Chapter 4: Chemical Kinetics

1. Chemical Kinetics: It is the branch of physical chemistry which deals with study of rate of reactions, the mechanism by which the reactions proceed and factors affecting rate of reaction.

2. Rate of Reaction: It is the change in concentration of reactant or product per unit time. It is always a positive quantity; negative sign represents decrease in concentration of reactant. The unit of rate of reaction is mole $L^{-1}s^{-1}$

$$\text{Rate of Reaction} = \frac{\text{Change in concentration of reactant or product}}{\text{Time taken in change}}$$

For a general reaction R → P, it can be expressed as

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

$$\text{Rate of appearance of P} = \frac{d[P]}{dt}$$

Where, d[R] is small change in concentration of P.

d[P] is small change in concentration of R.

dt is small interval of time.

3. Average Rate of Reaction: It is the rate of reaction measured over a long time interval. For a general reaction R → P, it can be expressed as

$$r_{av} = -\frac{\Delta[R]}{\Delta t} = \frac{\Delta[P]}{\Delta t} \quad \text{(where } \Delta t \text{ is large interval of time)}$$

4. Instaneous Rate of Reaction: It is the rate of reaction when the average rate is taken over a particular moment of time. For a general reaction R → P, mathematically it can be expressed as

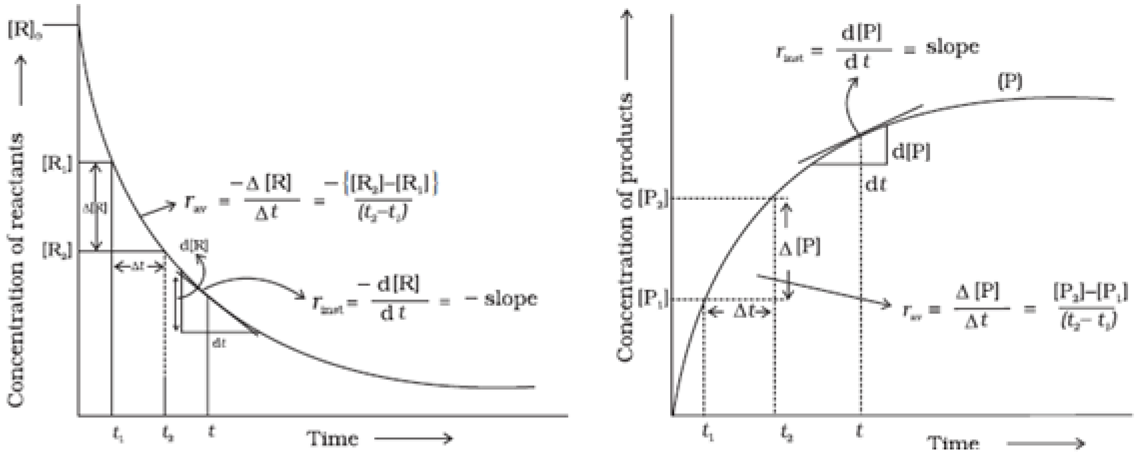
$$\text{Instaneous rate} = (\text{Average rate})_{\lim\limits_{\Delta t \to 0}}$$

$$r_{inst} = -\left(\frac{\Delta[R]}{\Delta t}\right)_{\lim\limits_{\Delta t \to 0}} = \left(\frac{\Delta[P]}{\Delta t}\right)_{\lim\limits_{\Delta t \to 0}}$$

$$r_{inst} = -\frac{d[R]}{dt} = \frac{d[P]}{dt}$$

- **General Expression for Rate of Reaction:** For a general reaction aA + bB → cC + dD

$$r_{inst} = \frac{-1}{a}\frac{d[A]}{dt} = \frac{-1}{b}\frac{d[B]}{dt} = \frac{1}{c}\frac{d[C]}{dt} = \frac{1}{d}\frac{d[D]}{dt}$$



Instaneous and average rate of reaction

5. Factors affecting the Rate of a Chemical Reaction:

a) **Nature of Reactants:** Ionic substances react more rapidly than the substance with covalent bond.

b) **Concentration of Reactants:** Rate of reaction increases with increase the concentration of reactants

c) **Temperature:** Rate of reaction increases with increase the temperature.

d) **Presence of Catalyst:** In presence of catalyst, the rate of reaction generally increases and the equilibrium state is attained quickly in reversible reaction.

e) **Surface area of Reactants:** The smaller the particle size, greater the surface area and faster is the reaction.

f) **Radiations:** Some reactions are considerable speed when exposed to sunlight or ultraviolet radiations, such reactions are called photochemical reactions. For examples, photosynthesis of carbohydrates, photography etc.

6. Rate Law (Rate equation) and Rate constant: The rate law or rate equation for a chemical reaction is an equation that links the reaction rate with the concentrations or pressures of the reactants and constant parameters (like rate coefficients and partial reaction orders). Consider a general reaction

$$aA + bB \rightarrow cC + dD$$

where a, b, c and d are the stoichiometric coefficients of reactants and products. The rate expression for this reaction is

$$\text{Rate} \propto [A]^x \ [B]^y$$

$$\text{Rate} = k \ [A]^x \ [B]^y$$

This equation, relates the rate of a reaction to concentration of reactants is called rate law or rate expression, where exponents x and y may or may not be equal to the stoichiometric coefficients (a & b) of the reactants and *k* is a proportionality constant known as rate constant.

If [A] = [B] = 1.0 mole L^{-1}, then

$$\text{Rate} = k$$

Thus the rate of reaction at unit concentration of reactants is called as rate constant or specific reaction rate. The value of '*k*' does not depend on concentration of reactant but it may depend on conditions such as temperature, catalyst etc

Above equation can also be written as

$$-\frac{d[R]}{dt} = k[A]^x[B]^y$$

This form of equation is known as differential rate equation,

7. Order of a Reaction:

- The sum of powers of the concentration of the reactants in the rate law expression is called the order of that chemical reaction.
- Order of a reaction can be zero, positive, negative and even a fraction.
- Order cannot be determined with a given balanced chemical equation. It can be determined experimentally.
- For a reaction $aA + bB \rightarrow cC + dD$

$$\text{Rate} = k[A]^x\ [B]^y$$

Here x = order of reaction with respect to A
y = order of reaction with respect to B
x + y = n (overall order of reaction)

8. Unit of Rate Constant: For n^{th} order reaction, $a \rightarrow$ Product

$$\text{Rate} = k[A]^n$$

$$k = \frac{\text{Rate}}{[A]^n}$$

$$k = \frac{\text{concentration}}{\text{time}} \times \frac{1}{\text{concentration}^n}$$

$$k = (\text{concentration})^{1-n}\ \text{time}^{-1}$$

While SI units of concentration is 'mol L^{-1}' and time is 's', the units of *k* for different reaction order are as

Zero order reaction, n = 0 so unit of $k = \text{mole } L^{-1}s^{-1}$
First order reaction, n = 1 so unit of $k = s^{-1}$
Second order reaction, n = 2 so unit of $k = \text{mole}^{-1}\ L\ s^{-1}$

Note: For gaseous reaction unit of k may be = $(\text{atm})^{1-n}\ \text{time}^{-1}$

9. Elementary Reaction (Simple Reaction): That reaction which completes in single step is called an elementary reaction. This type reaction have exponent in rate law equal to stoichiometric coefficients of the reactants.

If A + B → Product; is an elementary reaction for that rate law will be;

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

- Zero order reaction can never be elementary reaction.
- For elementary reactions fractional order is not possible.

10. Complex Reaction: Those reactions which complete in multistep are called complex reaction. For complex reactions the overall rate of reaction is controlled by the slowest step which is known as rate determining step.

For those reactions, rate law expression depends on concentration of reactants of slowest step which must be free from intermediate. Example-

$$2NO_2Cl \rightarrow 2NO_2 + Cl_2$$

This reaction is complex reaction b/c it carried out in following two steps-

$$NO_2Cl \rightarrow NO_2 + Cl \text{ (slow step)}$$
$$2NO_2Cl + Cl \rightarrow 2NO_2 + Cl_2 \text{ (fast step)}$$

For that reaction, the rate law is determine by the slowest step, so Rate = k [NO_2Cl].

11. Molecularity:

- Total number of molecules, atoms or ions (reacting species) participating in an elementary reaction is called as Molecularity of reaction.
- It is always in whole number (1, 2 or 3) and it cannot be zero or negative or fractional.
- Reactions are classified as Unimolecular, bimolecular and trimolecular for Molecularity 1, 2 and 3 respectively.
- Molecularity or order is never more than three b/c probabilities of more than three molecules colliding simultaneously is rare so it does not extend beyond three.
- Molecularity can be defined only for elementary reaction and has no meaning for a complex reaction.
- In elementary reactions Molecularity is equal to its order.
- In complex reaction generally Molecularity of slowest step is same as order of reaction which can be considered as Molecularity of reaction. (Except when slowest step contain intermediate).

12. Intermediates: The species which are produced in one step and consumed in another are called intermediates.

13. Zero Order Reaction: A zero order reaction means that the rate of reaction is independent of the concentration of reactants i.e. the rate does not change with the change in concentration of reactants.

$$\text{Rate} = k[A]^n$$
$$\text{Rate} = k \qquad \text{(while } n = 0)$$

Zero order reactions are relatively uncommon but they occur under special conditions. Some enzyme catalysed reactions and reactions which occur on metal surfaces are a few examples of zero order reactions. Some other examples of zero order reaction are as

- H_2 (g) + Cl_2 (g) → 2HCl (g)
- $2NH_3$ (g) → N_2 (g) + $3H_2$ (g)
- Reaction b/w acetone and bromine.
- Dissociation of HI on gold surface.
- Adsorption of gases on metal surface.

Integrated rate equation (rate law) for zero order reaction: Consider a general zero order reaction,

$$R \rightarrow P$$

For Zero order reaction, the rate of the reaction is proportional to zero power of the concentration of reactants.

$$-\frac{d[R]}{dt} = k[R]^0$$

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

$$-d[R] = k\,dt$$

Integrating both sides then

$$-[R] = k\,t + I \text{ ----------------- } (1)$$

where, I is integration constant.

At t = 0, the concentration of reactant [R] = $[R]_0$, where $[R]_0$ is the initial concentration of the reactant, then

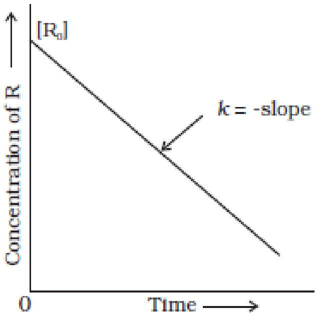
$$I = -[R]_0$$

Substituting the value of I in the equation (1) we get,

$$-[R] = kt - [R]_0$$

$$[R] = -kt + [R]_0 \text{ ------------- } (2)$$

Comparing above equation with a straight line equation, y = mx + c, if we plot [R] against t, we get a straight line with slope = $-k$ and intercept equal to $[R]_0$.



Further simplifying equation 2, we get the rate constant, k as

$$kt = [R]_0 - [R]$$

$$k = \frac{[R]_0 - [R]}{t}$$

$$\text{or} \qquad t = \frac{[R]_0 - [R]}{k} \qquad \text{----------------- (3)}$$

Half life period of a zero order reaction: It is the time in which the concentration of a reactant is reduced to half of its original value.

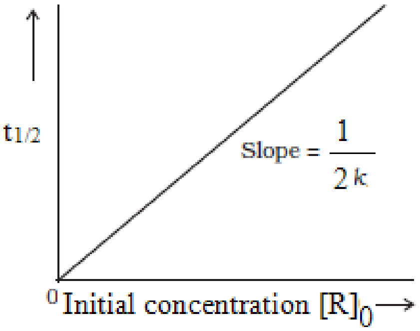
$$\text{When } t = t_{1/2}, \text{ then } [R] = \frac{[R]_0}{2}$$

Substituting these values in the equation (3), we get

$$t_{1/2} = \frac{1}{k}\left([R]_0 - \frac{[R]_0}{2}\right)$$

$$t_{1/2} = \frac{[R]_0}{2k}$$

$$t_{1/2} \; \alpha \; [R]_0$$



14. First Order Reaction: Reaction in which, the rate of the reaction is directly proportional to the first power of the concentration of reactants. Some examples are as

- All natural and artificial radioactive decay of unstable nuclei take place by 1st order kinetics.
- $C_2H_4\,(g) + H_2\,(g) \rightarrow C_2H_6\,(g)$
- $2N_2O_5 \rightarrow NO_2 + O_2$
- $2N_2O \rightarrow 2N_2 + O_2$
- $2H_2O_2 \rightarrow 2H_2O + O_2$

Integrated rate equation (rate law) for first order reaction: Consider a general first order reaction,

$$R \rightarrow P$$

In case of first order reactions, the rate is

$$-\frac{d[R]}{dt} = k\,[R]'$$

$$-\frac{d[R]}{[R]'} = k\,dt$$

Integrating both sides then

$$-\ln[R] = kt + I \qquad \text{------------- (1)}$$

At t = 0, $[R] = [R]_0$, where $[R]_0$ is the initial concentration of the reactant, then

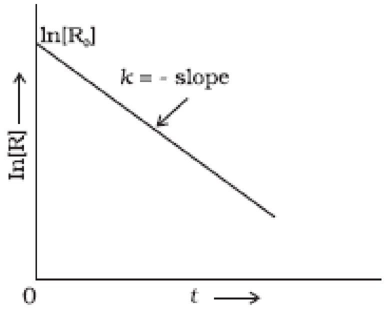
$$I = -\ln[R]_0$$

Substituting the value of I in the equation (1) we get,

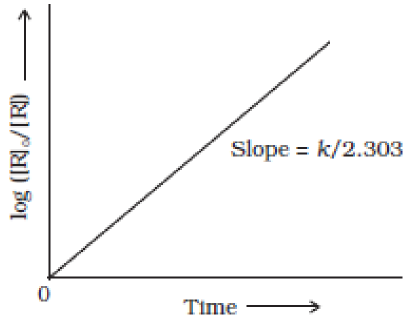
$$-\ln[R] = kt - \ln[R]_0$$

$$\ln[R] = -kt + \ln[R]_0 \text{ --------- (2)}$$

Comparing above equation with y = mx + c, if we plot ln [R] against *t* we get a straight line with slope = –*k* and intercept equal to ln $[R]_0$



A plot between ln[R] and t



Plot of log [R]$_0$/[R] vs time

Further simplifying equation 2, we get the rate constant, *k* as

$$kt = \ln\frac{[R]_0}{[R]}$$

$$kt = 2.303 \log\frac{[R]_0}{[R]}$$

$$k = \frac{2.303}{t}\log\frac{[R]_0}{[R]}$$

$$\text{or} \quad t = \frac{2.303}{k}\log\frac{[R]_0}{[R]} \text{ --------- (3)}$$

Where $[R]_0$ is initial concentration and [R] is the final concentration of the reactant.

Half life period of a first order reaction:

$$\text{When } t = t_{1/2}, \text{ then } [R] = \frac{[R]_0}{2}$$

Substituting these values in the equation (2), we get

$$t_{1/2} = \frac{2.303}{k}\log\frac{[R]_0}{[R]_0/2}$$

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

$$t_{1/2} = \frac{2.303}{k} \times 0.3010$$

$$t_{1/2} = \frac{0.693}{k}$$

Since no concentration term is involved, therefore $t_{1/2}$ for a first order reaction is independent of initial concentration.

15. Integrated rate equation for a Gaseous System: Consider a typical first order gas phase reaction

$$A(g) \rightarrow B(g) + C(g)$$

Let P_i be the initial pressure of A and P_t the total pressure at time '*t*' while P_A, P_B *and* P_C are the partial pressure of A, B and C respectively at time t.

Total pressure $P_t = P_A + P_B + P_C$

If x atm be the decrease in pressure of A at time *t* and one mole each of B and C is being formed, the increase in pressure of B and C will also be x atm each.

$$\begin{array}{lccccc} & A(g) & \rightarrow & B(g) & + & C(g) \\ \text{At } t = 0 & p_i \text{ atm} & & 0 \text{ atm} & & 0 \text{ atm} \\ \text{At time } t & (p_i - x) \text{ atm} & & x \text{ atm} & & x \text{ atm} \end{array}$$

where, p_i is the initial pressure at time $t = 0$.

$$p_t = (p_i - x) + x + x = p_i + x$$

$$x = (p_t - p_i)$$

where, $p_A = p_i - x = p_i - (p_t - p_i)$

$$p_A = 2p_i - p_t$$

$$k = \left(\frac{2.303}{t}\right)\left(\log \frac{p_i}{p_A}\right)$$

$$= \frac{2.303}{t} \log \frac{p_i}{(2p_i - p_t)}$$

16. Pseudo First Order Reaction: A chemical reaction in which value of order of reaction is one but molecularity is more than one is known as pseudo unimolecular / pseudo first order reaction. For example, the inversion of cane sugar is a bimolecular reaction but it is a first order reaction.

$$\underset{\text{Cane sugar}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H^+} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

So the rate equation for that reaction,

$$\text{Rate} = k' [C_{12}H_{22}O_{11}] [H_2O]$$

Due to water is in excess then its concentration remain constant during the reaction so $[H_2O]$ is taken as constant therefore rate equation is,

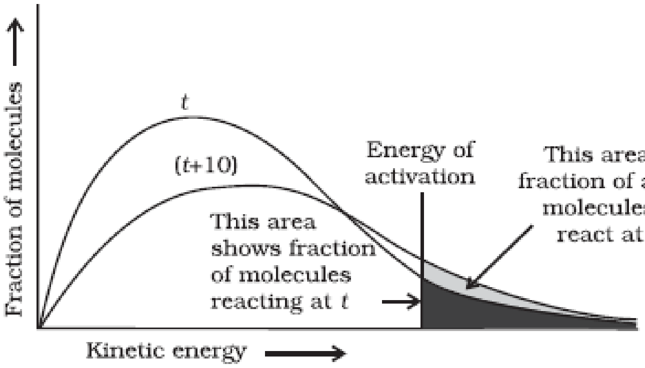
$$\text{Rate} = k \; [C_{12}H_{22}O_{11}] \qquad \text{where } k = k' [H_2O]$$

17. Effect of temperature on Rate of reaction: Generally it is found that for every rise in temperature by 10°C, the rate of reaction becomes two to three times. Before explain the temperature effect on rate of reaction require understand some definition,

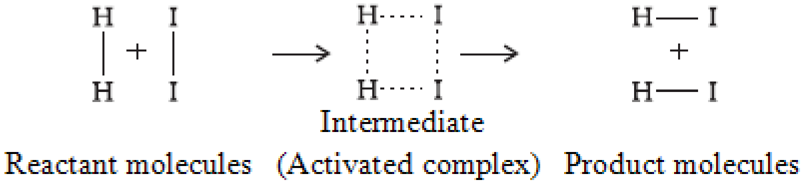
(i) Temperature Coefficient (μ): It is defined as the ration of rate constant of a reaction at two different temperatures which will be differ by 10°C. For most of the reaction, temperature coefficient lies b/w 2 and 3.

$$\mu = \frac{K_{T+10}}{K_T} \cdot \quad \text{and} \quad \frac{r_2}{r_1} = \frac{K_2}{K_1} = \mu^{\Delta T/10}$$

(ii) Maxwell and Boltzmann energy distribution curve: Increasing the temperature of a reaction mixture increases the fraction of molecules, which collide with energies greater than Ea. It is clear from the curve that with rise 10°C temperature, the area showing fraction of molecules having energy equal to or greater than activation energy gets double leading to doubling the rate of reaction.



(iii) Activated complex: It is an unstable intermediate formed b/w reacting molecules. Since it is highly unstable and it readily changes in to product.



(iv) Threshold Energy: The minimum energy that the reacting molecules must possess in order to undergo effective collision to form the product is called threshold energy.

(v) Activation Energy (Ea):

- It is extra energy which must be possessed by reactant molecules so that collision b/w reactant molecules is effective and leads to the formation of product molecules.
- For fast reaction activation energies are low while for slow reactions activation energies are high.

Activation energy (Ea) = Threshold energy – Average energy possessed by reacting molecules

$$\text{Reactants} \xrightarrow{\text{Activation energy}} \text{Activated complex} \xrightarrow{\text{Energy}} \text{Products}$$

18. Relation between Rate Constant & Temperature (Arrhenius Equation): It relates rate constant with temperature by following way

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

Where, A= Arrhenius factor or the frequency factor. It is also called pre-exponential factor.

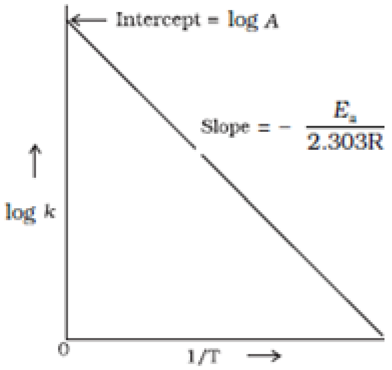
R = Gas constant

Ea = Activation energy measured in joules/mole (J mol –1).

$$\ln k = \ln A - E_a / RT$$

$$\log k = \log A - \frac{E_a}{2.303RT}$$

The plot of log k vs 1/T gives a straight line with
Slope = – Ea /2.303R and intercept = log A.
So we can calculate Ea and A by using these values



A plot between ln k and 1/T

If k_1 and k_2 are the values of rate constants at temperatures T_1 and T_2 then

$$\log k_1 = \log A - \frac{E_a}{2.303RT_1} \quad \text{------------ (1)}$$

$$\log k_2 = \log A - \frac{E_a}{2.303RT_2} \quad \text{------------ (2)}$$

Subtracting equation (1) from (2), we get

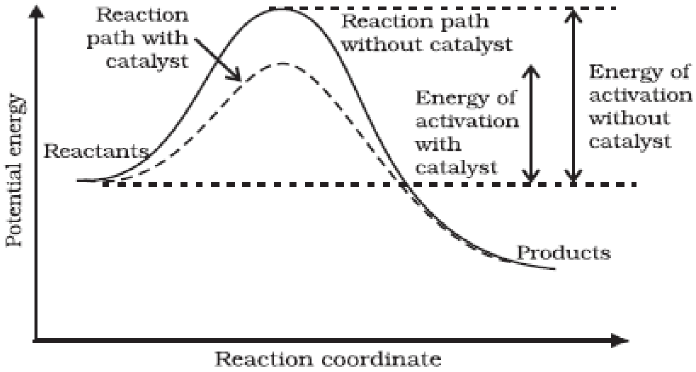
$$\log k_2 - \log k_1 = \frac{E_a}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303R}\left(\frac{T_2 - T_1}{T_1 T_2}\right)$$

19. Effect of catalyst on Rate of Reaction:

- A catalyst is a substance which increases the rate of a reaction without itself undergoing any permanent chemical change.
- The action of the catalyst can be explained by intermediate complex theory.
- According to this theory, a catalyst participates in a chemical reaction by forming temporary bonds with the reactants resulting in an intermediate complex. This has a transitory existence and decomposes to yield products and the catalyst.

- The catalyst provides an alternate pathway by reducing the activation energy b/w reactants and products and hence lowering the potential energy barrier which shown in figure.
- According to Arrhenius equation that lowers the value of activation energy faster will be the rate of a reaction.



Effect of catalyst on activation energy

20. Theory of Reaction Rate: Following are two theories:

(i) Collision theory of chemical reactions: This theory was developed by Max Trautz and William Lewis. It is based on kinetic theory of gases. According to this theory,

- For a reaction to occur there must be collision in b/w reacting molecules.
- The number of collision per second per unit volume of the reaction mixture is known as ***Collision frequency (Z)***.
- All collisions do not lead to the formation of products. Only effective collision brings about a chemical reaction.
- Collisions which lead to the formation of product molecules are called ***Effective collisions***.
- For effective collision reacting molecules must possess a minimum amount of kinetic energy (threshold energy) and proper orientation of collision
- For effective collisions, another factor *P*, called the probability or steric factor is also introduced. It takes into account the fact that in a collision, molecules must be properly oriented i.e.,

$$Rate = PZ_{AB}.e^{\frac{-E_a}{RT}}$$

Where, Z_{AB} represents the collision frequency of reactants, A and B and $e^{-Ea/RT}$ represents the fraction of molecules with energies equal to or greater than *E*a. And P is called the probability or steric factor.

(ii) Transition state theory:

21. Photochemical Reaction: