Q.1	**Give the main postulates of collision theory.**
Ans.	**Postulates of collision theory**: a) For any chemical reaction to occur, the molecules of reactants should collide with each other. b) The collision between the reactant molecules are perfectly elastic in nature. c) All collisions do not lead to product formation. Only those collisions where the reactant molecules possessing a minimum amount of energy called 'activation energy', lead to product formation. Such collisions are called effective collisions. d) The molecules of reactants are considered to be hard rigid spheres possessing only transitional energy. e) The collision molecules must be properly oriented for the reaction to occur. The energy required for effective collisions between the poorly oriented molecules is much more than the energy required for properly oriented molecules. f) The rate of reaction is directly proportional to number of collisions per cc per second.
Q.2	**Explain the application of collision theory to bimolecular reaction.**
Ans.	According to collision theory , for a chemical reaction to occur, the molecules must collide with each other. Consider a bimolecular reaction: $A + B \rightarrow$ Products It represents the number of binary collisions per cc per second between A and B and if E_a is the energy of activation then the rate of the reaction is given by : where, R = Gas constant , T = absolute temperature The total number of collisions per cc per second for two different molecules A and B is given by : Where, represent number of molecules A and B per cm^3 respectively. represent masses of individual molecules σ_{AB} is mean molecular diameter = k is Boltzmann constant = R/N where, R is gas constant and N is Avogadro's number

If the bimolecular reaction occur between similar molecules ie. For the reaction: **A + B → products**, then the number of collisions per cc per second between two similar molecules is given by:

By law of mass action, the rate of reaction for a bimolecular reaction of the type: A + B → products is given by:

Rate = k[A] [B]………………………………………………………(2)

where, k is specific reaction rate

From equation (1) and (2) above we get,

k[A] [B] =

If both the molecules are similar then

Where, **Z** represents collision frequency. It is defined as the number of collisions per cc per suffered by any one particle in one ml of gas.

Equation (5) is the fundamental equation for rate constant on the basis of collision theory.

<u>Test for collision theory</u>:

The validity of equation (5) can be tested by two ways:

i) By calculation of z from equation (5) and comparing it with the experimental values for a number of gaseous reactions.

ii) By comparing k calculated from equation (5) with the observed value.

Consider the bimolecular reaction, $2HI_{(g)} \rightarrow H_{2(g)} + I_{2(g)}$

At 283K, $k_{expt.} = 3.5 \times 10^{-7}\ mol^{-1}sec^{-1}$ while $k_{cal.} = 5.4 \times 10^{-7}\ mol^{-1}sec^{-1}$

Thus, $k_{expt.} \approx k_{cal.}$, thereby verifying the validity of collision theory.

Q.3	**Give the merits of collision theory.**
Ans.	**Merits**: 1) It is to apply and permits ready calculation of reaction rates. 2) It successfully explain the effect of temperature on the rate of reaction.

	3) It qualitatively explains the rates of gaseous unimolecular reaction. 4) For certain gaseous bimolecular reaction involving simple molecules, the experimentally determined rate constant is in closed agreement with that calculated on the basis of collision theory.
Q.4	**What are the drawbacks of collision theory?**
Ans.	The drawbacks of collision theory are as follows: 1) It fails to explain the chemical reactions involving complex molecules which are non-spherical. These molecules possess rotational as well as vibrational energy in addition to transitional energy. Hence energy is distributed in three modes of motion rather than assuming only transitional motion, as predicted by collision theory. Hence the experimentally determined rate is less than the theoretical calculated value. 2) It does not consider the fact that proper orientation of the molecule is the pre-requisite condition for a chemical reaction to occur. Due to lack of proper orientation, effective collision do not occur and hence the experimental observed rate is less than calculated on the basis of collision theory. 3) The collision theory assumes the rate of reaction is proportional to total number of collisions per cc per second. However, as all collisions are not fruitful, the rate of reaction is found to be proportional to number of effective collisions. 4) It does not account of fast reactions where the reactant molecules reacts in spite of having energy much less than the energy of activation. Such reactions are explained by quantum mechanics which assumes that the reaction occur due to transfer of electrons between reactant molecules. For such reactions, the experimentally determined rate is much greater than calculated on the basis of collision theory.
Q.5	**Discuss the application of collision theory to unimolecular reactions.** **OR** **Discuss Lindeman’s theory of unimolecular reaction.**
Ans.	Lindeman applied collision theory to explain unimolecular reactions in gas phase. It is based on following postulates: a) For a unimolecular reaction to occur, at least two molecules of the reactant should collide. In this process, there is a exchange of energy between them so that one of them acquires the energy of activation. b) The activated molecule do not get converted to products immediately. There is a

definite time lag between activation and decomposition.

c) If the time gap is large, the activated molecules loses its energy due to collision with other molecules and gets deactivated. If the time gap is short, the activated molecule decomposes to form product.

d) The activated molecules therefore disappear through two parallel processes namely through deactivation and through decomposition. Consider the following unimolecular reaction:

$$\mathbf{A \longrightarrow Products}$$

According to Lindeman, the reaction proceeds in the following two steps:

i) **$A + A$ —— $A^* + A$: A^* activated complex**

ii) A^* Product

Rate of formation of A^* = $\mathbf{k_1[A]^2}$

Rate of removal of A^* = $\mathbf{k_2[A^{**}][A] + k_3[A^*]}$

By steady state approximation , for a short lived activated complex,

Rate of formation of A^* = Rate of removal of A^*

ie. $\mathbf{k_1[A]^2 = k_2[A^*][A] + k_3[A^*]}$

Rate of formation of products = $k_3[A^*]$

Two cases arises:

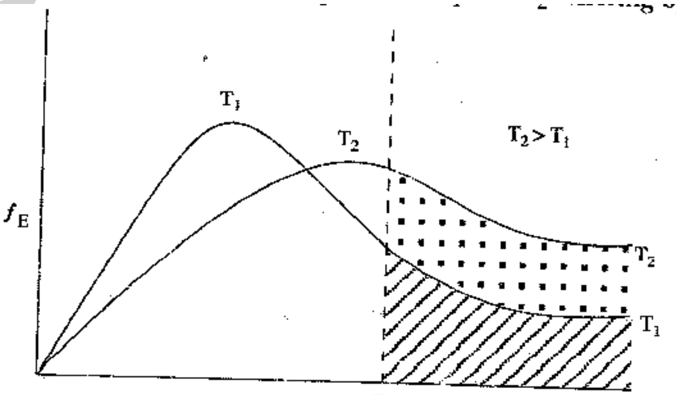
i) **At high pressures**

Rate of formation of products =

ie. Rate of formation of product α [A]

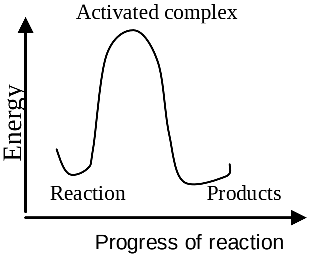
Thus the reaction is of first order at high pressures.

ii) **At low pressures**:

	Rate of formation of products = Thus reaction is of second order at low pressures. Thus according to Lindeman theory , there is a change from first order kinetics to second order as the pressure is lowered. This fact has been experimentally verified for large number of unimolecular gaseous reaction.
Q.6	**How does the collision theory explains the effect of temperature on rate of reaction?**
Ans.	According to collision theory, for a chemical reaction to occur, the molecule of the reactants must collide with each other. However , all collisions do not lead to formation of products. Only a fraction of the total number of molecules having energy equal to or greater than activation energy undergo effective collision and leads to the formation of products. At a given temperature, the reactants molecules have definite kinetic energy. Very few molecules possess too much high or too low kinetic energy. Majority of the molecules possess average kinetic energy. According to Maxwell-Boltzmann distribution law, at a given temperature there is distribution of kinetic energy between the reactant molecules. The fraction of the total molecules possessing a particular energy E can be plotted against the kinetic energy per mole for two temperatures. T_1 and T_2 differing by 10^0C as shown below. **Diagram**:  Fig. 1 : Variation of number of activated molecules with temperature

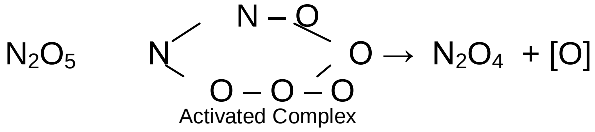
	From the graph it is observed that as the temperature is increased, the fraction of the molecules possessing the energy of activation E_a also increases. The number of effective collision also increase and hence the rate of reaction increases. Experimentally it is found that for every 10^0 rise in temperature, the rate of reaction becomes double or triple. The effective collisions is related to the total collision by the equation: Where the exponential factor is called Maxwell's factor. Thus , with the rise in temperature, there is an appreciable rise in Maxwell's factor which accounts for the increase in rate of reaction. Thus the collision theory explains the effect of temperature on the rate of reaction,
Q.7	**Discuss the activated complex theory or Transition state theory of bimolecular reactions.**
Ans.	The transition state theory, put forward by M. Polanyi and Henry Eyring is based on thermodynamic concept. It is based on the following postulates: a) All chemical reaction occur through the formation of an intermediate called the activated complex before the reactant gets converted into product. b) The activated complex is formed by the rearrangement of atoms and bonds of the reactant molecules c) The activated complex has transient existence and hence it is called transition state complex. It exist in equilibrium with the reactants and has high potential energy. **Reactants Activate complex** d) The activated complex decomposes into products. The rate of reaction is given by the rate of decomposition of the activated complex into products. Schematically, **Reactants Activated complex → Products** e) The energy of activation is the additional energy which the reactant molecules must acquire in order to form the activated complex. Ie. $E_a = E_{AC} - E_R$

Where, E_{AC} → energy of activated complex
E_R → energy of reactant molecules

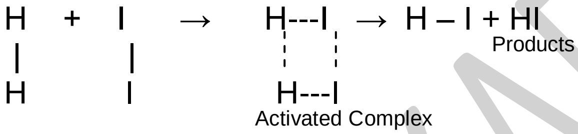


f) Examples of reactions involving activated complex formation:

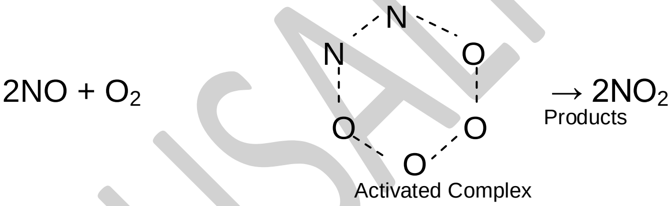
a) Unimolecular reaction



b) Bimolecular reaction:



c) Reaction involving more than two molecules:



Q.8 Derive an expression for rate constant of a bimolecular reaction on the basis of activated complex theory.

Ans. According to activated complex theory , all molecules before getting converted into products forms a transient species called activated complex. It represents highly unstable molecule formed by the rearrangement of atoms and bonds of reactant molecules.

Consider a bimolecular reaction between A and B

$$\underset{\text{Reactants}}{\mathbf{A + B}} \qquad \underset{\text{Activated complex}}{\mathbf{[X]^*}} \quad \rightarrow \mathbf{Products}$$

Rate of reaction =

The equilibrium constant K^* for the above reaction is given by:

The activated complex would decompose if enough vibrational energy is supplied to the system.

The frequency of decomposition of the activated complex is equal to —

Where $E_{vib.}$ = vibrational energy at temperature T
h = Planck's constant

but, $E_{vib.}$ = k.T where k is Boltzmann constant = R/N

Hence, frequency of decomposition of complex = —

Therefore rate of reaction = — —

By law of mass action , rate of reaction is given by —

From equation (3) and (4) we get,

From Vant Hoff relation

Where ΔG^0 is standard free energy change
K^* is equilibrium constant

Rearranging equation (6) we get,

But ,

Where, **= standard enthalpy change**

= **standard entropy change**

Substituting equation(7) in equation (5) we get,

<table>
<tr><td></td><td colspan="2">—
Equation (8) is the fundamental equation of transition state theory
The reaction between rate constant and standard free energy change is given by
—
ie.
If ΔG^0 is large, k will be small and vice versa. Hence, slow reaction have large free energy of activation.</td></tr>
<tr><td>Q.9</td><td colspan="2">Give the merits of transition state theory.</td></tr>
<tr><td>Ans.</td><td colspan="2">Merits:
a) It is applicable to simple as well as complex molecules.
b) It explains the slow rates of reactions involving large molecules in terms of entropy.
c) It takes into consideration the non spherical shape of molecules and the translational, rotational as well as vibrational energies associated with the molecules.
d) The theory is applicable to reaction in gas phase and in solution.</td></tr>
<tr><td>Q.10</td><td colspan="2">Compare the collision theory with the activated complex theory highlighting the relative merits of each theory.</td></tr>
<tr><td>Ans.</td><td>Collision Theory</td><td>Activated complex theory</td></tr>
<tr><td></td><td>1) It is applicable to reactions involving simple molecules in gaseous reactions and in solutions.</td><td>1) It is applicable to reactions involving simple as well as complex molecules (polyatomic molecules)</td></tr>
<tr><td></td><td>2) It considers molecules as hard rigid spheres possessing only translational energy</td><td>2) It considers molecule as non-spherical possessing translational, rotational as well as vibrational energy</td></tr>
<tr><td></td><td>3) The modified rate constant expression is given by k = P.Z. Where, P is Probability factor or steric factor</td><td>3) The rate constant expression is given by
—</td></tr>
<tr><td></td><td>4) For reactions involving large molecules, the experimentally determined rate is less than calculated ones. In such cases, the</td><td>4) It explains the discrepancy between experimental rate and calculated rate by using the idea of entropy decrease during the formation of activated complex. The probability factor P in terms of ΔS^0 is</td></tr>
</table>

probability factor is less than one.

given by P =— ——

Q.11 **How are chemical reactions classified? Give suitable examples.**

Ans. Chemical reactions are classified as slow, moderate , fast and ultrafast reactions depending upon their rates and time for reaction to occur.

Type of reaction	**Rate constant (k) (dm^3mol^{-1} sec^{-1})**	**Half life $t_{½}$ (s)**	**Examples**
1) Slow	10^{-7}	10^8(about 3 years)	$2H_2 + O_2 \rightarrow 2H_2O$
2) Moderate	10^{-4} to 10^{-1}	10^5(a day) to 10^2(about 2 min.)	Decomposition of H_2O_2 , HI etc.
3) Fast	10^{2} to 10^{5}	10^{-1} to 10^{-4}	$H^+ + OH^-$ H_2O
4) Ultrafast reaction	Around 10^{11}	10^{-12} (picoseconds) to 10^{-15} (femtosecond)	Explosion

Q.12 **What are fast reactions? Give suitable examples.**

Ans. The chemical reactions in which the rate constant lies between 10^1 to 10^{11} dm^3mol^{-1} sec^{-1} are called fast reaction. They have very short half life (10^{-1} to 10^{-4} sec).

eg. $H^+ + OH^-$ H_2O

a) for forward reaction $k_f = 1.4 \times 10^{11}$ dm^3mol^{-1} sec^{-1}
while for backward reaction $k_r = 2.5 \times 10^{-5}$ dm^3mol^{-1} sec^{-1}

therefore, the equilibrium constant K of the reaction is:

— ________

b) $NH_4^+ + OH^- \rightarrow NH_4OH$, $K = 3 \times 10^{10}$ dm^3mol^{-1} sec^{-1}

c) Bromination of aromatic amines and phenols

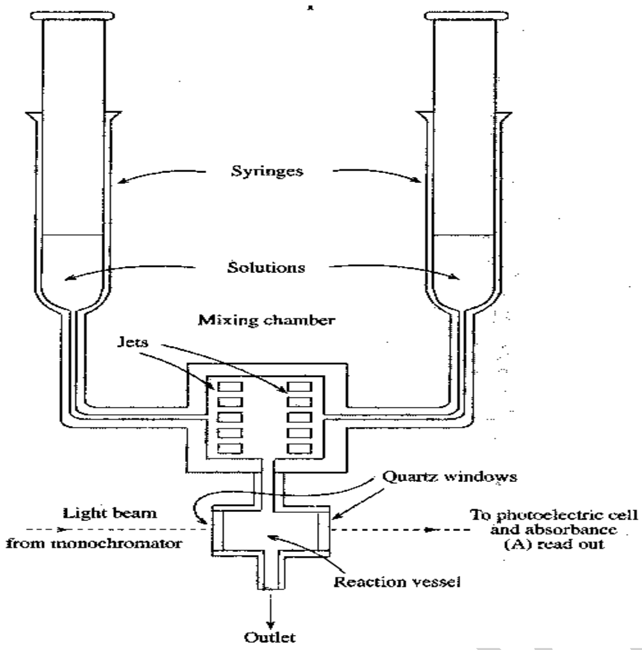
d) Reaction of haemoglobin with oxygen and carbon monoxide.

Q.13 **Explain the stop flow method used to study fast reactions.**

Ans. The stop flow technique is used to study the rates of fast reactions.

<u>Principle</u> : When two reactant solutions are allowed to mix in 10^{-3} seconds and their flow is suddenly stop, then the concentration changes during the reaction can be determined as a functions of time using spectrophotometer technique.

Diagram:



<u>Construction:</u> It consist of two vertically mounted syringes attached to the piston containing the solutions. The syringes are further connected to a mixing chamber through jets. The mixing chamber is further connected to a rectangular reaction vessel , which is fitted with quartz window on opposite sides. The reaction vessel is further joint to the outlet.

<u>Working:</u> The syringe are filled with the desired volume of two solutions to be mixed. The solutions are then force through jet into the mixing chamber where the two solutions mix in 10^{-3} second. The solution then pass through the reaction vessel and the flow is suddenly stopped. A beam of light is then allowed to pass through the quartz windows in the reaction vessel. The concentration changes occurring during the reaction are then noted down as a function of time by measuring the absorbance of solution using spectrophotometric technique.