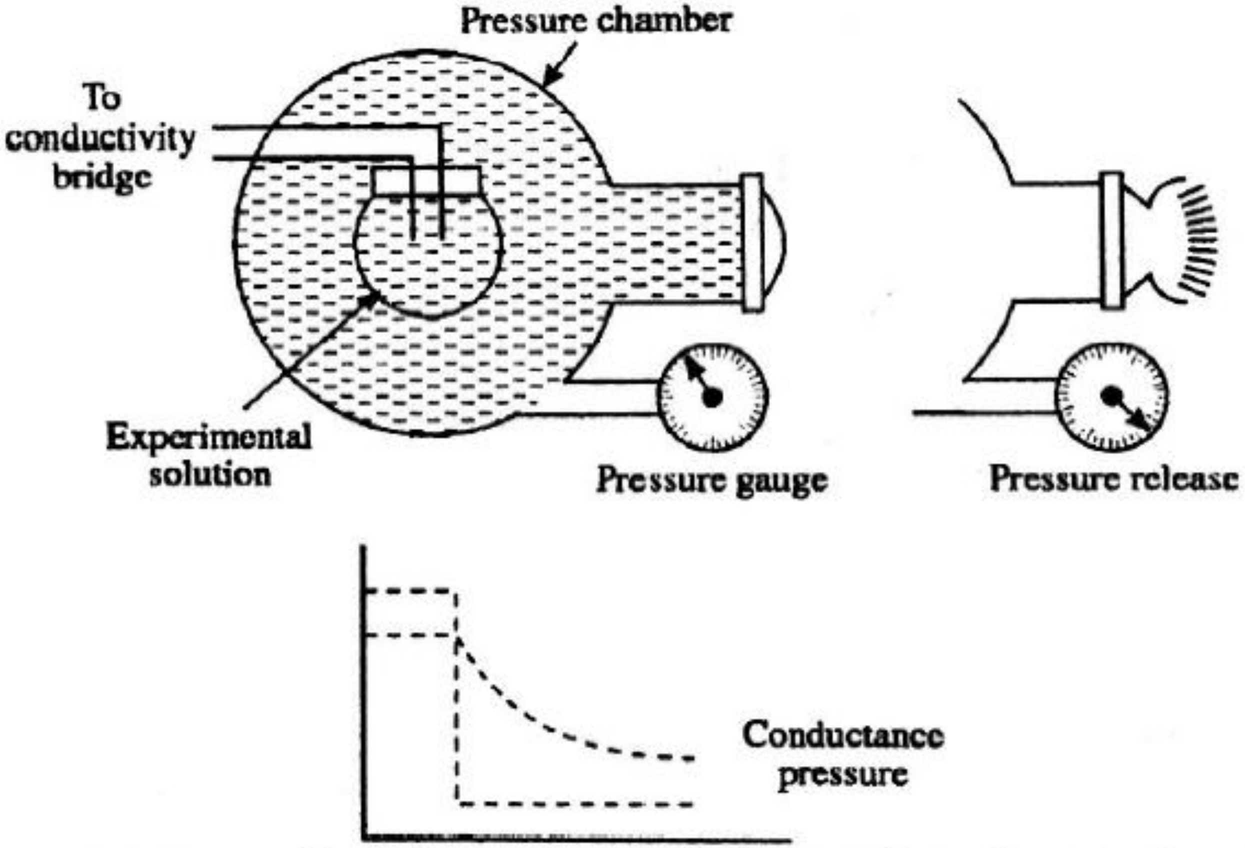


Fig. 9. Pressure-jump method shown for an ionic reaction; the reaction is followed by measuring the electrical conductance.

THEORIES OF UNIMOLECULAR REACTION RATES

LINDEMANN / LINDEMANN-HINSHELWOOD THEORY

This is the simplest theory of unimolecular reaction rates, and was the first to successfully explain the observed first-order kinetics of many unimolecular reactions. The proposed mechanism actually consists of a second-order bimolecular collisional activation step, followed by a rate-determining unimolecular step.

$$A + M \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} A^* + M$$

$$A^* \xrightarrow{k_2} P$$

Applying the steady-state approximation to the concentration of A* gives

$$[A^*] = \frac{k_1[A][M]}{k_{-1}[M] + k_2}$$

so that the overall rate is

$$\frac{d[P]}{dT} = k_2[A^*] = \frac{k_1k_2[A][M]}{k_{-1}[M] + k_2}$$

This is often written as

$$\frac{d[P]}{dT} = k_{eff}[A]$$

where $k_{eff} = \dfrac{k_1k_2[M]}{k_{-1}[M] + k_2}$ is an effective first-order rate constant. k_{eff} is, of course, a function of pressure. At high pressures, collisional deactivation of A^* is more likely than unimolecular reaction, k_{eff} reduces to k_1k_2/k_{-1} and the reaction is truly first order in A. At low pressures, bimolecular excitation is the rate determining step; once formed A^* is more likely to react than be collisionally deactivated. The rate constant reduces to $k_{eff}=k_1[M]$ and the reaction is second order.

Lindemann theory breaks down for two main reasons:

i) The bimolecular step takes no account of the energy dependence of activation; the internal degrees of freedom of the molecule are completely neglected, and the theory consequently underestimates the rate of activation.

ii) The unimolecular step fails to take into account that a unimolecular reaction specifically involves one particular form of molecular motion (e.g. rotation around a double bond for cis-trans isomerization). Subsequent theories of unimolecular reactions have attempted to address these problems. Hinshelwood theory offers a solution to problem i).

HINSHELWOOD THEORY

Hinshelwood modelled the internal modes of A by a hypothetical molecule having s equivalent simple harmonic oscillators of frequency and using statistical methods to determine the probabality of the molecule being collisionally activated to a reactive state.

The number of ways of distributing a given number of quanta, v, among the s oscillators (i.e. the number of degenerate states of the system at an energy $(v+\frac{1}{2})h\nu$) is

$$g_v = \frac{(v+s-1)!}{v!(s-1)!}$$

(a handwavy explanation of where this comes from is that (v+s-1)! is the number of permutations of all the quanta and all the harmonic oscillators. This has to be divided by the number of ways in which the quanta can be permuted amongst themselves, v!, and the number of ways the oscillators can be permuted amongst themselves, (s-1)!) The fraction of molecules in state v is given by the Boltzmann distribution

$$\frac{n_v}{N} = \frac{g_v e^{-vh\nu/kT}}{q} \quad \text{where} \quad q = \left(\frac{1}{1-e^{-h\nu/kT}}\right)^3$$

Hinshelwood now made the strong collision assumption. He assumed that the probability of deactivation of A* in any given collision is unity, so that the rate constant k_1 of the Lindemann mechanism is equal to the collision frequency Z. Because the collisions promote equilibrium, the probability of forming a state v in a collision is given by the Boltzmann distribution. The rate constant for activation to state v is therefore given by

$$k_1^v = Z\frac{g_v e^{-vh\nu/kT}}{q}$$

The overall rate of activation (i.e. rate of formation of collisionally excited A* with enough energy to react) is found by summing the k_1^v over all the energy levels which can dissociate i.e. all levels with an energy greater than the critical energy E_0 which the molecule needs to react. If the vibrational quantum number of the state with energy E_0 is m, we have

$$k_1 = \sum_m^{\infty} Z\frac{g_v e^{-vh\nu}/kT}{q}$$

The energies involved are usually large, with $E_0 \gg h\nu$. Hinshelwood developed equations for the case in which the energy levels can be assumed to be continuous ($kT \gg h\nu$). The expression then becomes

$$dk_1 = Z\frac{N(E)\, e^{-E/kT}\, dE}{q}$$

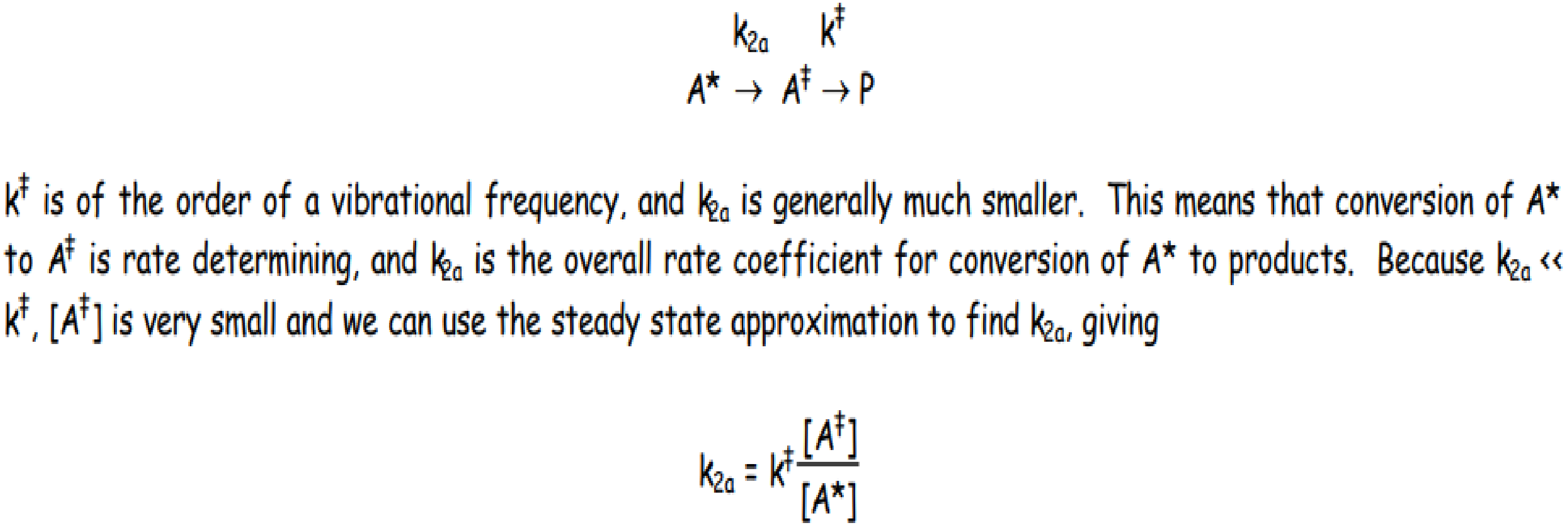
where $N(E)$ is the density of states; $N(E)dE$ is therefore the number of energy levels with energy between E and $E+dE$, and dk_1 is the rate constant for activation into this energy range. The total rate of activation is found by integrating dk_1 over all energies greater than the critical energy.

$$k_1 = \frac{Z}{(s-1)!}\left(\frac{E_0}{kT}\right)^{s-1} \exp(-E_0/kT)$$

This differs from the simple collision theory rate constant, $k_2 = Z\exp(-E_0/kT)$, by a factor of $\frac{1}{(s-1)!}\left(\frac{E_0}{kT}\right)^{s-1}$, leading to an increased theoretical value of k_1. The increase is more pronounced for large molecules, which have more oscillators, and is exactly what is required to overcome the first failure of the Lindemann theory.

RRK THEORY

Problem ii) can be addressed by recognising that a minimum amount of energy must be localised in specific modes of molecular motion in order for the unimolecular step to take place. A new step is added to the Lindemann mechanism, in which the generally excited molecule A* is converted into the specifically excited ‘activated complex’ A‡ .



$$A^* \xrightarrow{k_{2a}} A^\ddagger \xrightarrow{k^\ddagger} P$$

$k^\ddagger$ is of the order of a vibrational frequency, and k_{2a} is generally much smaller. This means that conversion of A^* to $A^\ddagger$ is rate determining, and k_{2a} is the overall rate coefficient for conversion of A^* to products. Because $k_{2a} \ll k^\ddagger$, $[A^\ddagger]$ is very small and we can use the steady state approximation to find k_{2a}, giving

$$k_{2a} = k^\ddagger \frac{[A^\ddagger]}{[A^*]}$$

RRK theory assumes that energy can flow freely from one vibrational mode to another within the molecule (this is a fairly reasonable assumption, since molecular vibrations are highly anharmonic at chemical energies and are therefore coupled). As before in the discussion of the Hinshelwood theory, for a molecule with s equivalent oscillators, the degeneracy of the vth vibrational level is $\frac{(v+s-1)!}{v!(s-1)!}$. If we have to locate at least m quanta in one particular mode for dissociation to occur (i.e. $E_0 = mh\nu$), this simply reduces our choice of quanta to (v-m), and the total number of ways of arranging these is $\frac{(v-m+s-1)!}{(v-m)!(s-1)!}$. The probability P_m^v of locating at least m quanta out of v in the dissociation mode is the ratio of these two quantities.

$$P_m^v = \frac{(v-m+s-1)!}{(v-m)!(s-1)!}\,\frac{v!(s-1)!}{(v+s-1)!} = \frac{(v-m+s-1)!v!}{(v-m)!(v+s-1)!}$$

Because the quantum numbers involved are very large (i.e. v and m are ››s) we have

$$\frac{(v-m+s-1)!}{(v-m)!} \rightarrow (v-m)^{s-1} \qquad \text{and} \qquad \frac{v!}{(v+s-1)!} \rightarrow v^{-(s-1)}$$

so that

$$P_m^v = (v-m)^{s-1} v^{-(s-1)} = \left(\frac{v-m}{v}\right)^{s-1} = (1- m/v)^{s-1}$$

Since $E=vh\nu$ and $E_0=mh\nu$, this expression can be rewritten in terms of energies.

$$P_{E_0}^{E} = (1 - E_0/E)^{s-1}$$

$P_{E_0}^{E}$ is the probability of locating a minimum amount of energy E_0 out of the total energy E in the dissociation mode. If energy randomisation takes place rapidly enough for the vibrational energy to be distributed statistically, then $\frac{[A^{\ddagger}]^E}{[A^*]^E} = P_{E_0}^{E}$, and the rate constant is

$$k_2(E) = k^{\ddagger}(1 - E_0/E)^{s-1}$$

k_2 increases with energy, since the probability of localising a given amount of energy E_0 in one particular mode increases as E increases. The localisation probability decreases as s increases since there are more modes to spread the energy across. Consequently, k_2 becomes smaller as the molecule becomes more complex, in contrast to the behaviour of the rate constant for activation k_1.

RRKM THEORY

Based on the results of Hinshelwood and RRK theory, the reaction mechanism can be rewritten to take account of the fact that the rates of collisional activation and unimolecular dissociation are energy dependent.

$$A + M \underset{k_{-1}}{\overset{dk_1(E)}{\rightleftharpoons}} A^*(E) + M$$

$$A^*(E) \xrightarrow{k_2(E)} P$$

Applying the steady state approximation to [A*(E)] leads to the rate expression

$$\frac{d[P(E)]}{dt} = \frac{k_2(E)dk_1(E)[A][M]}{k_{-1}[M]+k_2(E)}$$

from which we can identify the unimolecular rate coefficient for the energy range from E to E+dE as

$$k(E) = \frac{k_2(E)dk_1(E)[M]}{k_{-1}[M] + k_2(E)}$$

The thermal rate coefficient is obtained by integrating over E from E_0 to ∞

$$k = \int_{E_0}^{\infty} \frac{k_2(E)dk_1(E)[M]}{k_{-1}[M]+k_2(E)} = \int_{E_0}^{\infty} \frac{k_2(E)dk_1(E)[M]}{k_{-1}(1 + k_2(E)/k_{-1}[M])}.$$

In RRKM theory, the energy of the molecule is partitioned into fixed and non-fixed components. Only the non-fixed component E*, which can flow freely around the various modes of motion of the molecule, can contribute to reaction. The various terms of the rate expression are now evaluated using statistical mechanics.

i) $\frac{dk_1(E^*)}{k_{-1}}$ is the equilibrium constant for energization of the A molecules into the energy range E* to E*+dE*, and can be calculated from the partition function ratio $Q_{A^*(E^*)}/Q_A$.

ii) $k_2(E^*)$ is obtained by applying the steady state treatment to the activated complex $A^‡$ as in RRK theory, with the modification that the overall reaction is broken down into energy contributions from translation and from rotation/vibration. The rate constant $k^‡$ and ratio of concentrations $[A^‡]/[A^*]$ are evaluated using partition functions ($k^‡$ is treated as a translation along the reaction coordinate).

In the high pressure limit, RRKM theory reduces to transition state theory. In the general case, RRKM theory admits equilibrium between A* and A‡ , but not between A* and A. However, at high pressures A* and A are also in equilibrium. Transition state theory assumes that the activated complex A‡ is in thermal equilibrium with the reactants. This is equivalent to assuming that the thermal Boltzmann distribution is maintained at all energies, which is true at sufficiently high pressures at high pressures the RRKM model becomes the same as the transition state theory model, and the results of the two theories coincide.


Thank you