CHAPTER # 9
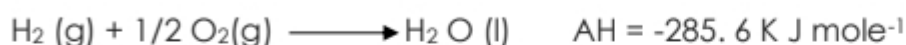
CHEMICAL KINETICS

Q1.What information we get from thermodynamics and why it is not enough to understand the stoichiometry and thermodynamics of a reaction?

Ans: Thermodynamics can tell us whether a reaction occurs spontaneously or not For example thermodynamics tells us that the follow ng reaction is highly spontaneous at room temperature and 1 atm pressure

$$H_2 (g) + 1/2\ O_2(g) \longrightarrow H_2 O\ (l) \qquad AH = -285.\ 6\ K\ J\ mole^{-1}$$

Explanation:

If we mix these gases under these conditions, we will have to wait a very long time for the reaction to occur Even a life time would not be long enough to observe any change in the reactants. However, if an electric spark is passed through the mixture, a reaction will occur with explosive violence.

Thus it is not enough to understand the stoichiometry and thermodynamics of a reaction.

We must also under and the factors that affect the rate of the reaction.

Chemical kinetics:

The branch ot Chemistry that concerns reaction rates and factors affecting reaction rates is chemical kinetics.

Q2. Define chemical kinetics and also give its significance.

Ans: Chemical Kinetics:

"The study of rates of chemical reactions and the factors that affect the rates of chemical reactions is known as kinetics or chemical kinetics.

Rates of chemical reaction:

Chemical reactions occur at a variety of rates from very rapid to very slow.

Slow reaction:

Some reactions are very slow and may require several weeks to produce enough products.

Example:

Fermentation is a slow reaction,

Fast reaction:

Some reactions complete in few seconds these reaction are called fast reactions.

Example:

Acid-base neutralization reactions are completed in microseconds.

Moderate reactions:

Some reactions proceed at moderate speed and these reactions are called moderate reactions.

Example:

The reactions that contract muscles and transmit impulses along nerves and record photographic images are the examples of moderate reactions.

Significance:

In industry it is important to know the conditions under which the reaction will proceed most economically Rate information is the most important kind of information used in the deduction of mechanism of a chemical reaction.

Mechanism:

Mechanism means sequence of all chemical steps which leads reactants to products.

Q3. Differentiate between average rate of reaction and instantaneous rate of reaction.

Ans:

Average rate of reaction	Instantaneous rate of reaction
i. "Thus rate of reaction between two specific time intervals is called the average rate of reaction."	i. The rate of reaction at a particular instant of time is called instantaneous

	rate of reaction
ii. The average rate of reaction over any time interval can be determined from the difference in concentrations divided by the difference between the measurement times	ii. It is determined from the slope of tangent to the curve at that time
iii. It is a constant value	iii. In the beginning of the time intervals, the instantaneous rate is higher than the average rate. At the end of the interval the instantaneous rate is lower than the average rate
iv. It is represented by Average rate of reaction $= \dfrac{x_2 - x_1}{t_2 - t_1} = \dfrac{\Delta x}{\Delta t}$	iv. It is represented by Instantaneous rate of reaction $= \dfrac{dx}{dt}$

Note:

i. The average rate and the instantaneous rate are equal for only one instant in any time interval

ii. As the time interval becomes smaller, average rate becomes close to the instantaneous rate.

iii. The average rate will be the same as instantaneous rate when the time interval approaches zero.

Q4. Write and explain the expression for the rate of reaction.

Ans: Rate of reaction:

"The rate of reaction is defined as the instantaneous change in concentration of a reactant or product at a given time".

Explanation:

If dx is very small change in concentration of a product in a very small time interval dt, the rate of reaction is expressed as.

Rate of reaction = dx / dt

Consider a general reaction

$$A \longrightarrow B$$

The rate of reaction can be expressed in term of the rate of disappearance of reactant A or the rate of appearance of product B.

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

$$\frac{dx}{dt} = +\frac{d[B]}{dt}$$

Where d [A] and d [B] are the changes in the concentrations of A and B respectively.

The **negative sign indicates** a decrease in the concentration of the reactant A. whereas the **positive sign indicates** the increase in the concentration of product B.

Q5. How initial rates can be determined? Explain it with the help of following table which shows the concentration of phenolphthalein in a solution that was initially 0.005 M in phenolphthalein and 0.6 M in OH⁻ ions. When a solution that contains phenolphthalein in the presence excess base is allowed to stand for a few minutes, the solution which has initially a pink colour, it gradually turns colourless as the phenolphthalein reacts with OH⁻ ions in solution.

Use this data to determine the initial rate.

Experimental data for the reaction between Phenolphthalein and excess Base.

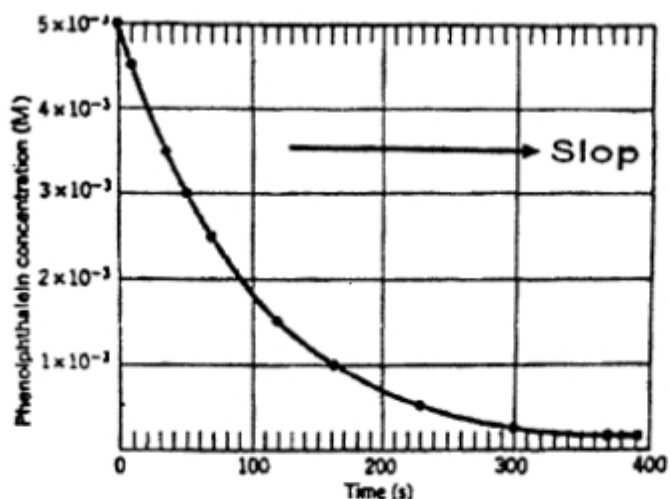| Concentration of Phenolphthalein (M)	Time (s)
0.0050	0.00
0.0045	10.5
0.0040	22.3
0.0035	35.7
0.0030	51.1
0.0025	69.3
0.0020	91.6
0.0015	120.4
0.0010	160.9
0.00050	230.3

Ans: Determination of Initial Rates:

"Initial rate is the instantaneous rate at the moment the reactants are mixed (i.e. at $t = 0$)"

Under these condition product concentrations are negligible. The initial rate is measured by determining the slope of line tangent to the curve at zero time.
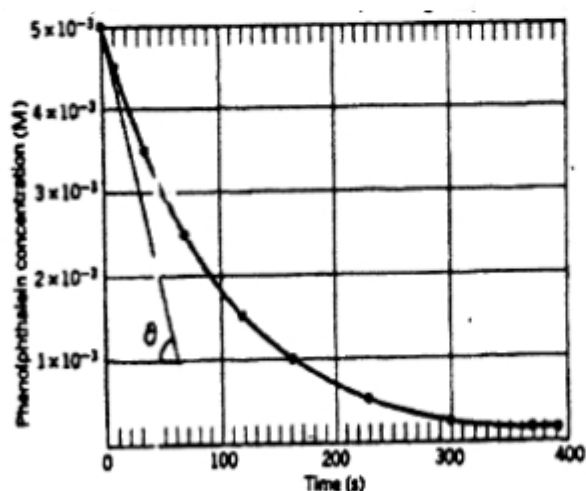
Explanation:

Plot a graph between time on x-axis and concentration of Phenolphthalein on y-axis, following curve will be obtained.

A Plot of concentration versus time for the reaction between

phenolphthalein and excess OH⁻ ions

Draw tangent to the curve through the point at which t = 0 and determine the slope of the line. Slope is equal to initial rate (see figure).
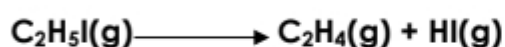

A Plot of concentration versus time showing tangent to the curve when t=0

for the reaction between phenolphthalein and excess OH⁻ ions

$$Slope = \frac{\Delta x}{\Delta t}$$
$$= \frac{4 \times 10^{-3}}{60}$$
$$6.67 \times 10^{-5} \, mole \, dm^{-3} . s^{-1}$$

Ethyl Iodide decomposes at a certain temperature as follows

$C_2H_5I(g) \longrightarrow C_2H_4(g) + HI(g)$

From the following data determine the initial rate of decomposition:

| Time(min)	[C₂H₅I] (M)
0	0.36
15	0.30
30	0.25
48	0.19
75	0.13

Solution:

(i) Plot a graph between time and concentration of C_2H_5I take time on on x-axis and concentration of C_2H_5I on y-axis following curve will be obtained.
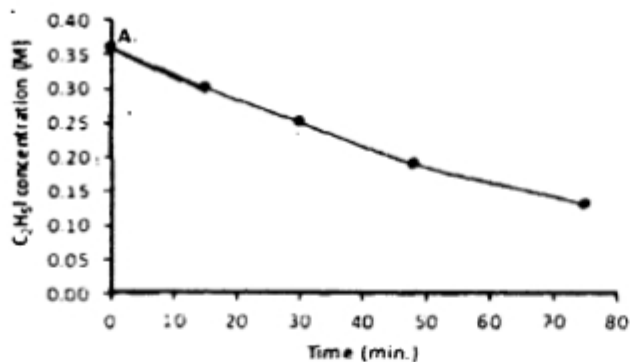
(ii) Draw tangent to the curve through the point at which t = 0 and determine the slope of the line. The slope of line is equal to initial rate.

$$Slope = \frac{\Delta x}{\Delta t} = \frac{0.36 - 0.23}{30 - 0} = 4.33 \times 10^{-3} mole \ dm^{-3}.min^{-1}$$
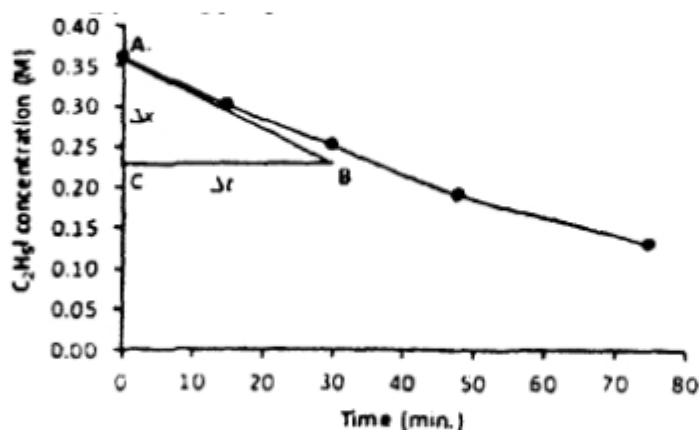
Q6. **Explain zero order, first order and second reactions with the help of examples.**

Ans: **Zero order reaction:**

A reaction that is independent of the concentration of reactant molecules is called zero order reaction.

Examples:

i.   An example is the decomposition of ammonia on heated tungsten.

9

$$2NH_{3(g)} \longrightarrow N_{2(g)} + 3H_{2(g)}$$

$$\text{Rate} = k\,[NH_3]^0$$

The concentration of ammonia decreases at a steady rate until it reaches zero.

ii.   The combination of H_2 and Cl_2 in presence of sunlight is also a zero order reaction.

iii.   The reactions catalyzed by enzymes also follow zero order kinetics.

First order reactions.

A reaction whose rate of reaction is directly proportional to the first power of concentration of single reaction molecule is called first order reaction.

$$\text{Rate} \propto [A]^1$$

Examples:

i)   Thermal decomposition of N_2O_5

$$2N_2O_{5(g)} \longrightarrow 2N_2O_{4(g)} + O_{2(g)}$$

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

ii)   Decomposition of ammonium nitrite in aqueous solution

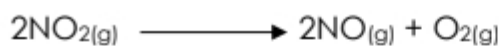$$NH_4NO_2 \longrightarrow N_2 + 2H_2O$$

$$\text{Rate} = k\,[NH_4NO_2]$$

Second order reactions:

A reaction for which sum of exponents of rate equation is two is called second order reaction.

$$\text{Rate} \propto [A]^2 \text{ or Rate} \propto [A]^1\,[B]^1$$

Examples:

i.   Decomposition of nitrogen dioxide.

$$2NO_{2(g)} \longrightarrow 2NO_{(g)} + O_{2(g)}$$

$$\text{Rate } = k\,[NO_2]^2$$

ii. $$NO_{(g)} + O_{3(g)} \longrightarrow NO_{2(g)} + O_{2(g)}$$

$$\text{Rate} = k\,[NO][O_3]$$

$$\text{Order of reaction} = 1 + 1 = 2$$

iii. $$2NO_{2(g)} + O_{3(g)} \longrightarrow N_2O_{5(g)} + O_{2(g)}$$

$$\text{Rate} = k\,[NO_2][O_3]$$

Q7.   Explain third order, fractional order and negative order reactions with the help of examples,

Ans: Third order reactions:

A reaction for which sum of exponents of rate equation is three is is called third order reaction.

$$\text{Rate} \propto [A]^3 \text{ or Rate} \propto [A]^2[B]^1 \text{ or Rate} \propto [A]^1\,[B]^1[C]^1$$

Examples:

i.   The oxidation of NO by O_2 is an example of a third order reaction.

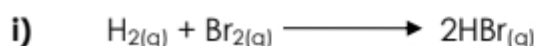$$2NO_{(g)} + O_{2(g} \longrightarrow 2NO_{2(g)}$$

$$\text{Rate} = k\,[NO]^2\,[O_2]$$

ii. $$2FeCl_{3(q)} + 6KI_{(aq)} \longrightarrow 2FeI_{2(aq)} + 6KCl_{(aq)} + I_{2(s)}$$

$$\text{Rate} = k\,[FeCl_3]\,[KI]^2$$

Fractional order reactions:

Examples:

i) $$H_{2(q)} + Br_{2(q)} \longrightarrow 2HBr_{(q)}$$

Rate = $k[H_2] [Br_2]1/2$

Order of reaction is $1 + 0.5 = 1.5$

ii. $CHCl_{3(l)} + Cl_{2(g)} \longrightarrow CCl_{4(l)} + HCl_{(g)}$

Rate = $k [CHCl_3][Cl_2]1/2$

Negative order reaction:

Example: $2O_{3(g)} \longrightarrow 3O_{2(g)}$

Rate = $k [O_3]^2[O_2]^{-1}$

$2H_2 + 2NO \longrightarrow N_2 + 2H_2O$

Solution: Given: $H_2 = $ Rate $\propto [H_2]$

NO = Rate $\propto [NO]^2$

Rate $\propto [H_2][NO]^2$

Rate = $k [H_2][NO]^2$

$=1+2=3$.

Important information

the atmospheric nitrogen, (N^{14}) to produce radioactive C^{14}

carbon dioxide, $^{14}CO_2$. The half-life of this decay is 5.75×10^3 years.

Example 9.1:

Jet engines release Nitrogen (II) oxide in the upper atmosphere. In the ozone layer of upper atmosphere Nitrogen (II) oxide reacts with ozone to form nitrogen (IV) oxide and oxygen.

$$NO(g) + O_3(g) \longrightarrow NO_2(g) + O_2(g)$$

The following data was obtained for this reaction at 25°C.

Experiment	Initial [NO]	Initial [O₃]	Initial rate (mole dm⁻³s⁻¹)
1	1.00×10^{-6}	9.00×10^{-6}	1.98×10^{-4}
2	2.00×10^{-6}	9.00×10^{-6}	3.96×10^{-4}
3	1.00×10^{-6}	3.00×10^{-6}	6.60×10^{-5}

Use this data to determine the rate law for the reaction.

Solution:

To determine the order of reaction with respect to a reactant, we examine the relationship between initial concentration and the rate of reaction while holding the concentration of the other reactant constant

Experiments 1 and 2:

in experiments 1 and 2 initial concentration of ozone is kept constant at

9.00×10^{-6} from 1.00×10^{-6} M to 2.00×10^{-6} M: increases from 1.98×10^{4} to 3.96×10^{-4} moles dm⁻³s⁻¹

M. the initial rate increases from 198x10 to 3.99x10 moles dm's' The ratio between these two rates is

$$1.98 \times 10^{-4} : 3.96 \times 10^{-4}$$
$$\frac{1.98 \times 10^{-4}}{1.98 \times 10^{-4}} : \frac{3.96 \times 10^{-4}}{1.98 \times 10^{-4}}$$
$$1 : 2$$

Rate $\propto$ [NO]

Experiments 1 and 3:

In experiments 1 and 3 initial concentration of NO is kept constant at 1.00×10^{-6} i.e. and concentration of ozone is decreased to one third from 9.00×10^{-6} to 3.00×10^{-6} M. The initial rate decreases from 1.98×10^{-4} to 6.60×10^{-5} moles $dm^{-3}s^{-1}$. The ratio between these rates is

$$1.98 \times 10^{-4} : 6.60 \times 10^{-5}$$

$$\frac{1.98 \times 10^{-4}}{1.98 \times 10^{-4}} : \frac{6.60 \times 10^{-5}}{1.98 \times 10^{-4}}$$

$$1 : \frac{1}{3}$$

Conclusion:

Thus the rate of reaction also decreases one third. This means the rate of reaction is directly proportional to the first power of concentration of Os

Rate $\propto [O_3]$

Rate $\propto [NO] [O_3]$

Thus, the rate law for the reaction is Rate < (NO) (O) Hence in s reaction is a second order reaction,

Example 9.2:

The following reaction is first order in H_2 and half order in Br_2 write rate law for the reaction

$$H_2 + Br_2 \longrightarrow 2HBr$$

Solution: Given information indicates that

Rate $\propto [H_2]$ --------(i)

Rate $\propto [Br_2]^{1/2}$ --------(ii)

Combining (i) and (ii)we get the rate for the reaction

Rate $\propto [H_2][Br_2]^{1/2}$

Rate $= k [H_2][Br_2]^{1/2}$

1. Phosgene is a toxic gas. It has been used in World War II. This gas is prepared by the reaction of carbon monoxide with chlorine.

1. $CO(g) + Cl_2 (g) \longrightarrow COCl_2(g)$
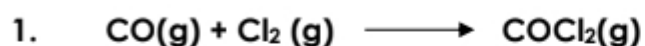
The following data were obtained for kinetic study of this reaction.

Experiments	Initial [CO]	Initial [Cl$_2$]	Initial rate (moles dm^{-3} s^{-1})
1	1.000	0.100	1.29×10^{-29}
2	0.100	0.100	1.30×10^{-30}
3	0.100	1.000	1.30×10^{-30}

Experiments 1 and 2:

In Experiments 1 and 2 initial concentration of Cl2 is kept constant at O 100 M. The concentration of CO is decreased ten times ie, from 1.29×10^{-29} to 1.30×10^{-30} mole dm^{-3}s^{-1}

The ratio between these two rates is

1.29×10^{-29} 1.30×10^{-30}

$\dfrac{1.29 \times 10^{-29}}{1.29 \times 10^{-29}}$ $\dfrac{1.30 \times 10^{-30}}{1.29 \times 10^{-29}}$

1 $\dfrac{1}{10}$

Conclusion:

Thus, the rate of reaction also decreases ten times when concentration of CO is decreased ten times. This means that the rate of reaction is directly proportional to the first power of concentration of CO

Thus **Rate $\propto$ [CO]**

Experiments 2 and 3:

in Experiments 2 and 3, initial concentration of CO is kept constant at 0.100 M The concentration of Cl, is increased ten times ie from 0.100 M to 1.000 M The initial rate remains constant at 1.30×10^{-30} mole $dm^{-3}s^{-1}$.

Conclusion:

This means that the ratio between them does not change and thus the rate is independent of concentration of CO.
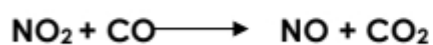
Rate $\propto$ $[Cl_2]^0$

Rate $\propto$ $[CO][Cl_2]^0$

Rate = k [CO]

Hence it is a first order reaction

2.   **The following reaction is second order in NO_2 and is independent of the concentration of CO. Write rate law for the reaction. What is the overall order of the reaction?**

$NO_2 + CO \longrightarrow NO + CO_2$

The given information shows that

Rate $\propto$ $[CO]^0$ ....(1)

Rate $\propto$ $[NO_2]^2$ ....(2)

Combining (1) and (2)we have

Rate $\propto$ $[CO]^0 [NO_2]^2$ Or Rate k $[NO_2]^2$

Hence it is a second order reaction.

29. Explain in detail the various factors which can affect the rate of reactions.

Ans: Factors Affecting Rate of Reactions:

All the factors, which change the number of effective collisions per second, affect the rate of a chemical reaction. Some of the important factors are as follows

1) Nature of Reactants:

Chemical reactivity:

i. The chemical reactivity of elements is based on their electronic configurations

ii. Alkali metals have one electron in their outer most orbital.

iii. They are highly electropositive, react with water violently as compared to alkaline earth metals.

iv. Alkaline earth metals have two electrons in their outermost s-orbital and are less electropositive than alkali metals.

Ionic and covalent reactions:

Reactants having ionic bonds undergo faster reactions than those having covalent bonds.

Reason:

This is because ionic reactions involve the combination of opposite ions, without involving rearrangement of electronic cloud. Whereas the reaction between covalent molecules involves electronic redistribution, proceed slowly.

2) Concentration of Reactants:

The rate of a chemical reaction depends upon the collisions among the reacting molecules.

The frequency with which the molecules collide depend upon their concentrations.

iii. This fact is expressed by the law of Mass Action.

iv. It states that the rate of chemical reaction is proportional to the product of

molar concentration of the reactants.

vi. Hence, the higher the concentration, the greater the rate of reaction.

Examples:

i. A mixture of H_2 and Cl_2 will react twice as fast if the partial pressure of H_2 and Cl_2 is doubled in the presence of excess of the other component.

ii. Combustion occurs more rapidly in pure oxygen than in air (21% oxygen).

iii. Limestone ($CaCO_3$) reacts al different rales with different concentrations of HCl. Quantitatively the effect of concentration on reaction rate is expressed by order of the reaction with respect to each reactant.

3) Surface Area:

The basic concept of collision theory is that reactant particles atoms, ions and molecules must collide with each other in order to react.

The rate of a reaction increases with increasing surface area of reactants.

Reason:

This is because increased surface area of reactants increases the possibilities of contacts between their particles. Finely divided solid, therefore react more rapidly than its big pieces.

Examples:

i. **Powdered zinc reacts more rapidly with dil HCl than a large piece of zinc.**

$$Zn_{(s)} + 2HCl_{(aq)} \longrightarrow ZnCl_{2(aq)} + H_{2(g)}$$

The reason is that powdered zinc exposes a greater surface area to collide with HCl molecules.

This increases the number of collisions between the reacting particles, since rate of a chemical reaction depends upon the collision among the reacting molecules. Thus increase in number of collisions increase the reaction rate. Hence powdered zinc reacts faster.

ii. For the same reason aluminium foil reacts with NaOH moderately on warming but powdered aluminium reacts rapidly with cold NaOH.

$$2Al_{(s)} + 2NaOH_{(aq)} + 6H_2O_{(l)} \longrightarrow 2Na[Al(OH)_4]_{(aq)} + 3H_{2(g)}$$

4) Temperature:

i. Reaction rates generally increase with the increase in temperature.

ii. According to the collision theory, the rate of a reaction is proportional to the number of collisions among the reactant molecules.

iii. An increase in temperature increases the average kinetic energy of the molecules This increases average speed of reacting molecules.

iv. An increase in kinetic energy of reactant molecules increases the collision frequency i.e. the number of effective collisions and hence the reaction rate However, only effective collisions bring about the reaction.

Conditions for effective collision:

For a collision to be effective molecules must possess

i. The activation energy

ii. Must be properly oriented

Maxwell Boltzmann curve of kinetic energy:

i. At ordinary temperature very few molecules possess the energy of activation

ii. All the molecules of a reactant do not possess the same energy at a particular temperature.

iii. Most of them possess average energy.

iv. A fraction of molecules have kinetic energy more than the average energy.

v. The number of molecules having at least kinetic energy equal to Ea at temperature Tis proportional to the shaded area under the Maxwell Boltzmann curve of kinetic energy.

vi. As the temperature is increased the area of the shaded region increases and more molecules have kinetic energy greater than Ea.

vii. An increase in temperature increases the number of reactants molecules that have enough energy for effective collision.

viii. It is found that in general the reaction rate increases two to three folds for each 10K increase in temperature.
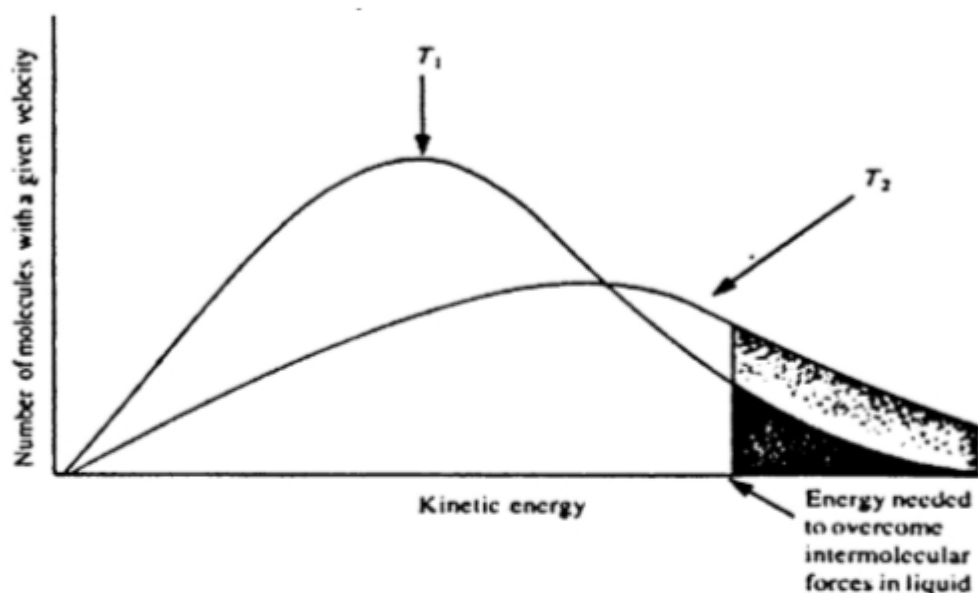
Q11. Explain Arrhenius equation and also give its applications.

Ans: Arrhenius (1889) studied the effect of temperature on read found that the effect of temperature on rate of reaction is given by the following equation. This equation is known as Arrhenius equation

Mathematically: $k = Ae^{-Ea/RT}$

K = rate constant,

Ea is energy of activation,

R is the gas constant ($R = 8.3143 JK^{-1}mole^{-1}$).

A is constant known as Arrhenius constant

It is related with the frequency of collision and orientation of the reacting molecules Therefore, rate constant k varies with the temperature it increases with temperature which in turn increases rate of reaction.

Applications:

i. The Arrhenius equation can be used to understand the role of rate constant in the theoretical determination of reaction rates.

ii. This equation can be used to calculate rate constants for a reaction at different temperatures.

iii. The factor by which a rate constant increases with the increase in temperature is also the factor by which rate of reaction increases.

iv. This is because the rate of a reaction is proportional to the rate constant.

Activity

Calculate the factor by which the rate of the following reaction will increase as a result of increase in temperature from 37°C to 47° C. The activation energy for the reaction is 106 K).

$$C_{12}H_{22}O_{11} (aq) + H_2O(l) \longrightarrow C_6H_{12}O_6 (aq) | + C_6H_{12}O_6 (aq)$$

Solution:

Glucose Fructose

Solution: Using the Arrhenius equation, derive an equation for the ratio of rate constants k_1 at temperature T_1 and k_2 al temperature T_2. For this purpose write the Arrhenius equation at two temperatures

$$k_1 = Ae^{\frac{Ea}{RT_1}} \qquad ....(1)$$

$$k_2 = Ae^{\frac{Ea}{RT2}} \qquad ....(2)$$

Divide equation (2) by the equation (1)

$$\frac{k_2}{k_1} = \frac{Ae^{\frac{Ea}{RT_2}}}{Ae^{\frac{Ea}{RT_1}}}$$

$$\frac{k_2}{k_1} = \frac{e^{\frac{Ea}{RT_2}}}{e^{\frac{Ea}{RT_1}}}$$

$$\frac{k_2}{k_1} = e^{\frac{Ea}{RT_2} + \frac{Ea}{RT_1}}$$

$$\frac{k_2}{k_1} = e^{\left(\frac{Ea}{RT_1} - \frac{Ea}{RT_2}\right)}$$

Take natural logarithm of both sides

$$In\frac{k_2}{k_1} = Ine^{\left(\frac{Ea-Ea}{RT_1 \ RT_2}\right)}$$

$$In\frac{k_2}{k_1} = \frac{Ea}{RT_1} - \frac{Ea}{RT_2}$$

Convert natural logarithm into common logarithm

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

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

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

E_a = 106KJ mole^{-1}

   =106x10^{3}Jmole^{-1}

R=8.314Jmole^{-1}K^{-1}

T_1=37^{0}C+273=310K

T_2=47^{0}C+273=320K

$$\log \frac{k_2}{k_1} = \frac{106 \times 10^3}{2.303 \times 8.314}\left(\frac{320-310}{310 \times 320}\right)$$

$$\log \frac{k_2}{k_1} = \frac{106000}{2.303 \times 8.314}\left(\frac{10}{310 \times 320}\right)$$

$$\log \frac{k_2}{k_1} = 0.5581$$

$$\frac{k_2}{k_1} = Anti\log 0.5581$$

$$\frac{k_2}{k_1} = 3.6$$

Conclusion:

As the factor by which the ratio of rate constants increases as a result of 10°C increase in temperature is also the ratio of increase in reaction rates. Thus the rate of reaction at 47° C is 3.8 times the rate of 37°C.

Q12. Briefly explain rate determining step with the help of example.

Ans: Rate Determining Step:

"The slowest step of a reaction mechanism which determines the overall rate of reactions called as rate determining step."

Explanation:

The path followed by the reactants in forming the products in a chemical reaction is called the mechanism. The rate equation for a reaction is very useful because it provides information about the mechanism of the reaction. A reaction may occur in a single step or in many steps. Wren the reaction proceeds through two or more steps one of the steps is the slowest.

Reason:

The rate of the slowest step determines the overall rate of reaction This is because places a limit on the rate at which the overall reaction can occur. No

reaction can proceed faster than the rate-determining step All the other steps of the reaction mechanism are generally fast.
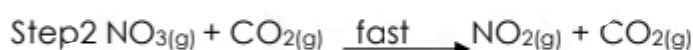
Example:

For react on

$$NO_{2(g)} + CO_{(g)} \longrightarrow NO_{(g)} + CO_{2(g)}$$

$$Rate = k[NO_2]^2$$

The rate equation gives us following information

1) The reaction is second order with respect to NO, and zero with respect to CO. Therefore it is independent of the concentration of CO.

ii) Two molecules of NO are involved in the rate-determining step.

iii) Reaction must proceed n more than one step.

The proposed mechanism for the reaction is as follows

Step1 $NO_{2(g)} + NO_{2(g)} \xrightarrow{\text{slow}} NO_{3(g)} + NO_{(g)}$

Step2 $NO_{3(g)} + CO_{2(g)} \xrightarrow{\text{fast}} NO_{2(g)} + CO_{2(g)}$

Reaction intermediate:

The first step is the rate determining step Species NO, that does not appear in the overall reaction and is consumed during the course of reaction and is called reaction intermediate.

example also proves that a balanced chemical equation may rot give any information about the reaction mechanism.

Example9.4:

Hypochlorite ionClO$^-_3$in aqueous solution decomposes to chlorate ion ClO$^-_3$ and chloride ion

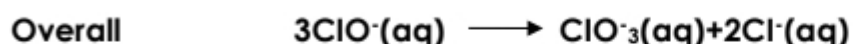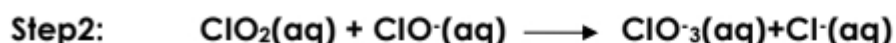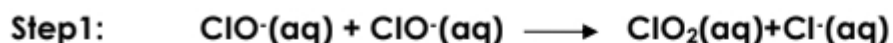$$3ClO^-(aq) \longrightarrow ClO_3^- + 2Cl^-$$

The rate of the reaction is second order in **ClO$^-_3$** ion

Rate = k [ClO$^-$]^2

The following two-step mechanism is consistent with the rate law for the reaction.

Step1: $ClO^-(aq) + ClO^-(aq) \longrightarrow ClO_2(aq) + Cl^-(aq)$

Step2: $ClO_2(aq) + ClO^-(aq) \longrightarrow ClO_3^-(aq) + Cl^-(aq)$

**Overall** $3ClO^-(aq) \longrightarrow ClO_3^-(aq) + 2Cl^-(aq)$

Identify the rate-determining step.

Solution:

Rate law for this reaction indicates that two ClO ions must participate in the rate determining step. Therefore Step is the rale-determining step in this mechanism.

Example 9.5:

Rate $=k[NO_2][O_3]$ for the following reaction indicates that one molecule of NO, and one molecule ot o, participate in the determining step

$2NO_2(g) + O_3 \longrightarrow N_2O_5(g) + O_2(g)$
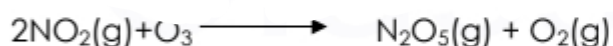
Thus rate law includes the concentration of each of the reactants raised to the power that equals the coefficient for the reactant in the equation for the rate-determining step
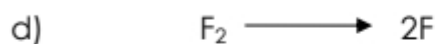
For the following reaction,

$2NO_2(g) + F_2(g) \longrightarrow 2NO_2F(g)$

Rate = k[NO] (F2]

Which of the following mechanism is consistent with the rate law?

a) $2NO_2 + F_2 \longrightarrow 2NO_2F$

b) $\quad NO_2 + F_2 \longrightarrow NO_2F + F$

$\quad NO_2 + F \longrightarrow NO_2F$

c) $\quad NO_2 + F_2 \longrightarrow NO_2F + F$

$\quad NO_2 + F \longrightarrow NO_2F$

d) $\quad\quad\quad F_2 \longrightarrow 2F$

$\quad 2NO_2 + 2F \longrightarrow 2NO_2F$

Solution:

The rate equation shows that in the slowest step (rate determining step), one molecule of NO_2 and ore molecule of F_2 will participate thus option c correspond to the rate equation. Hence mechanism (c) is correct for this reaction

Example 9.6:

NO reacts with Hy according to the following equation:

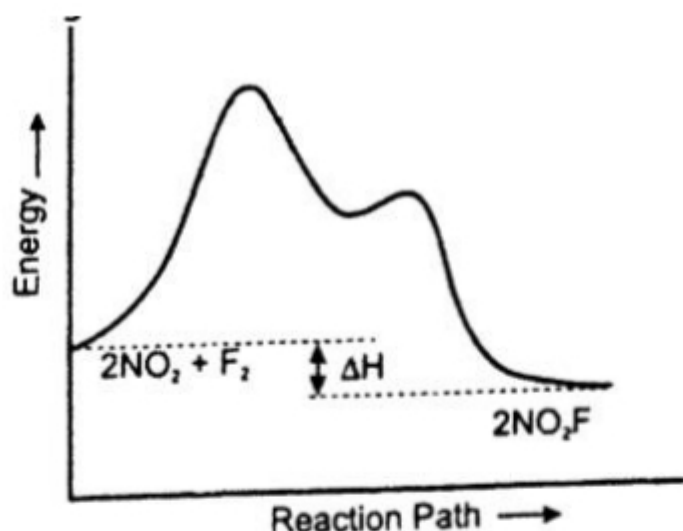$2NO(g) + 2H_2(g) \longrightarrow N_2(g) + 2H_2O(g)$

The mechanism for this reaction involves two steps:

$2NO + H_2 \longrightarrow N_2 + H_2O_2$

$H_2O_2 + H_2 \longrightarrow 2H_2O$

What is the experimental rate law for this reaction?

Potential Energy Diagram and Reaction Mechanism:

Potential energy diagram for the reaction between NO_2 and F_2

Example 9.7:

Potential energy diagram for the reaction between NO, and F is given below:

The experimental rate law for this reaction is given below:

Reaction:

$$2NO_2(g) + F_2(g) \longrightarrow 2NO_2F(g) \quad Rate=k[NO_2][F_2]$$

Propose reaction mechanism.

Solution:

Step 1: Determine the number of elementary steps

As potential energy diagram shows two peaks. the reaction mechanism must involve two elementary steps.

Step 2: Identify the rate determining step

As activation energy for step 1 is higher than step 2. Therefore, step 1 will be slow and rate determining step.

Step 3: Use rate law to determine the number of molecules involved in the rate-determining step Given rate law suggests that one molecule of NO, and one include of F:are involved in this step.

Step 4: Propose two elementary steps for the mechanism. In the overall reaction two molecules of NO, and one molecule of F2 react to form two molecules of NO F But

in the rate determining step only one NO, molecule and one F, molecule must react to form one NO, and a reaction intermediate. In the second elementary step reaction intermediate must react with another molecule of NO, to form another molecule of NO, F (A species which is formed during a chemical reaction in one step and is consumed in another step is called reaction intermediate).

Thus proposed mechanism is,

$$NO_2 + F_2 \longrightarrow NO_2F + F$$

$$NO_2 + F \longrightarrow NO_2F$$

Step 5: Add the two steps to get the overall reaction which must be same as the reaction under consideration.

$$NO_2 + F_2 \longrightarrow NO_2F + F$$

$$NO_2 + F \longrightarrow NO_2F$$

_____

$$2NO_2 + F_2 \longrightarrow 2NO_2F$$

Since sum of elementary steps give the reaction under consideration, the proposed mechanism may be acceptable

SELF-CHECK EXERCISE 9.5

1. The following data was collected for the reaction between H, and NO at 700° C.

$$2H_2 + 2NO \longrightarrow 2H_2O + N_2$$

Experiment	[H$_2$]	[NO]	Initial rate (moles dm^{-3}s^{-1})
1	0.010	0.025	2.4x10^{-6}
2	0.0050	0.025	1.2x10^{-6}

3		0.010	0.0125	0.6x10⁻⁶

Suggest a plausible mechanism that is consistent with the rate law. (Hint: assume the oxygen atom is reaction intermediate). Potential energy diagram for this reaction is given below.
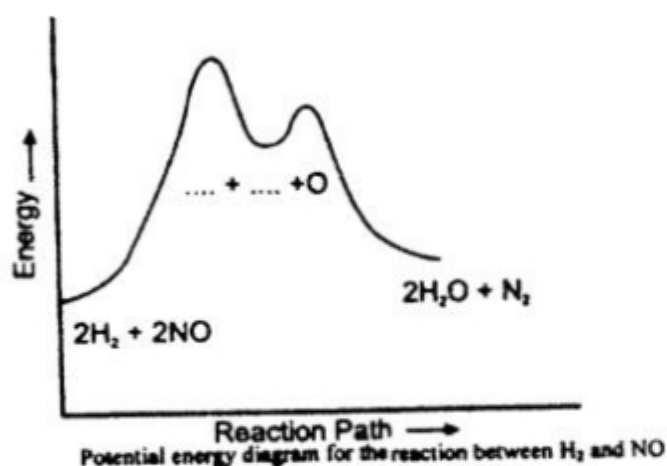
Potential energy diagram for the reaction between H_2 and NO

Experiments 1 and 2:

in Experiments 1 and 2, initial concentration of NO is kept constant at 0.025 M. The concentration of H2 is decreased to one half from 0.010 M 10 0.0050 M. The initial rate decreases from 2.4×10^{-6} to 1.2×10^{-6} mole dm⁻³s⁻¹

The ratio between these two rates is

$$\frac{2.6 \times 10^{-6}}{2.4 \times 10^{-6}} \qquad \frac{1.2 \times 10^{-6}}{1.2 \times 10^{-6}}$$

$$\frac{2.4 \times 10^{-6}}{2.4 \times 10^{-6}} \qquad \frac{1.2 \times 10^{-6}}{2.4 \times 10^{-6}}$$

$$1 \qquad \frac{1}{2}$$

Conclusion:

Thus, the rate of reaction decreases to one half when concentration of H_2 is decreased to one half It shows that the rate of reaction is directly proportional to the first power of concentration of H_2

Rate $\propto H_2$

Experiments 1 and 3:

in Experiments 1 and 3, initial concentration of Hy is kept constant at 0.010

M and concentration of NO is decreased to one half le from 0.025 M to 0.0125 M

The initial rate decreases from 2.4×10^{-6} to 0.6×10^{-6} mole dm^{-3}s^{-1}

The ratio between these rates is

$$\frac{2.6 \times 10^{-6}}{2.4 \times 10^{-6}} \qquad \frac{0.6 \times 10^{-6}}{0.6 \times 10^{-6}}$$

$$\frac{2.4 \times 10^{-6}}{2.4 \times 10^{-6}}$$

$$1 \qquad \frac{1}{4}$$

Conclusion:

Thus, the rate of reaction decreases to one fourth when concentration of NO

is decreased to one nalf. It shows that the rate of reaction is directly proportional to

the second power of concentration of NO.

Rate $\propto [NO]^2$

Rate law:

The rale law for the reaction is

Rate $\propto [NO]^2[H_2]$

Rate $= k [NO]^2[H_2]$

Overall order of reaction=2+1=3.

Hence it is a third order reaction.

(b) Mechanism:

Step 1: Determine the number of elementary steps.

The potential energy diagram shows two peaks, the reaction mechanism

must involve two elementary steps.

Step 2: Identify the rate determining step.

As activation energy for step 1 is higher than step 2. Therefore, step 1 will be slow and rate determining step.

Step 3: Identify the number of molecules involved in ratio-determining step.

Use rate law to determine the number of molecules involved in the rate determining step Rate law suggests that two molecules of NO and one molecule of Hy are involved in this step.

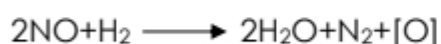Step 4: Propose elementary steps for the mechanism.

The overall reaction shows that two molecules of NO and one molecules of H_2 react to form products. However, the rate law equation shows the determining step two molecules of NO and one molecule of Hy is involved. Thus the mechanism may be written in two steps as given below.

In one elementary step, 2 molecules of NO react with 1 molecule of Hz to for 2 molecules of H2O, one molecule of Na and one oxygen atom. This is the slow rate determining step. In second step, one molecule of H2 reacts with one atom of oxygen to give one molecule of water. This is the fast step.

Atomic oxygen is the intermediate in the reaction.
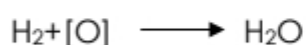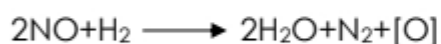
$$2NO+H_2 \longrightarrow 2H_2O+N_2+[O]$$

$$H_2+[O] \longrightarrow H_2O$$

Step5: Add the two steps to get the overall reaction.

$$2NO+H_2 \longrightarrow 2H_2O+N_2+[O]$$

$$H_2+[O] \longrightarrow H_2O$$

_____

$$2NO+2H_2 \longrightarrow 2H_2O+N_2$$

Since sum of elementary steps give the reaction under consideration, the proposed mechanism may be acceptable.

2. Following mechanism has been proposed for a reaction.
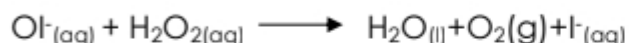
$H_2O_2(aq) + I^-(aq) \longrightarrow H_2O_{(l)} + OI^-_{(aq)}$

$OI^-_{(aq)} + H_2O_{2(aq)} \longrightarrow H_2O_{(l)} + O_2(g) + I^-_{(aq)}$
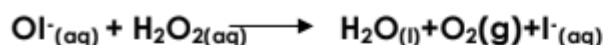
Identify catalyst, reaction intermediate and rate determining step.

Solution:

Add the two half reactions

$H_2O_2(aq) + I^-(aq) \longrightarrow H_2O_{(l)} + OI^-_{(aq)}$

$OI^-_{(aq)} + H_2O_{2(aq)} \longrightarrow H_2O_{(l)} + O_2(g) + I^-_{(aq)}$

_____

$2H_2O_2(aq) \longrightarrow H_2O(l) + O_2(g)$

Reaction intermediate:

The Orion is produced and consumed during the course of reaction and is not appeared in the net reaction Hence OI⁻ ion is the reaction intermediate
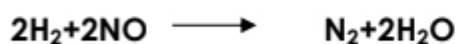
Rate-determining steps:

Without experimental rate law we cannot suggest the rate determining step.
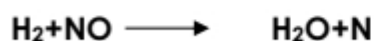
Catalyst:

The I' ion is used as a reactant in the first step but regenerates in the last step and is not consumed in the reaction. Thus, I ion is the catalyst.

3. The rate law for the following reaction

$2H_2 + 2NO \longrightarrow N_2 + 2H_2O$

$Rate = k[H_2][NO]^2$

Is the following mechanism is consistent with the rate law? Give reason.

$H_2 + NO \longrightarrow H_2O + N$

$N + NO \longrightarrow N_2 + O$

$O + H_2 \longrightarrow H_2O$

Solution:

The rate equation shows that there must be 2 molecules of NO and one molecule of H_2 in the slowest step (rate-determining step) But there is only one molecule of NO in the slowest step (rate-determining step). Thus the above mechanism is incorrect.

4. The rate law for the reaction,

$$2N_2O \longrightarrow 2N_2 + O_2$$

Rate = k[N_2O] Reaction occurs in two elementary steps. Assume o atom as a reaction intermediate, Write mechanism for the reaction.

Solution:

According to the rate equation slowest and the fast step will be

$$N_2O \longrightarrow N_2 + [O]$$

$$N_2O + [O] \longrightarrow N_2 + O_2$$
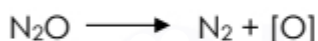
Mechanism:

Add the two steps to get the overall reaction.

$$N_2O \longrightarrow N_2 + [O]$$

$$N_2O + [O] \longrightarrow N_2 + O_2$$

_____

$$2N_2O \longrightarrow 2N_2 + O_2$$

Q13. Explain collision theory, transition state and activation energy.

Ans: Collision Theory:

Chemical reactions involve the breaking and making of chemical bonds

These changes are accompanied by changes in energies.

Collision theory has been proposed to explain the observed kinetics of

reactions.

Conditions for a chemical reaction:

i. For a chemical reaction to occur, the combining atoms or molecules must collide with one another. These collisions may be effective or ineffective depending upon the energy and orientation of the colliding particles.

ii. The effective collision can take place only if the energy of the colliding particles is high enough to overcome the repulsion between electrons around the reacting particles.

iii. Proper orientation means that at the time of collision, the atoms which are required to make new bonds should collide with each other.

Activation Energy:

The minimum amount of energy, in addition to the average kinetic energy, which the particles must possess for effective collisions, is called activation energy.

Explanation:

The reaction will not occur if the energy of reacting particles in less than activation energy.
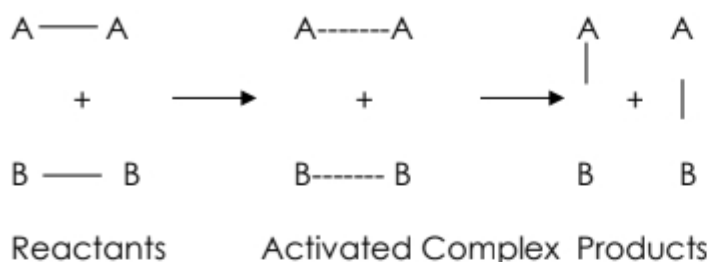
Thus the rate of a reaction depends upon its energy of activation. The greater the activation energy, the lesser will be the rate of reaction. This is because only a small fraction of molecules possesses enough energy to react. On the other hand, it activation energy is small then a large number of molecules can bring about effective collisions Hence, higher will be the rate of reaction.

Consider a reaction between Az and B, molecules to form a new molecule AB

If these molecules possess energy equal to or more than the activation energy, then upon collisions their bands will break and new bonds will be formed

Activated complex or Transition state:

In an effective collision the molecules form an unstable species called activated complex. Since it is high an energy species, it is short lived and quickly breaks down to the products. Activated complex is also called a transition state

```
A —— A          A------A          A    A
                                        |
   +       ⟶       +      ⟶     +  |
                                             
B —— B          B------ B         B    B
```

Reactants   Activated Complex Products

Effective collision of molecules.

Explanation of effective collision:

in an effective collision the colliding molecules come close to each other slow down just before collisick Their kinetic energy decreases and this results in the corresponding increase in their potential energy. The activation energy appears as a hill between reactants and products. Molecules must first climb the energy barrier before they can roll down the hill to form products Only the colliding molecules with proper activation energy do so. On the other hand if they lack proper activation energy, they will be unable to reach the top of the hill and fall back chemically unchanged

Potential energy diagram for exothermic reaction:

The potential energy diagram can also be used to understand the enthalpy changes in chemical reactions. The heat of reaction is equal to the difference of energies of reactants and products in an exothermic reaction product are at a lower energy level than the reactants. In both exothermic and endothermic reactors activation energy (Ea) is an energy barrier which must be crossed over before the products can be formed of energy of activation is not available to the reacting particles, the reaction will not start.

Potential energy diagram for endothermic reaction:

In endothermic reactions a continuous source of energy is needed to complete the reaction.

In an endothermic process the products are at higher energy level than the reactants.

Fig shows energy profile for exothermic and endothermic reactions

Energy

(a)   Reaction path →   (b)   Reaction path →
(a) Exothermic reaction   (b) Endothermic reaction
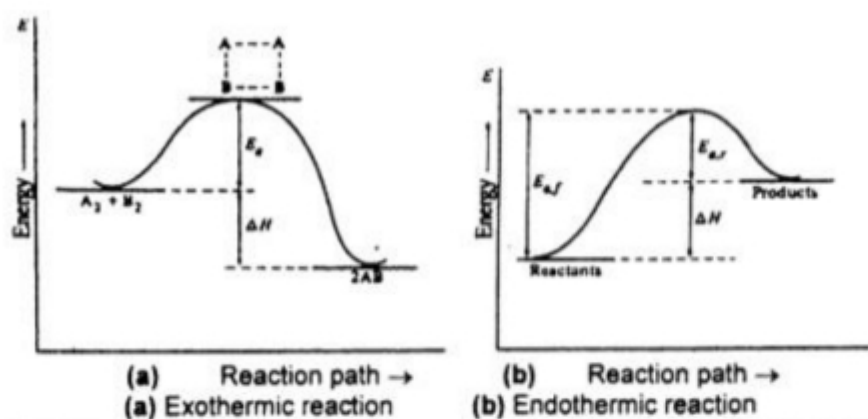
Q14. Write a note on catalyst how can the increase the rate of reaction?

Ans: Catalysis:

A substance which accelerates a chemical reaction but remains chemically unchanged all the end of a reaction is-called as catalyst.


Effect of Catalyst on energy of activation
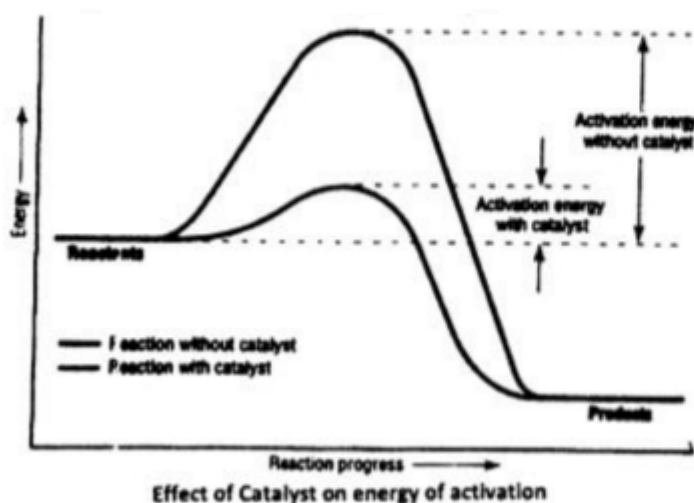
Explanation:

A catalyst provides a new mechanism for the reaction with low energy of activation. Thus catalyst increases the rate of reaction by decreasing if energy of activation. A catalyst has no effect on the total thermodynamic or enthalpy of the
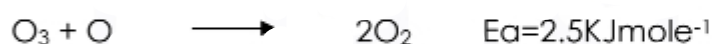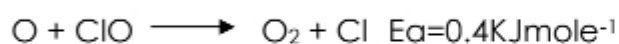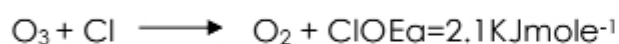
reaction. For this reason, a catalyst cannot be used to bring about a chemical reaction, which is not favored thermodynamically
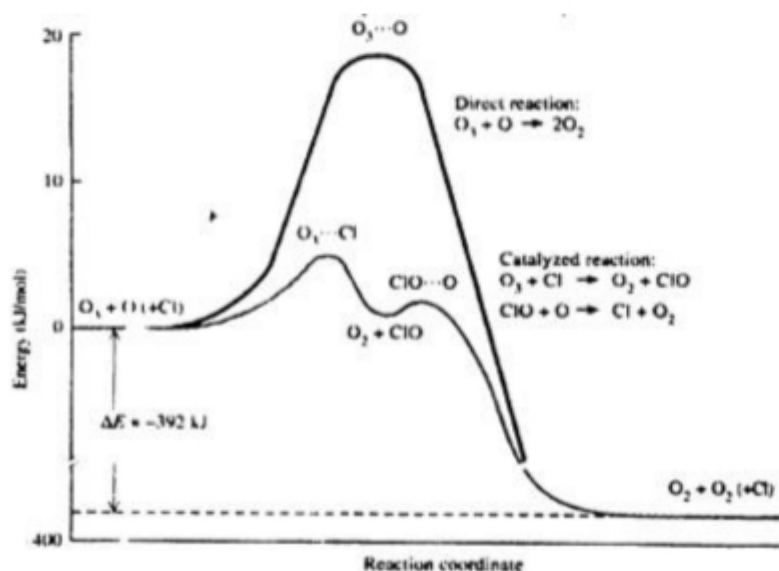
Example:

In the stratosphere, conversion of an ozone molecule by an oxygen atom into two O, molecules occur. This reaction has higher energy of activation,

$$O_3 + O \longrightarrow 2O_2 \quad E_a = 17.1 KJmole^{-1}$$
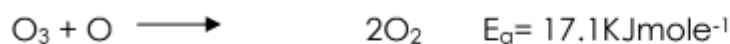
Chlorofluorocarbon compounds diffuse up into the stratosphere. These compounds absorb short wave length ultraviolet light from the sum, that breaks carbon-chloride bords and produce chlorine atoms. Ci atom catalyze the mechanism requiring less energy of activation.

$$O_3 + Cl \longrightarrow O_2 + ClO \quad E_a = 2.1 KJmole^{-1}$$

$$O + ClO \longrightarrow O_2 + Cl \quad E_a = 0.4 KJmole^{-1}$$

$$O_3 + O \longrightarrow 2O_2 \quad E_a = 2.5 KJmole^{-1}$$

It shows that the direct reaction between o, and has a substantially higher activation energy than the chlorine catalyzed reaction sequence.

Energy level diagram for the decomposition of ozone in the stratosphere.

Q15. Explain the following terms in detail with the help of examples.

Homogeneous catalysis.

ii. Heterogeneous catalysis.
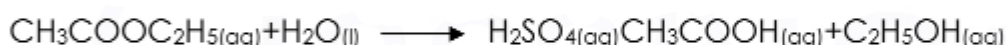
Ans: i. Homogeneous catalysis:

A catalysis in which the catalyst and the reactants are in the same phase is known as homogeneous catalysis, a metal halide or a metal oxide.

Examples of homogeneous catalysis:

In the lead chamber process for the manufacture of sulphuric acid, NO gas catalyzes oxidation of SO_2 gas

$$2SO_{2(g)} + O_{2(g)} \underset{}{\overset{NO_{(g)}}{\rightleftharpoons}} 2SO_{3(g)}$$

ii) Hydrolysis of esters is catalyzed by H_2SO_4

$$CH_3COOC_2H_{5(aq)} + H_2O_{(l)} \xrightarrow{} H_2SO_{4(aq)} CH_3COOH_{(aq)} + C_2H_5OH_{(aq)}$$

iii) An aqueous solution of sucrose is stable for years provided that bacterial growth is inhibited But when a small amount of an enzyme sucrase is added to the sucrose solution, it is rapidly converted to glucose and fructose

$$C_{12}H_{22}O_{11}(aq) + H_2O\ (l) \xrightarrow{sucrase} C_6H_{12}O_6(aq) + C_6H_{12}O_6(aq)$$

iv) in the upper atmosphere nitric oxide s responsible for the depletion of ozone It catalyzes the decomposition of ozone
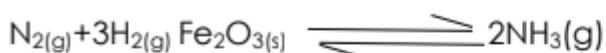
$$2O_3(g) \xrightarrow{} NO(g) \quad 3O_2(g)$$

**ii. Heterogeneous catalysis:**

The catalysis, in which catalyst and the reactants are in different phases, is known as heterogeneous catalysis. Heterogeneous catalysis often contains transition metals as pure metals.
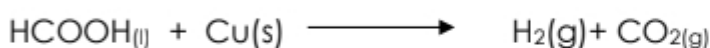
Examples of heterogeneous catalysis:

i) in the manufacture of ammonia, finely divided Fe_2O_3 is used as catalyst

$$N_{2(g)} + 3H_{2(g)} \xrightarrow{Fe_2O_{3(s)}} 2NH_3(g)$$

ii) in contact peaces for the manufacture of H_2SO_4 oxidation of $SO_2(g)$ is catalyzed by $V_2O_5(s)$

$$2SO_{2(g)} + O_{2(g)} \xrightarrow{V_2O_5(s)} 2SO_{3(g)}$$
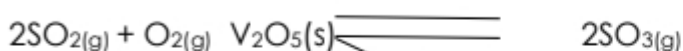
iii) Formic acid decomposes into H_2O and CO in presences of Al_2O_3 but it decomposes into H2 and CO in presence of Cu.

$$HCOOH_{(l)} + Al_2O_3(s) \longrightarrow H_2O_{(l)} + CO_{(g)}$$

$$HCOOH_{(l)} + Cu(s) \longrightarrow H_2(g) + CO_{2(g)}$$

iv) The petroleum, plastic and food industries use catalytic hydrogenation to change the great variety of compounds into more useful substances The conversion of vegetable oil into margarine is one example. Finally,

$$\text{Vegetable Oil (l)} + H_2(g) \xrightarrow{Ni/Pt/Pd(s)} \text{Margarine(s)}$$

SELF-CHECK EXERCISE 9.6

Most of new cars are equipped with catalytic converters in exhaust system. These converters contain Pt or Pd or transition metal oxide such as CuO or Cr2O3, as catalyst. It oxidizes co and unburnt a gasoline to CO2 and H2O.
It also reduces NO and NO, to N, and Oz. Identify type of catalysts.
Solution:
In these reactions reactants are in gases state and the catalyst are in solid state Therefore, these reactions are the example of heterogeneous catalysis.

Q16. Explain the term enzymes.

Ans: **Enzymes:**

These are biochemical catalysts i.e, substances that increase the rate of chemical reactions within living things.

Most of the chemical reactions that occur in living organisms are regulated by molecules called enzymes.

Explanation:

Enzymes like catalysts are not consumed during chemical reactions, Virtually all reactions in living cells are catalyzed by enzymes. An enzyme is a specialized protein that catalyzes specific biochemical reaction. Each enzyme catalyzes only one reaction.

Occurrence:

Most of the enzymes are found inside the cells. However, some are found in extra cellular fluids such as saliva, gastric juice etc.

Enzymes may speed up reactions by a factor of 10"

Constitution of enzymes:

Some enzymes consist of protein only, but most enzymes contain non-protein components such as carbohydrates, lipids, metals, phosphates etc. The complete enzyme is called holoenzyme.

Apoenzyme and co-factor:

The protein part is called apoenzyme and non-protein as co-factor or co-enzyme.

Mechanism of enzyme action:

Enzyme catalysis can be represented by the series of reaction. In the first step, a reactant binds to a specific location on the enzyme called the active site. Hydrogen bonding plays a key role in this binding.

$$E \ + \ R \ \rightleftharpoons \ ER$$
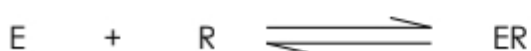
Enzyme   reactant   Enzyme-Reactant Complex

Binding cause chemical changes in the structure of reactants and forms a product species. The enzyme then releases the product and is ready to repeat the process.

$$ER \rightleftharpoons E + P$$

Enzyme-Reactant Complex Enzyme   reactant

Because an enzyme plays a catalytic role over and over and very rapidly, only a tiny amount of enzyme is required.

Q17. Give daily life application of enzymes:

i. Since some enzymes can also act outside the cells, therefore, they can be used commercially

ii. Enzymes are effective in removing stains from fabrics. For this purpose, suitable enzymes that can act on substances that are present in the stains are used. These enzymes decompose components of stains to simpler m which are soluble in water and can be removed by washing with water.

Example:

Enzymes like pepsin, trypsin, lipase, and amylase etc are used to remove food stains from fabrics. The food strain may contain carbohydrates, proteins and fats. Amylase acts on starch, pepsin and trypsin acts on protein and lipase on fats

iii. All these enzymes convert complex water insoluble components of food into simple water-soluble components

SUMMARY OF KEY TERMS

1. The rate of a chemical reaction is a change in the concentration of reactant

or product in the given time the instantaneous rate of reaction is the infinitesimally small change in concentration that occurs over an infinite infinitesimally small period of time.

2. The rate law is an expression that relates the rate of a reaction to the rate constant and the concentration of reactants raise to an appropriate power.
It can only be determined experimentally.

3. Overall reaction order is sum of the powers to which reactant concentrate on are raised in the rate law.

4. A reaction mechanism is the sequence of elementary steps that describe the reaction. The rate of reaction is determined by the slowest elementary step called the rate determining step in the reaction mechanism.

5. The rate of a chemical reaction depends upon the activation energy for the reaction. The rate constant and activation energy are related by the Arrhenius equation

$$k = Ae^{\frac{Ea}{RT}}$$

6. Reaction rates are influence by the catalyst, which change mechanism of the reaction by decreasing energy of activation.

7. In homogenous catalysis, the catalyst and the reactant are in the same phase whereas in heterogeneous catalysis the catalyst and reactants are in different phases.

8. Enzymes are catalysts in living organism.