

CHAPTER

9

CHEMICAL KINETICS

Q1: Explain the terms, chemical kinetics, rate of reaction, elementary reaction, rate determining step and rate law.

Ans: Chemical Kinetics:

Definition: "The branch of chemistry which deals with the rate of reaction, mechanism of reaction and factors that affect the rate of reaction is called chemical kinetics."

Explanation: The rate of reaction tells us that how fast or slow the reaction occurs.

Mechanism tells us the sequence of steps in which old bonds are broken and new bonds are formed until the products are obtained. It means that mechanism is a stepwise description of a chemical reaction.

The knowledge of chemical kinetics is important for the industry, engineering, biological reactions and other fields. For example; industrial chemists are interested in speeding up of reaction and obtaining products in shorter period of time.

Rate of Reaction: (ETEA: 2010, BISE Kohat, Swat)

"The change in concentration of reactants or products per unit time is called the rate of reaction." It is equal to change in concentration of reactants or products divided by change in time.

$$\text{Rate of reaction} = \frac{\text{Change in concentration}}{\text{Change in time}}$$

$$\text{Rate of reaction} = \frac{\Delta C}{\Delta t}$$

The symbol " Δ [delta]" means the change in.

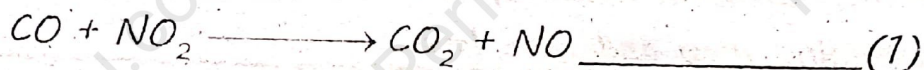
Units of Rate of Reaction:

The rate of reaction has the unit of concentration divided by unit of time.

Unit of rate of reaction = $\frac{\Delta C}{\Delta t} = \frac{\text{mol} \cdot \text{dm}^{-3}}{\text{sec}} \Rightarrow (\text{mol} \cdot \text{dm}^{-3} \cdot \text{s}^{-1})$ for gaseous reaction, the unit is "atm·s⁻¹".

Example:

Consider the reaction between carbon monoxide and nitrogen dioxide. The products are carbon dioxide and nitric oxide [NO]. The chemical equation is as under:



The rate of this reaction can be taken to be the change in concentration per unit time of the products, let's say CO₂

$$\text{Rate} = \frac{\text{Change in conc. of CO}_2}{\text{Change in time}} = \frac{\Delta[\text{CO}_2]}{\Delta t} \quad (i)$$

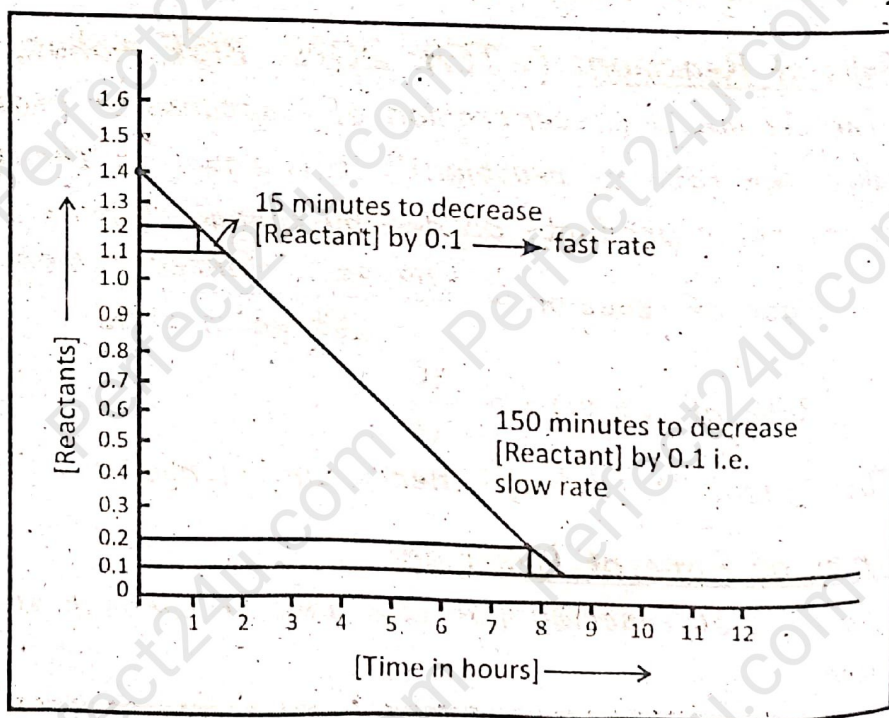
$$\text{Rate} = \frac{\text{Quantity of CO}_2 \text{ produced}}{\text{Time interval}} \quad (ii)$$

The rate of reaction is equal to the decrease in concentration of reactants, let's say CO,

$$\text{Rate} = \frac{-\Delta[\text{CO}]}{\Delta t} \quad (iii)$$

From equation (1), it is clear that, for every one mole of CO₂ formed, one mole of CO is consumed. If in one second the concentration of CO₂ were to increase by 0.02 mol·dm⁻³ [$\Delta(\text{CO}_2) = 0.02 \text{ mol} \cdot \text{dm}^{-3}$] then the concentration of CO would have to decrease by the same amount ($\Delta[\text{CO}] = -0.02 \text{ mol} \cdot \text{dm}^{-3}$). The rate of reaction is calculated from either equation (ii) or equation (iii) would be +0.02 mol·dm⁻³·sec⁻¹.

The rate of reaction is not a constant quantity but changes with the



concentration of reactant molecules present. When the concentration of reactants is high, the rate of reaction is also high. The rate gradually decreases and eventually becomes zero when all of the reactants have been consumed completely.

Plot of concentration against time showing that the reaction rate decreases as the concentration decreases. It takes 15 minutes to decrease the concentration from 1.2 to $1.1 \text{ mol} \cdot \text{dm}^{-3}$ while it takes 150 minutes to decrease the concentration by the same amount from 0.2 to $0.1 \text{ mol} \cdot \text{dm}^{-3}$.

Elementary Reaction and Rate Determining Step:

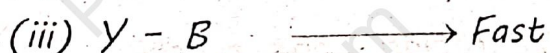
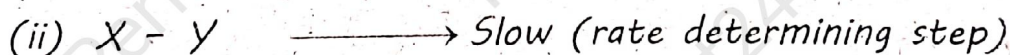
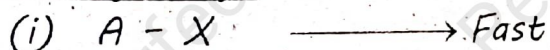
Most of the chemical reactions take place in series / various steps. These steps are called elementary steps. A complete sequence (ترتيب) of these elementary reactions is called a reaction mechanism. The overall reaction is the sum of these elementary steps. In each step, some chemical species [reaction intermediates] are produced. These reaction intermediates are consumed in subsequent steps. The overall reaction equation is obtained by adding these elementary reactions.

While adding these reactions, the intermediate species are cancelled out and in the final equation only reactants and products are left. Each of these elementary reactions will have their own rate. The overall rate of the complete reaction will be determined by the step which has the lowest rate, the slowest step will be the rate determining step.

Example:

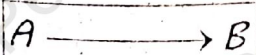
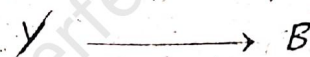
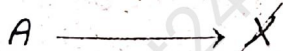


Elementary steps:

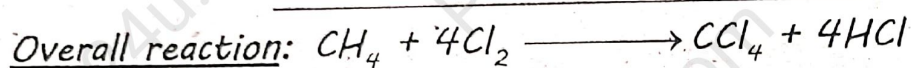
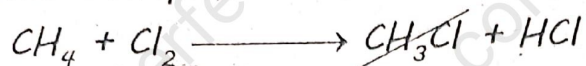


Overall Reaction:

Add all the three steps:



The reaction intermediates X and Y are present on both sides. Therefore, they will be cancelled out and net reaction will be " $A \rightarrow B$ ".
Let's take another example,



In the above reaction, the reaction intermediates CH_3Cl , CH_2Cl_2 and CHCl_3 are present on both sides so cancelled.

Rate Expression or Rate Law [Rate Equation]:

"An equation that gives relationship between rate of reaction and concentration of reactants is called rate equation or rate law."

Rate Law:

It states that "the rate of a chemical reaction is directly proportional to the product of molar concentrations of the reacting substances raised to an appropriate power."

Explanation: For a reaction the rate law is not written from balanced chemical equation, it is determined experimentally. It has been proved experimentally that the rate of reaction decreases as the concentration of reactants decreases. Increasing the concentration of reactants increases the reaction rate.

Justification:

In order to study the effect of concentration upon reaction rate we may conduct a series of experiments in which we measure the initial concentration of $\text{CO} - \text{NO}_2$ reaction at different concentration of CO , holding the concentration of NO_2 constant.



Data for three such series are presented in the given table:

Series-I			Series-II			Series-III		
[CO]	[NO ₂]	Rate	[CO]	[NO ₂]	Rate	[CO]	[NO ₂]	Rate
0.10	0.10	0.005	0.10	0.20	0.010	0.10	0.30	0.015
0.20	0.10	0.010	0.20	0.20	0.020	0.20	0.30	0.030
0.30	0.10	0.015	0.30	0.20	0.030	0.30	0.30	0.045
0.40	0.10	0.020	0.40	0.20	0.040	0.40	0.30	0.060

Initial rates of reaction $[\text{mol} \cdot \text{dm}^{-3} \cdot \text{s}^{-1}] K = 0.50 \text{ litre/mol} \cdot \text{s}^{-1}$.

Looking at the vertical columns in the above table, we observe that the rate is directly proportional to the concentration of CO. For example, if the concentration of CO is doubled [from 0.1 – 0.2 $\text{mol} \cdot \text{dm}^{-3}$] the rate also become double [From 0.005 – 0.010 $\text{mol} \cdot \text{dm}^{-3} \cdot \text{s}^{-1}$] in series-I. Now it becomes clear that the rate of reaction is directly proportional to the concentration of CO i.e.

$$\text{Rate} \propto [\text{CO}] \dots\dots\dots (a)$$

In the same way we can deduce the effect of NO₂ concentration upon rate by examining the horizontal rows of data in the given table.

When the concentration of CO is held constant at 0.1 $\text{mol} \cdot \text{dm}^{-3}$ [first horizontal rows] the rate increases in direct proportion to the concentration of NO₂, thus

$$\text{Rate} \propto [\text{NO}_2] \dots\dots\dots (b)$$

Thus we conclude that, the rate of this reaction is directly proportional to the concentration of both the reactants CO and NO₂ combining the two equations (a) and (b)

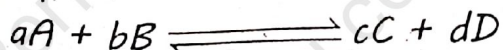
$$\text{Rate} \propto [\text{CO}] [\text{NO}_2]$$

$$\text{Rate} = K [\text{CO}] [\text{NO}_2] \dots\dots\dots (c)$$

The above equation (c) is called rate law, rate equation or rate expression.

Specific Rate Constant / Velocity Constant:

"The rate of reaction, when concentration of reactants are unity is called specific rate constant of a reaction." Consider a general reaction



$$\text{Rate of reaction} \propto [A]^a [B]^b$$

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

The above equation is called rate equation, where the proportionality constant "K" is called the rate constant. The "a" and "b" may be either whole numbers, zero or fraction. If the concentration of "A" and "B" are taken as unity, the rate constant is equal to the rate of reaction. "K" has a fixed value for a reaction under given condition of temperature:

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

$$\text{Let } [A] = 1 \text{ mol} \cdot \text{dm}^{-3}$$

$$\text{OR } \frac{\Delta C}{\Delta t} = K[1]^a [1]^b$$

$$[B] = 1 \text{ mol} \cdot \text{dm}^{-3}$$

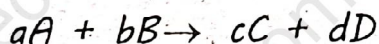
$$\text{OR } \left[\frac{\delta x}{\delta t} = K \right]$$

Q2: What is the order of reaction? Explain various types of order of reactions with the help of examples. (ETEA: 2008)

Ans: Order of Reaction:

Definition: "The sum of the powers of concentration of reactants in the rate law is called order of reaction."

The order of reaction is not predicted from the equation of reaction but it is determined experimentally.



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

The sum of "a" & "b", [a + b] is called the order of reaction. Order of reaction may be zero, 1st order, 2nd order, 3rd order & fractional order.

First order Reaction: (ETEA: 2009,12,19)

"The reaction in which the rate of reaction is proportional to the 1st power of the concentration of a single reactant is called 1st order reaction." e.g.



$$\frac{dx}{dt} = K[\text{Br}_2]$$



$$\frac{dx}{dt} = K[\text{Ra}]$$

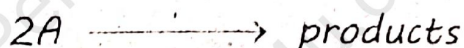


$$\frac{dx}{dt} = K[\text{N}_2\text{O}_5]$$

Second order Reaction:

"The reactions for which the rate of reaction is proportional to the second power of concentration of one reactant or to the concentration of two reactants each raised to the 1st power, are called 2nd order reactions."

Example:

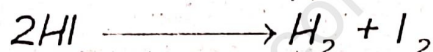


(i) Thermal decomposition of nitrogen dioxide



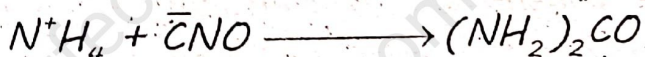
$$\frac{dx}{dt} = K[\text{NO}_2]^2$$

(ii) Thermal decomposition of hydrogen iodide



$$\frac{dx}{dt} = K[\text{HI}]^2$$

(iii) Formation of urea in solution phase



$$\frac{dx}{dt} = K[\text{N}^+\text{H}_4]^1 [\text{C}\bar{\text{N}}\text{O}]^1 \quad (1+1) = 2 \cdot 2^{\text{nd}} \text{ order reaction}$$

Third order Reaction: (ETEA: 2015,17)

(i) Those reactions for which the rate of reaction is proportional to the 3rd power of concentrations of three reactants each raised to the 1st power are called 3rd order reaction.



$$\frac{dx}{dt} = K[A]^1 [B]^1 [C]^1 \quad 1 + 1 + 1 = (3)$$

It is 3rd order reaction, although it is first order with respect to concentration of each of the reactants A, B and C.

(ii) The reactions in which the rate of reaction is directly proportion-

al to the 3rd power, of the concentration of the one reactant are called 3rd order reactions.



$$\frac{dx}{dt} = [A]^3$$

(iii) Those reactions in which the rate of reaction is directly proportional to the 2nd power of concentration of one reactant and to the 1st power of concentration of the 2nd reactant are called third reactions.

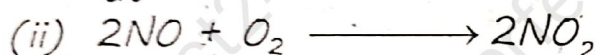


Examples:



$$\frac{dx}{dt} = [NO]^2 [H_2]^1$$

$2 + 1 = (3)$. 3rd order reaction



$$\frac{dx}{dt} = K[NO]^2 [O_2]^1$$

$(2 + 1 = 3)$. 3rd order reaction

Q3: Explain the role of rate constant in theoretical determination of reaction rate.

Ans We know that, the rate equation give relationship between rate of reaction, concentration of reactants and the rate constant "K".

Rate constant is temperature dependent and is constant for a given reaction at a particular temperature. The rate equation can only be obtained experimentally. The data obtained experimentally is used to find out the rate of reaction. For a reaction involving only one reactant.

(i) If the rate doubles when the concentration of reactants doubles then the reaction is 1st order.

(ii) If the rate increases four times when the concentration doubles, the reaction is 2nd order with respect to the reactant.

For a reaction involving more than one reactant, we can find the order by measuring the dependence of the reaction rate on the concentration of each reactant, one at a time, keeping the concentrations of all other reactants constant. Any change in the rate must be due to changes in the concentration of that substance.

Once the rate equation has been established, with the knowledge of the order of reaction experimentally, then the rate equation can be used to calculate rate of reaction theoretically for the given concentration of reactants, with the help of known value of rate constant.

Example: For a first order reaction, $A \longrightarrow B$, the rate constant is 0.0458 s^{-1} , calculate rate of the reaction if the concentration of reactant is $0.35 \text{ mol} \cdot \text{dm}^{-3}$.

Solution:

$$\text{Rate constant "K"} = 0.0458 \text{ s}^{-1}$$

$$\text{Concentration of reactant [A]} = 0.35 \text{ mol} \cdot \text{dm}^{-3}$$

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

$$\text{Rate} = 0.0458 \text{ s}^{-1} \times 0.35 \text{ mol} \cdot \text{dm}^{-3}$$

$$(\text{Rate} = 0.016 \text{ mol} \cdot \text{dm}^{-3} \cdot \text{s}^{-1})$$

EXAMPLE 9.5: For the decomposition of nitrogen pentoxide, N_2O_5 , dissolved in carbon tetrachloride: $2\text{N}_2\text{O}_5 \rightarrow 4\text{NO}_2 + \text{O}_2$

The following data was obtained at 30°C .

Concentration	Rate of reaction
$0.170 \text{ mol} \cdot \text{dm}^{-3}$	$0.050 \text{ mol} \cdot \text{dm}^{-3} \cdot \text{hour}^{-1}$
$0.340 \text{ mol} \cdot \text{dm}^{-3}$	$0.100 \text{ mol} \cdot \text{dm}^{-3} \cdot \text{hour}^{-1}$
$0.680 \text{ mol} \cdot \text{dm}^{-3}$	$0.200 \text{ mol} \cdot \text{dm}^{-3} \cdot \text{hour}^{-1}$

(a) Write the rate equation for the reaction. What is the order of reaction?

(b) Calculate the rate constant for the reaction at 30°C .

Solution:

The experimental data shows that doubling the concentration of N_2O_5 from 0.170 to 0.340 and from 0.340 to $0.680 \text{ mol} \cdot \text{dm}^{-3}$ double the rate of reaction i.e. from $0.050 \text{ mol} \cdot \text{dm}^{-3} \cdot \text{h}^{-1}$ to $0.100 \text{ mol} \cdot \text{dm}^{-3} \cdot \text{h}^{-1}$. Therefore the rate of this reaction is directly proportional to 1st power of N_2O_5 concentration. OR

$$\text{Rate} = K[\text{N}_2\text{O}_5]^1$$

Since the rate of reaction is proportional to the 1st power of concentration of one reactant concentration, the reaction is 1st order.

(b) To calculate the rate constant, we now solve the rate equation

for "K". Then substitute any of the three sets of data

$$\text{Rate} = K[N_2O_5]$$

$$K = \frac{\text{Rate}}{[N_2O_5]}$$

$$K = \frac{0.050 \text{ mol} \cdot \text{dm}^{-3} \cdot \text{h}^{-1}}{0.170 \text{ mol} \cdot \text{dm}^{-3}} = (0.29 \text{ h}^{-1})$$

$$K = \frac{0.100 \text{ mol} \cdot \text{dm}^{-3} \cdot \text{h}^{-1}}{0.340 \text{ mol} \cdot \text{dm}^{-3}} = (0.29 \text{ h}^{-1})$$

$$K = \frac{0.200 \text{ mol} \cdot \text{dm}^{-3} \cdot \text{h}^{-1}}{0.680 \text{ mol} \cdot \text{dm}^{-3}} = (0.29 \text{ h}^{-1})$$

Note: In 1st order reaction the rate reactant has only the unit of time.

Q4: Explain factors affecting the rate of reactions. (BISE Mkd 2018)

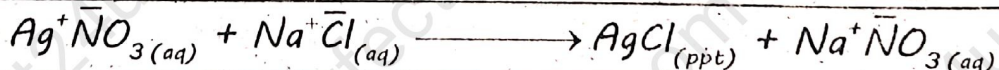
Ans: Factors Affecting the Rate of Reactions:

The following factors affect the rate of reaction:

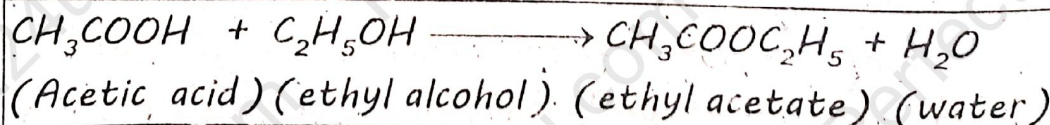
1. Nature of the Reactants:

Reactants vary (تختلف) among themselves in chemical reactivity:

1. Sodium metal reacts quickly with water as compared to iron at room temperature.
2. Ionic compounds react faster than covalent compounds. As in the aqueous medium ions are only exchanged which are already separated in aqueous solution. For example,



On the other hand, reaction between covalent compounds takes place slowly because they require energy for breaking of existing bonds and for the formation of new bonds. The molecules must come in contact at specific orientations. For example, esterification [formation of esters] process is slow due to the given reasons.



3. The reaction of magnesium with oxygen in the presence of flame

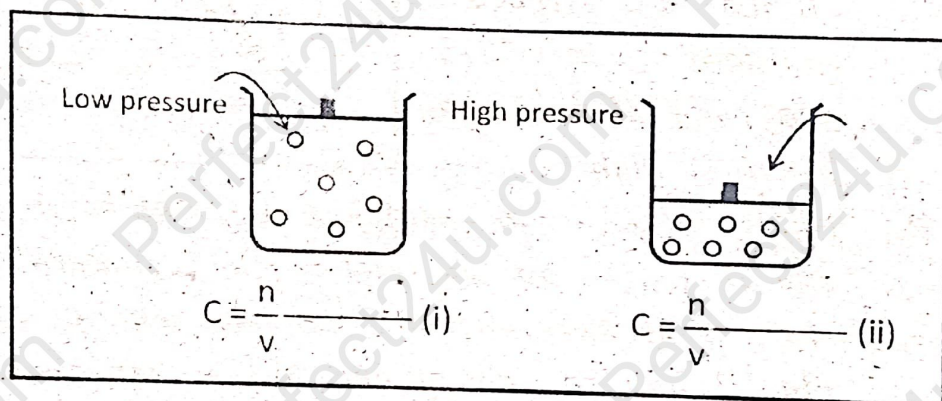
proceeds very rapidly to form magnesium oxide, while the reaction of copper with oxygen is very slow under the same conditions.

2. Effect of Concentration of Reactants:

The rate of almost all reactions increases with increase in the concentration of reactants. According to the law of mass action "the rate of a chemical reaction is directly proportional to the molar concentration of the reactants."

Reactions occurring in gaseous mixtures or in solutions are said to be homogenous. If the gaseous mixture or solution is concentrated it contains more active particles per unit volume and reaction is faster as in dilute mixture.

Combustion is more rapid in pure oxygen [100% O_2] as compared to air [air contain 21% O_2]. For gases the concentration can be increased by increasing external pressure.



In case (ii) volume becomes low so concentration becomes high, as both have inverse relation.

3. The Particle Size of a Solid Reacting in Homogenous Reactions:

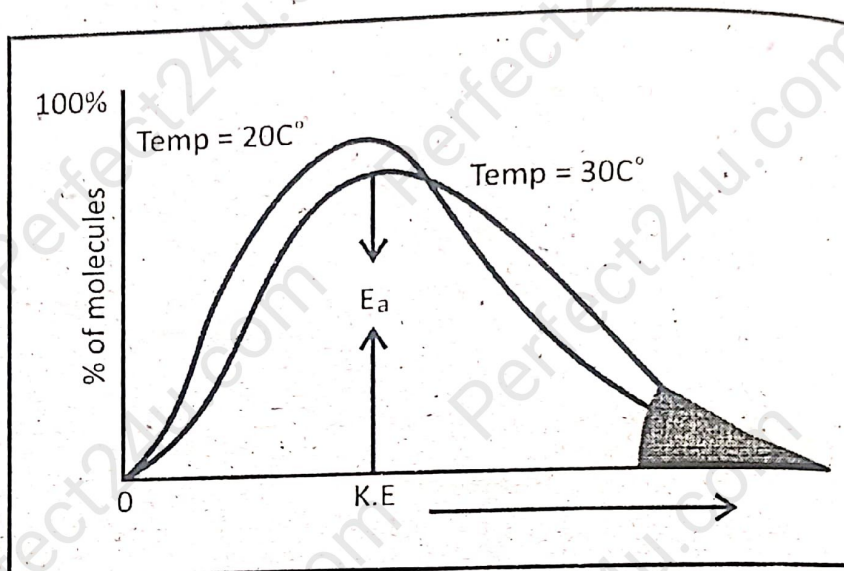
Generally larger the size of the reacting particles, the greater is the total surface area exposed for reaction and as a result faster will be the reaction. The reason is that with increased surface area of reactants, more atoms and molecules come in contact with each others.

1. Aluminium foil reacts with NaOH solution slowly but aluminium powder reacts fast.
2. A piece of $CaCO_3$ react with dilute H_2SO_4 very slowly but powdered $CaCO_3$ reacts quickly.
3. Lumps (تکڑے) of soft coal, do not burn readily in air and burn explosively when taken in powdered form.

4. Effect of Temperature:

Generally an increase in temperature increases the rate of chemical reaction. When we increase temperature by 10K, the rate of reaction almost becomes double. Temperature affects the rate of reaction in two ways:

1. With increase in temperature, kinetic energy of molecules increases and hence molecular motion speeds up. The number of effective collisions increases and rate of reaction becomes high.



2. With increase in temperature, more molecules gain activation energy (E_a). So the higher the temperature, the greater is the chances of the reactants to have energy equal to or greater than the activation energy and hence faster will be the rate of reaction.

Activation Energy (E_a):

It is the minimum amount of energy more than the average kinetic energy which is sufficient to convert the reactants into products.

Effective Collisions = [Fruitful Collisions]:

Effective collisions are those which lead towards chemical reaction.

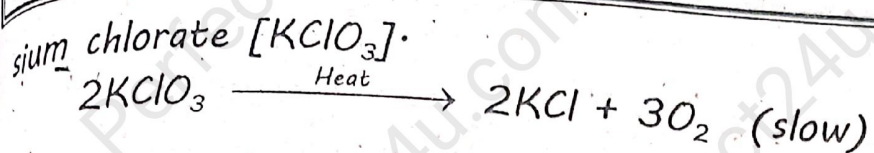
Ineffective Collisions = [Fruitless Collisions]:

Ineffective collisions are those which do not result in the formation of products.

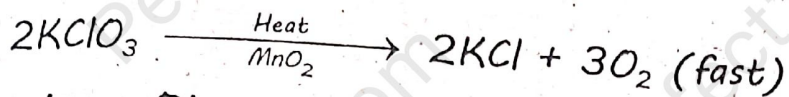
5. Presence or Absence of a Catalyst:

“A substance which changes the rate of a chemical reaction and remains unchanged by mass and composition at the end of a chemical reaction is called a catalyst.”

A catalyst generally speeds up the chemical reaction and save time. For example; oxygen is obtained by the thermal decomposition of potas-



The reaction is slow in the absence of a catalyst. When a small amount of manganese dioxide $[MnO_2]$ is added, the rate of reaction increases.

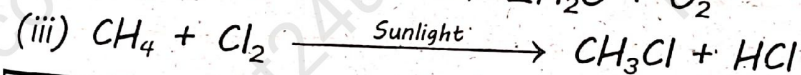
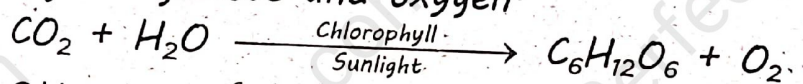


6. Light = Photochemical Reactions:

"Chemical reactions which are taking place in the presence of sunlight are called photochemical reactions." As photo means light, example are:

1. Photosynthesis and photography
2. Decomposition of hydrogen peroxide
3. Chemical reaction between methane and chlorine

(i) **Photosynthesis:** The leaves of plant contain a green pigment called chlorophyll. Chlorophyll absorbs light energy, convert it into chemical energy. Chlorophyll use this energy to convert CO_2 and H_2O into sugar / glucose and oxygen.



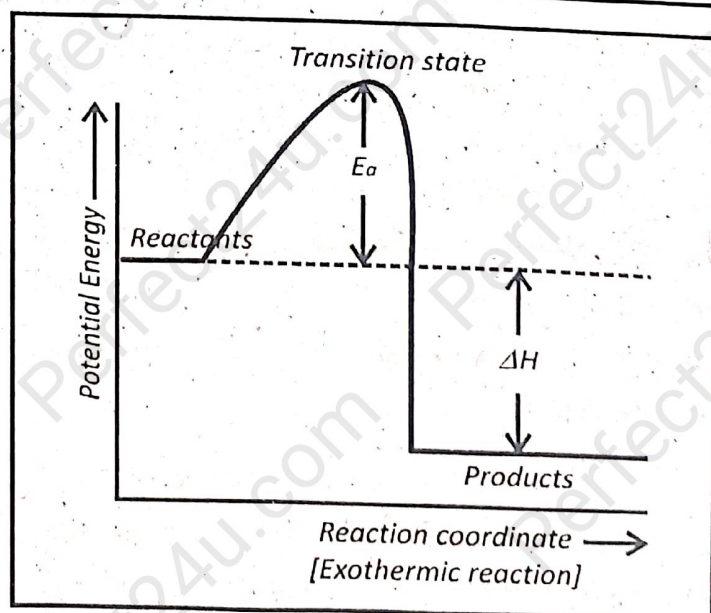
Q5: Write a note on activation energy and transition state.
(ETEA: 2018,19, Mardan 2018)

Ans. Activation Energy:

Definition: "The minimum amount of energy more than the average kinetic energy which is sufficient to convert reactants into products is called activation energy."

(OR)

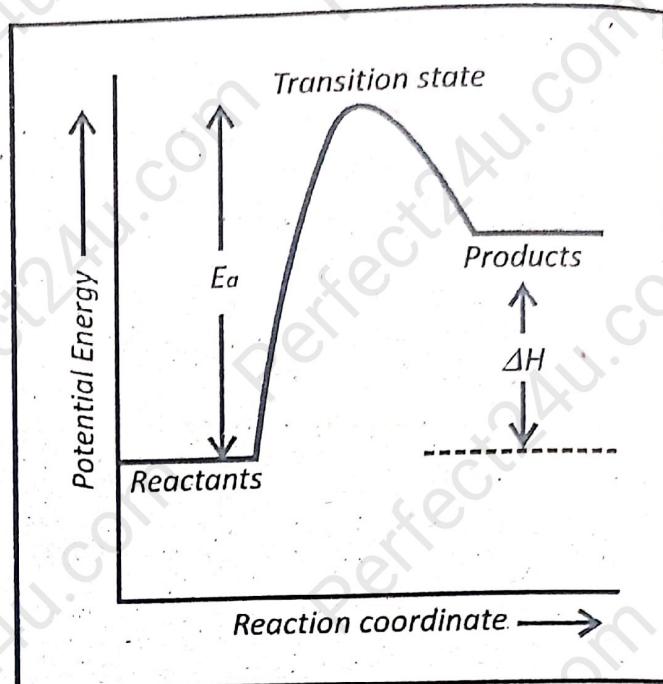
"The minimum amount of energy required to initiate a chemical reaction is called activation energy."



Explanation: Activation energy is represented by E_a . Its unit is kJ/mole . For example energy of activation for the decomposition of N_2O_5 is $103.4 \text{ kJ}\cdot\text{mol}^{-1}$.

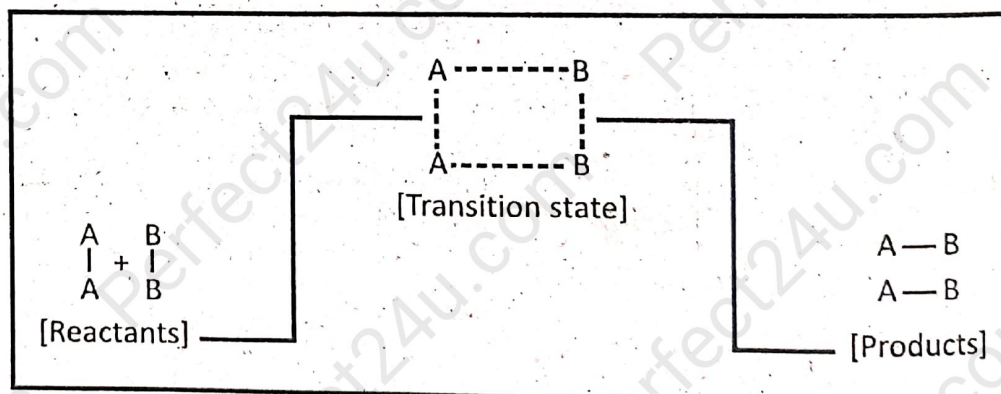
We may say that energy of activation is an energy hill (energy barrier) between reactants and products. The reactants have to pass over [climb up] this hill for the formation of products. If energy of molecules is less than " E_a ", they will not reach to the top of the hill and falls back, without forming products. For an exothermic reaction, the products are at lower energy level than the reactants, so heat is evolved.

For an endothermic reaction, the products are at higher energy level than the reactants. So heat is absorbed. It is shown in the front figure.



Transition State / Activated Complex:

The unstable and short lived combination of atoms which possess high potential energy and ready to form the prod-



ucts is called transition state or activated complex." For example, when two reactants A_2 and B_2 with sufficient energy collide to form an activated complex, the collision will result in a chemical reaction to form products.

In the beginning the $\text{A}-\text{A}$ and $\text{B}-\text{B}$ bond length increases and the bonds become weak. Energy is absorbed during this process, and an unstable high energy state called transition state is formed.

Then A-type and B-type atoms, attract each other, bond lengths decrease and A-B molecules, [products] are formed with the release of energy. So products are at lower energy than transition state.

$E_{\text{transition}}$ is greater than $E_{\text{(reactants)}}$

$E_{\text{(products)}}$ is lower than $E_{\text{(transition)}}$

The transition state always lies at the highest point of the reaction energy diagram.

- The transition state may either return to the initial reactants or it proceeds to form products.
- Transition state does not represent a real molecule because it is impossible to isolate transition state. However some of its properties are common to molecules like;
 1. Molecular weight
 2. Interatomic distance
 3. Definite enthalpy
 4. Definite composition
 5. The ability of rotation and vibration

Q6: Explain collision theory of reaction rate.

(ETEA: 2015, BISE Abbottabad 2016, Malakand 2018, Swat 2018)

Ans. Collision Theory of Reaction Rate:

The main points of collision theory are as:

1. A chemical reaction is the result of collisions between reactant molecules.
2. Not all, only effective collisions can give rise to the products. Two conditions are necessary for an effective collision. The molecules must have sufficient energy and they must have proper orientation.
3. The number of collisions per second is called collision frequency. Higher the collision frequency, faster will be the rate of reaction.
4. By 10°C rise in temperature, collision frequency becomes double.
5. If all the collisions among reacting molecules are effective, the reaction will be completed in a short time.

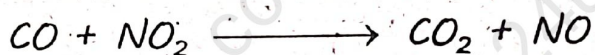
Explanation:

According to point number 1, if we increase the number of molecules, the number of collisions increases, as a result rate of reaction increases.

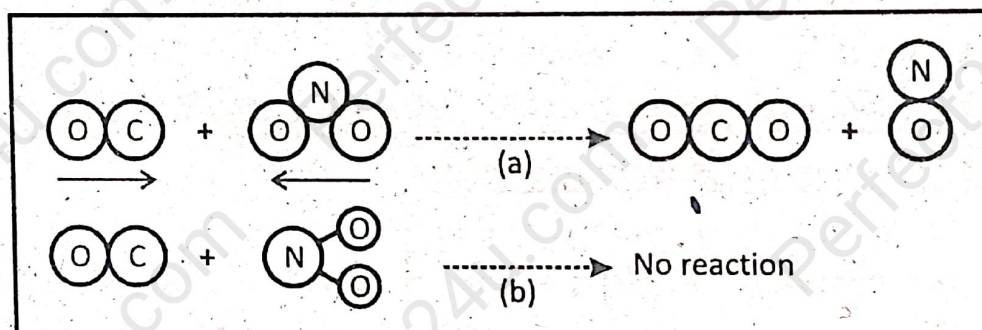
$\text{No. of molecules} \propto \text{No. of collisions} \propto \text{Rate of reaction}$

2. According to collision theory, molecules react only if upon collision, they possess a certain minimum amount of energy i.e. the energy of activation which is necessary for old bonds breaking in the reactant molecules. If the energy of colliding molecule is equal to or greater than the energy of activation, the reaction would occur otherwise not.

3. According of collision theory, proper orientation of molecules is necessary so, some molecules must be oriented in a very specific manner for a reaction to occur. Similarly the combination of two hydrogen atoms to form H_2 -molecule, require no specific orientation. Lets consider a Bi-molecular reaction,



The two reactant molecules must be oriented in a proper way if they are to react upon collision. When CO reacts with NO_2 , one of the oxygen atoms of NO_2 will be transferred to CO molecule. But it will be only possible when carbon atom of CO collide with one of the oxygen atoms of NO_2 .



Q7: What is catalysis? Explain its various types.
(ETEA: 2009,10,13,14,18,19).

Definition: "The process or chemical reaction, which occurs in the presence of a catalyst, is called catalysis."

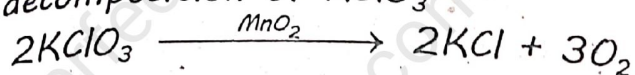
Catalyst:

"A catalyst is a substance, which generally increases the rate of a chemical reaction and recovered at the last unchanged by mass and composition is called a catalyst."

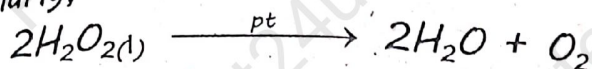
Positive Catalyst:

"A substance which increases the rate of a chemical reaction is called positive catalyst." For example, MnO_2 act as a positive catalyst for

the decomposition of KClO_3 :

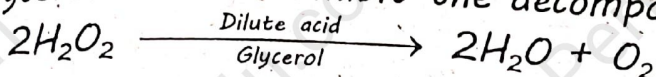


Similarly,



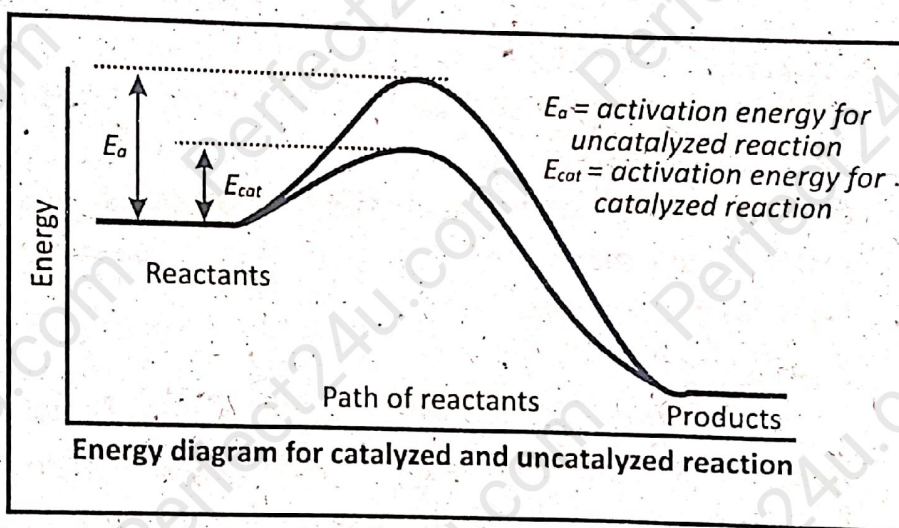
Negative Catalyst:

"A substance which decreases the rate of a chemical reaction is called negative catalyst." It is also called inhibitor. For example, dilute acids or glycerol retard / inhibit the decomposition of H_2O_2 .



Characteristics of a Catalyst:

1. Catalyst generally increases the rate of a chemical reaction.
2. A catalyst remains unchanged during a chemical reaction. The total mass and chemical composition of catalyst remains unchanged.
3. A catalyst is more effective when used in powdered form, because in ground state its surface area is large.
4. A catalyst is very much specific in its function.
5. A very small amount of catalyst is needed for speeding up the reaction.
6. A catalyst works by changing the reaction path through a lower energy activated complex, requiring lower activation energy than the uncatalysed reaction.



By changing the path by which a reaction occurs, a catalyst can lower the activation energy that is required and so speeds up the reaction.

The figure shows that E_a is the activation energy in the presence of catalyst. Many molecules that do not have kinetic energy to overcome the " E_a " potential energy barrier are able to cross the lower E_{cat} path, making the reaction faster.

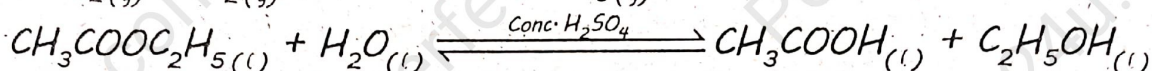
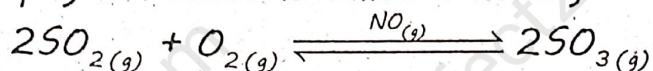
Types of Catalysis:

Catalysis are of two types:

1. Homogenous catalysis
2. Heterogeneous catalysis

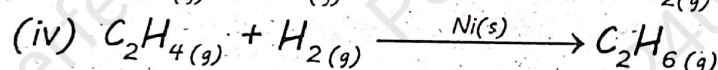
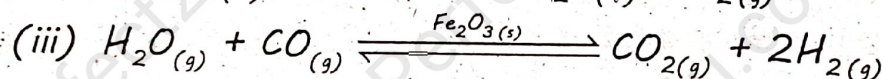
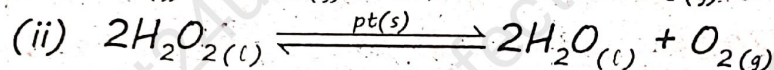
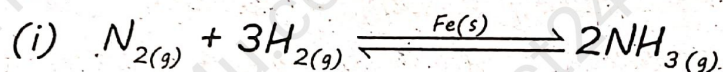
1. Homogeneous Catalysis:

"A chemical reaction in which, the catalyst and reactants are in the same physical state is called a homogeneous catalysis." For example,



2. Heterogeneous Catalysis:

"A chemical reaction in which the reactants and catalyst are in different physical states [phases] is called heterogeneous catalysis." Example are:



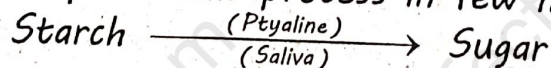
Enzymes Catalysis:

"A chemical reaction in which enzymes act as a catalyst is called enzymes catalysis."

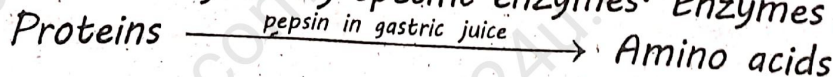
Enzymes are complex protein molecules which accelerate organic reactions. Enzymes are found in living tissues. Enzymes are proteins of high molecular mass.

Examples:

1. Ptyaline (پتالین) an enzyme found in saliva accelerates the conversion of starch into sugar. Although starch will react with water to form sugar but several weeks will be required for this process in the absence of ptyaline. At body temperature, very little amount of ptyaline complete this process in few minutes.



2. Similarly pepsin in gastric juice break down protein into simpler molecules which can be utilized by the body cells. Nearly every step of breakdown of a complex molecule to a series of smaller ones, in biological systems is catalyzed by specific enzymes. Enzymes are specific in function.



Exercise

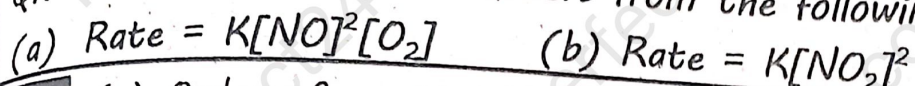
1. Choose the correct option from the given options:

1. Activated complex in a substance which is:
(a) Stable ✓ (b) Unstable
(c) Can be isolated (d) Can exist as product
2. A reaction is 1st order with respect to "A" and second order with respect to "B". The rate equation is:
✓ (a) Rate = $K[A][B]^2$ (b) Rate = $K[A]^2[B]$
(c) Rate = $K[A][B]$ (d) Rate = $K[A]$
3. For a reaction $A \longrightarrow$ products, doubling the concentration of "A" quadruples the rate, the reaction is:
(a) First order ✓ (b) 2nd order
(c) Zero order (d) 3rd order
4. With increase in temperature, the rate of reaction increases, due to:
(a) Decrease in collision
(b) Decrease in activation energy
(c) Increase in kinetic energy of molecules
✓ (d) More number of molecules attains activation energy
5. You can speed up a reaction by,
(a) Using less concentrated solution
(b) By lowering concentrated solution
✓ (c) Using more concentrated solution
(d) Stopping stirring
6. When the catalyst and reactants are in different physical states / phases, we call the catalysis,
✓ (a) Heterogeneous (b) Homogenous
(c) Concentrated (d) Positive catalysis
7. Increasing temperature, increase the rate of reaction by,
(a) Lowering the activation energy
(b) Increasing the activation energy
(c) Lowering the frequency of effective collisions between reacting molecules
✓ (d) Increasing the frequency of effective collisions between reacting molecules

8. The energy needed to start the reaction is called:
(a) Potential energy ✓ (b) Activation energy
(c) Kinetic energy (d) Ionization energy
9. As the number of effective collisions between the reacting particles increases, the rate of reaction:
(a) Decreases ✓ (b) Increases
(c) Remains same (d) Both "b" and "c"
10. Which condition will increase the rate of reaction?
(a) Decrease in temperature and concentration of reactants
✓ (b) Increase in temperature and increase in concentration of reactants
(c) Increase in temperature and decrease in concentration of reactants
(d) Increase in temperature and increase in concentration of reactants
11. A catalyst:
(a) Decrease the activation energy and decrease of the rate of reaction
(b) Decrease the activation energy and increase the rate of reaction
(c) Increase the activation energy and decrease the rate of reaction
✓ (d) Increase the activation energy and increase the rate of reaction
12. Which aluminium sample would react most rapidly with 1M CuSO_4 solution under the same conditions?
(a) 1 gram Al rod
(b) 1 gram Al pellets (نکڑے)
(c) 1 gram Al ribbon
✓ (d) 1 gram Al powder
13. 1 mole of a reactant reacts with a rate of $0.6 \text{ mol} \cdot \text{dm}^{-3} \cdot \text{s}^{-1}$. What is the rate constant of this reaction if reaction is 1st order
(a) 1 s^{-1} (b) 0.3 s^{-1}
✓ (c) 0.6 s^{-1} (d) 0.9 s^{-1}

Short Questions

Q1: Determine the overall orders from the following rate equation:



Ans: (a) Order of reaction = $1 + 2 = 3 = 3^{\text{rd}}$ order

(b) Order of reaction = $2 \rightarrow 2^{\text{nd}}$ order

Q2: Explain why a molecular collision should be sufficiently energetic to cause a reaction?

Ans: We know that rate of reaction increases by increasing temperature. By increasing temperature the kinetic energy increases and more molecules get activation energy which is required to convert reactants into products.

Secondly by increasing temperature collision frequency of molecules increases and thus the number of effective collisions increases which results in the formation of products. So molecular collisions must be sufficiently energetic to cause a reaction because energy is needed for old bonds breaking.

Q3: Name the four factors that increase the rate of reaction.

Ans: The following four factors increase the rate of a chemical reaction:

1. The nature of reactants [Higher the reactivity of reactants faster will be reaction]
2. High concentration of reactants
3. Large surface area
4. High temperature

Q4: In the light of collision theory of reaction rate, give reasons of increase in the rate by the increase of temperature.

Ans: By increasing temperature, rate of reaction increases because:

1. Kinetic energy of molecules increases and hence molecular motion speed up.
2. Number of effective collisions increases and hence chances of reaction increases.
3. More molecules attain activation energy which is necessary for reactants to overcome the barrier (حائل) and to form products.

Q5: Consider two gases "A" and "B" in a container at room temperature. What effect would the following changes have on the rate of the reaction between these gases?

- (a) The pressure is doubled
- (b) The number of molecules of gas "A" is doubled
- (c) The temperature is decreased by 10°C

Ans: (a) When pressure is doubled, volume will be decreased, molecules will come close to each other. Collision frequency and concentration become high and hence the rate of reaction will be increased.
(b) By increasing the number of molecules of gas "A" concentrations will increase. The chances of effective collisions increase and hence the rate of reaction will become fast.
(c) By decreasing temperature, kinetic energy of molecules decreases and hence the rate of reaction will be decreased.

Q6: The rate constant for the reaction:



At 400°C is $0.50 \text{ dm}^3 \cdot \text{mol}^{-1} \cdot \text{sec}^{-1}$ and the reaction is 1st order with respect to both "CO" and "NO₂".

- (a) What is the overall order of reaction?
- (b) What is the rate of the reaction at 400°C

When the concentration of CO is $0.025 \text{ mol} \cdot \text{dm}^{-3}$ and that of NO₂ is $0.040 \text{ mol} \cdot \text{dm}^{-3}$.

Ans: (a) For the given reaction, rate equation is:

$$\text{Rate} = k[\text{CO}]^1[\text{NO}_2]^1$$

As the sum of the exponents of the reactants in the rate equation is "2" so order of reaction is 2.

- (b) $[\text{CO}] = 0.025 \text{ mol} \cdot \text{dm}^{-3}$, $[\text{NO}_2] = 0.040 \text{ mol} \cdot \text{dm}^{-3}$

$$\text{Rate constant} = k = 0.5 \text{ dm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$$

$$\text{Rate} = k[\text{CO}][\text{NO}_2]$$

$$\text{Rate} = 0.5 \text{ dm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1} (0.025 \text{ mol} \cdot \text{dm}^{-3}) (0.040 \text{ mol} \cdot \text{dm}^{-3})$$

$$\text{Rate} = 0.0005 \text{ mol} \cdot \text{dm}^{-3} \cdot \text{s}^{-1}$$

$$[\text{Rate} = 5 \times 10^{-4} \text{ mol} \cdot \text{dm}^{-3} \cdot \text{s}^{-1}]$$

Q7: Explain briefly why all collisions between reactant molecules do not lead to reaction.

Ans: For effective collisions, activation energy and proper orientation is

necessary, only then reactants will form products otherwise not. Some molecules in the reaction mixture do not have proper orientation and sufficient kinetic energy, so all molecular collisions don't lead to reaction.

Descriptive Questions

Q1: Define the following terms:

- | | |
|-----------------------|-------------------------------|
| (a) Rate of reaction | (b) Rate constant |
| (c) Order of reaction | (d) Rate law or rate equation |
| (e) Catalyst | |

Ans: (a) Rate of Reaction:

"The change in concentration of reactants or products per unit time is called rate of reaction."

(b) Rate Constant:

"The rate of reaction, when concentration of reactants are unity is called rate constant."

(c) Order of Reaction:

"The sum of the powers of concentration of reactants in the rate law is called order of reaction."

(d) Rate Law / Rate Equation:

"An equation that shows relationship between rate of reaction and concentration of reactants is called rate equation."

(e) Catalyst:

"A substance which generally increases the rate of a chemical reaction and remains unchanged by mass and composition is called catalyst."

Q2: (a) Define the activation energy. What role does it play in chemical reaction?

(b) Household gas [methane] burns in the presence of oxygen and give energy for our daily use. If a mixture of methane and oxygen is kept in a container for indefinite period, no reaction takes place, explain.

Ans: Activation Energy:

Definition: "The minimum amount of energy more than the average kinetic energy which is required to convert reactants into products is

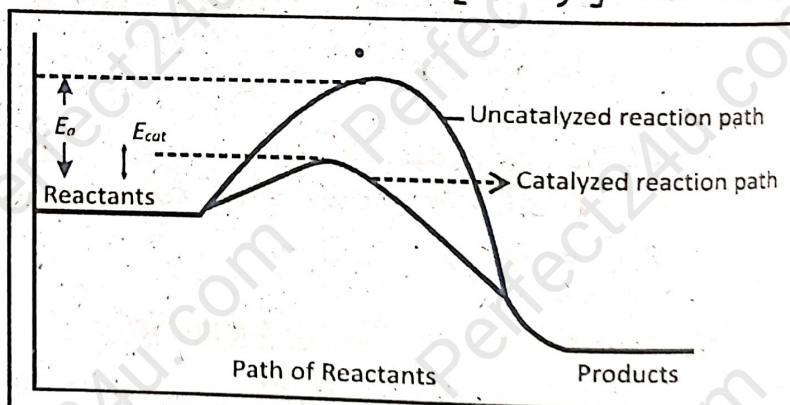
called activation energy.”

It plays an important role in chemical reaction. Activation energy is an energy hill between reactants and products. Energy is required to activate reactant molecules, to climb up the hill and form products. Without proper activation energy reactant do not convert into products. So it is necessary for reaction proceeding.

(b) During chemical reaction, old bonds breaking and new bond formation takes place. Heat / energy must be provided to the reacting species for old bond breaking. When a mixture of methane and oxygen is kept for long time at room temperature, no reaction takes place, because there is no sufficient activation energy to form products. Similarly molecular collisions are ineffective at room temperature.

Q3: Explain how does a catalyst increase the rate of reaction? Compare a catalyzed and uncatalyzed reaction on a potential energy diagram.

Ans: Actually a catalyst is a substance which alters [change] the rate of a reaction. A catalyst works by changing the reaction path through a lower energy activated complex, requiring lower activation energy than the uncatalyzed reaction.



Q4: Explain the relationship between reactant concentration and rate of the reaction.

Ans: Please see question number 4.

Q5: (i) Discuss why [according to collision theory of chemical reactions], some molecular collisions result in a chemical reaction while others do not?

(ii) Draw and explain a reaction energy diagram [reaction profile] for
 (a) an exothermic reaction (b) an endothermic reaction

(iii) Also show on the diagram:

- (a) Position of the reactants energy (E_A)
- (b) Position of the energy of products

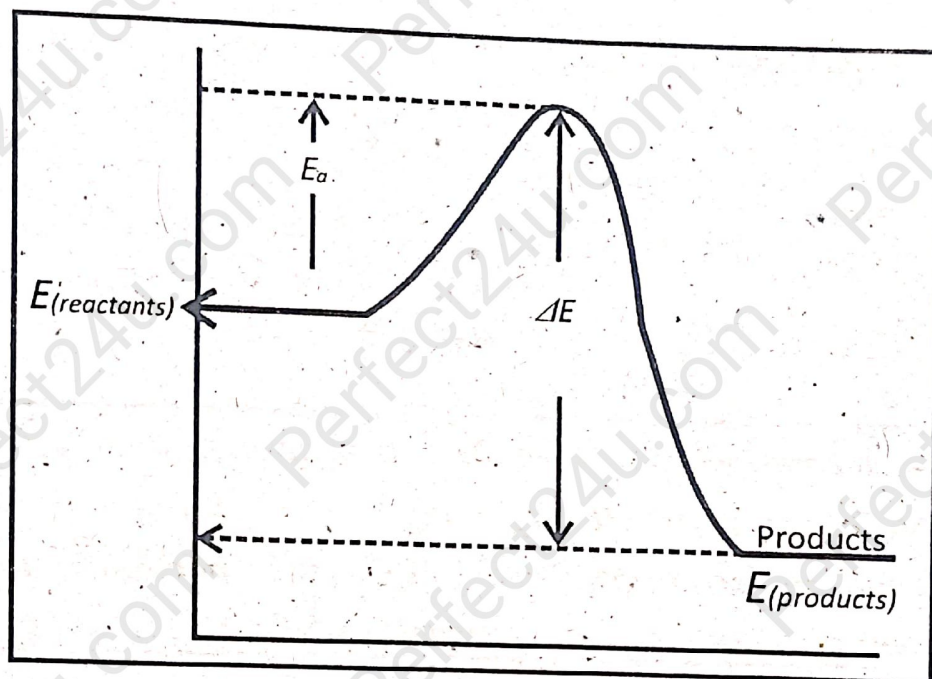
(c) Activation energy

(d) ΔH of the reaction

Ans: (i) For effective collisions, activation energy and proper orientation is necessary only then reactants will form products otherwise not. Some molecules in the reaction mixture do not have proper orientation and sufficient kinetic energy so all molecular collisions do not lead to reaction.

(ii) Please see question number 5.

(iii)



Numerical Questions

Q1: The conversion of x to y , follows second order kinetics. If concentration " x " is increased 3 times to what factor the rate of formation of " y " will be increased?

Ans: We know that, in second order reaction the rate of reaction is proportional to the 2nd power of the concentration of one reactant.

$$\text{Rate} \propto [\text{Reactants}]^2$$

It means that when concentration is double then the rate increases 4 times and when the concentration of reactant (x) is increased 3 times then the rate of reaction increases 9 times.

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

Reaction: $x \rightarrow y$

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

If concentration of "X" is increased 3-times then;

$$\text{Rate} = [3X]^2$$

As reaction is 2nd order with respect to X

$$\text{Rate} = (3)^2 [X]^2$$

$$\text{Rate} = 9K [X]^2 = (9 \text{ rate})$$

Q2: A first order reaction ($A \rightarrow \text{products}$) has a rate of 0.008 M s^{-1} , with $[A] = 0.002 \text{ M}$, what is the rate constant of this reaction?

Solution:

$$\text{Rate} = 0.008 \text{ M s}^{-1}$$

$$[M = \text{mol} \cdot \text{dm}^{-3}]$$

$$[A] = 0.002 \text{ M}$$

$$\text{Rate constant } K = ?$$

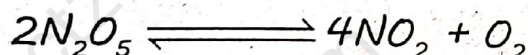
$$\text{Rate} = K [A]$$

$$K = \frac{\text{Rate}}{[A]} = \frac{0.008 \text{ M s}^{-1}}{0.002 \text{ M}} = [4 \text{ s}^{-1}]$$

Q3: (a) The decomposition of N_2O_5 proceeds according to the following equation: $2\text{N}_2\text{O}_5 \rightleftharpoons 4\text{NO}_2 + \text{O}_2$

(b) If the rate of decomposition of N_2O_5 at a particular instant is $4.2 \times 10^{-7} \text{ M} \cdot \text{s}^{-1}$, what is the rate of appearance of (a) NO_2 , (b) O_2 ?

Ans: The given equation is,



$$2 : 4 : 1$$

$$\left[1 : 2 : \frac{1}{2} \right]$$

As the concentration of NO_2 is twice as that of N_2O_5 , so the rate of appearance of NO_2 will be double i.e. $2 \times 4.2 \times 10^{-7} = [8.4 \times 10^{-7} \text{ M} \cdot \text{s}^{-1}]$

(b) Similarly the concentration of O_2 is half as compared to N_2O_5 , so the rate of appearance of O_2 as compared to the rate of disappearance of N_2O_5 will be half i.e.

$$\frac{1}{2} \times 4.2 \times 10^{-7} \text{ M} \cdot \text{s}^{-1} \Rightarrow [2.1 \times 10^{-7} \text{ M} \cdot \text{s}^{-1}]$$

