3. Chemical Kinetics and Catalysis

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Chemical Kinetics and Catalysis.

History of Chemical Kinetics:-

In 1864, Peter Waage and Cato Guldberg pioneered the development of chemical kinetics by formulating the law of mass action, which states that the speed of a chemical reaction is proportional to the quantity of the reacting substances Van 't Hoff studied chemical dynamics and in 1884 published his famous **"Études de dynamique chimique"**.In 1901 he was awarded by the first Nobel Prize in Chemistry "in recognition of the extraordinary services he has rendered by the discovery of the laws of chemical dynamics and osmotic pressure in solutions". After van't Hoff, chemical kinetics deals with the experimental determination of reaction rates from which rate laws and rate constants are derived. The activation energy for a reaction is experimentally determined through the Arrhenius equation and the Eyring equation. The main factors that influence the reaction rate include: the physical state of the reactants, the concentrations of the reactants, the temperature at which the reaction occurs, and whether or not any catalysts are present in the reaction.

Scope of chemical kinetics:-

Chemical kinetics is the study of the rates and the mechanism of chemical reactions. Commonly the measure of how fast the products are formed and the reactants consumed is given by the rate values. Chemical kinetics is the study of the rates and the mechanism of chemical reactions. **Chemical kinetics** is an important phenomenon in physical **chemistry**. The term **kinetics** is referred to as the study of motion. It is a study of **chemical** reaction with respect to reaction rates, effect of different variables such as temperature and concentration.

Chemical kinetics is the study of the rates and the mechanism of chemical reactions. Commonly the measure of how fast the products are formed and the reactants consumed is given by threated values. The study of chemical kinetics has been highly useful in determining the factors that influence the rate, maximum yield and conversion in industrial processes. The mechanism or the sequence of steps by which the reaction occurs can be known. It is also useful in selecting the optimum conditions for maximum rate and yield of the chemical process. One reason for the **importance** of **kinetics** is that it provides evidence for the mechanisms of **chemical** processes. Besides being of intrinsic scientific interest, knowledge of reaction mechanisms is of practical use in deciding what is the most effective way of causing a reaction to occur.

Rate of reaction:-

The speed or **rate** of a **chemical reaction** is the change in concentration of a reactant or product per unit time. To be specific, it can be expressed in terms of: the **rate** of decrease in concentration of any of the reactants.The **rate** of increase in the concentration of any of the products.
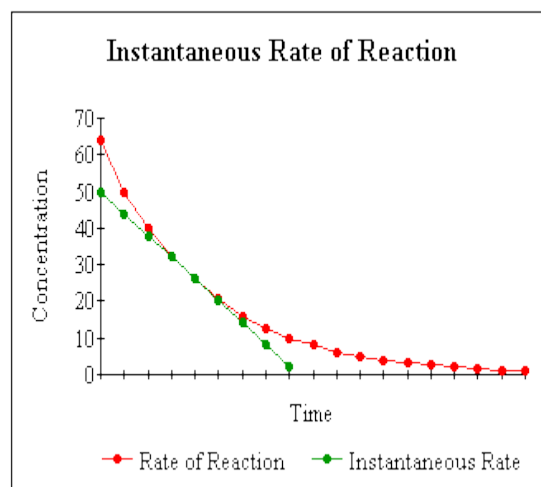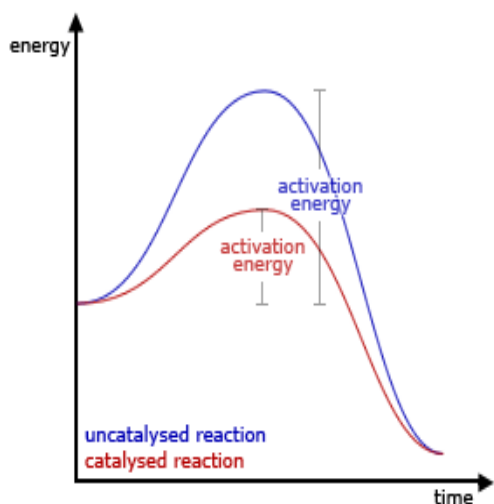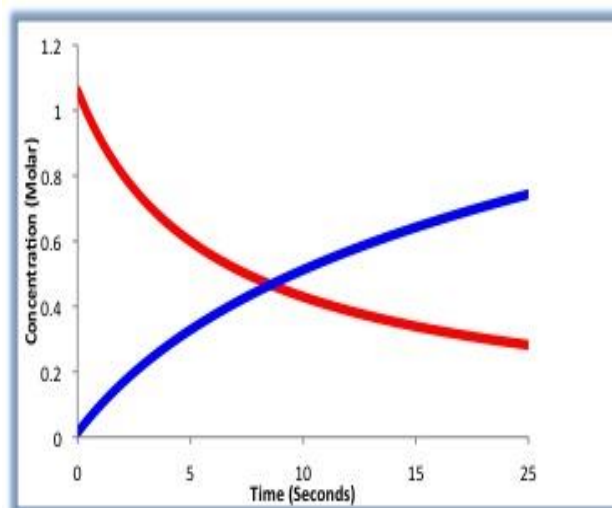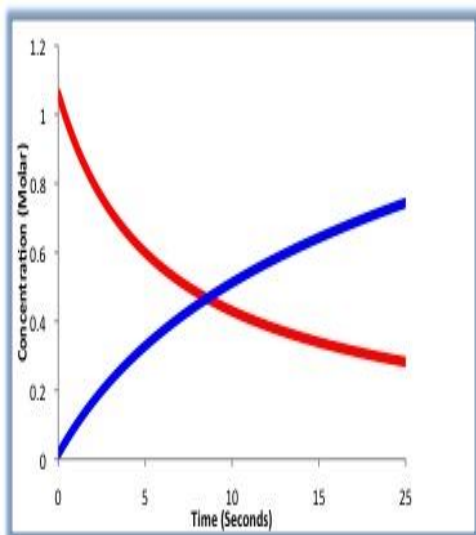
For example, the oxidative rusting of iron under Earth's atmosphere is a slow reaction that can take many years, but the combustion of cellulose in a fire is a reaction that takes place in fractions of a second. For most reactions, the rate decreases as the reaction proceeds.

Order of Reaction:-

The **Order of Reaction** refers to the power dependence of the rate on the concentration of each reactant. Thus, for a first-**order reaction**, the rate is dependent on the concentration of a single species. ... The **order of reaction** is an

experimentally determined parameter and can take on a fractional value. The Order of Reaction refers to the power dependence of the rate on the concentration of each reactant. Thus, for a first-order reaction, the rate is dependent on the concentration of a single species. A second-order reaction refers to one whose rate is dependent on the square of the concentration of a single reactant. The rate of a first-order reaction is dependent solely on the concentration of one species in the reaction.

Some characteristics of the reaction order for a chemical reaction are listed below.

- Reaction order represents the number of species whose concentration directly affects the rate of reaction.
- It can be obtained by adding all the exponents of the concentration terms in the rate expression.
- The order of reaction does not depend on the stoichiometric coefficients corresponding to each species in the balanced reaction.
- The reaction order of a chemical reaction is always defined with the help of reactant concentrations and not with product concentrations.
- The value of the order of reaction can be in the form of an integer or a fraction. It can even have a value of zero.

In order to determine the reaction order, the power-law form of the rate equation is generally used. The expression of this form of the rate law is given by $r = k[A]^x[B]^y$.

In the expression described above, 'r' refers to the rate of reaction; 'k' is the rate constant of the reaction, [A] and [B] are the concentrations of the reactants.

The exponents of the reactant concentrations x and y are referred to as partial orders of the reaction. Therefore, the sum of all the partial orders of the reaction yields the overall order of the reaction..

Molecularity of Reaction:-

The **molecularity** of an elementary **reaction** is defined as the minimum number of molecules, atoms or ions of the reactants(s) required for the **reaction** to occur and are equal to the sum of the stoichiometric coefficients of the reactants in the chemical equation of the **reaction**.

In general, molecularity of simple reactions is equal to the sum of the number of molecules of reactants involved in the balanced stoichiometric equation or..

The molecularity of a reaction is the number of reactant molecules taking part in a single step of the reaction.

$PCl_5 \rightarrow PCl_3 + Cl_2$	Unimolecular
$2HI \rightarrow H_2 + I_2$	Bimolecular
$2SO_2 + O_2 \rightarrow 2SO_3$	Trimolecular
$NO + O_3 \rightarrow NO_2 + O_2$	Bimolecular
$2CO + O_2 \rightarrow 2CO_2$	Trimolecular
$2FeCl_3 + SnCl_2 \rightarrow SnCl_2 + 2FeCl_2$	Trimolecular

Order of a reaction	Molecularity of a reaction
1. It is the sum of powers raised on concentration terms in the rate expression.	1. It is the number of molecules of reactants taking part in elementary step of a reaction.
2. Order of a reaction is an experimental value, derived from rate expression.	2. It is a theoretical concept.
3. Order of a reaction can be zero, fractional or integer.	3. Molecularity can neither be zero nor fractional.
4. Order of a reaction may have negative value.	4. Molecularity can never be negative.
5. It is assigned for overall reaction.	5. It is assigned for each elementary step of mechanism.
6. It depends upon pressure, temperature and concentration (for pseudo order)	6. It is independent of pressure and temperature.

Note:

- Molecularity is a theoretical concept.
- Molecularity cannot be zero, -ve, fractional, infinite and imaginary.
- Molecularity cannot be greater than three because more than three molecules may not mutually collide with each other.

Factors influencing the rate of reaction:-

A) Physical state:

The physical state (solid, liquid, or gas) of a reactant is also an important factor of the rate of change. When reactants are in the same phase, as in aqueous solution, thermal motion brings them into contact. However, when they are in separate phases, the reaction is limited to the interface between the reactants. Reaction can occur only at their area of contact; in the case of a liquid and a gas, at the surface of the liquid. Vigorous shaking and stirring may be needed to bring the reaction to completion. This means that the more finely divided a solid or liquid reactant the greater its surface area per unit volume and the more contact it with the other reactant, thus the faster the reaction. To make an analogy, for example, when one starts a fire, one uses wood chips and small branches — one does not start with large logs right away. In organic chemistry, on water reactions are the exception to the rule that homogeneous reactions take place faster than heterogeneous reactions (are those reactions in which solute and solvent not mix properly)

B) Surface area of solid state

In a solid, only those particles that are at the surface can be involved in a reaction. Crushing a solid into smaller parts means that more particles are present at the surface, and the frequency of collisions between these and reactant particles increases, and so reaction occurs more rapidly. For example, Sherbet (powder) is a mixture of very fine powder of malic acid (a weak organic acid) and sodium hydrogen carbonate. On contact with the saliva in the mouth, these chemicals quickly dissolve and react, releasing carbon dioxide and providing for the fizzy sensation. Also, fireworks manufacturers modify the surface area of solid

reactants to control the rate at which the fuels in fireworks are oxidized, using this to create diverse effects. For example, finely divided aluminum confined in a shell explodes violently. If larger pieces of aluminum are used, the reaction is slower and sparks are seen as pieces of burning metal are ejected..

C) Concentration

The reactions are due to collisions of reactant species. The frequency with which the molecules or ions collide depends upon their concentrations. The more crowded the molecules are, the more likely they are to collide and react with one another. Thus, an increase in the concentrations of the reactants will usually result in the corresponding increase in the reaction rate, while a decrease in the concentrations will usually have a reverse effect. For example, combustion will occur more rapidly in pure oxygen than in air (21% oxygen).

The rate equation shows the detailed dependence of the reaction rate on the concentrations of reactants and other species present. The mathematical forms depend on the reaction mechanism.

D) Temperature:-

Temperature usually has a major effect on the rate of a chemical reaction. Molecules at a higher temperature have more thermal energy. Although collision frequency is greater at higher temperatures, this alone contributes only a very small proportion to the increase in rate of reaction. Much more important is the fact that the proportion of reactant molecules with sufficient energy to react (energy greater than activation energy: $E > E_a$) is significantly higher and is explained in detail by the Maxwell–Boltzmann distribution of molecular energies.

The effect of temperature on the reaction rate constant usually obeys the Arrhenius equation where 'A' is the pre-exponential factor or A-factor, 'E_a is the activation energy, 'R' is the molar gas constant and 'T' is the absolute temperature

E) Catalyst:-

A catalyst is a substance that alters the rate of a chemical reaction but it remains chemically unchanged afterwards. The catalyst increases the rate of the reaction by providing a new reaction mechanism to occur with lower activation energy. In autocatalysis a reaction product is itself a catalyst for that reaction leading to positive feedback. Proteins that act as catalysts in biochemical reactions are called enzymes. A catalyst does not affect the position of the equilibrium, as the catalyst speeds up the backward and forward reactions equally.

In certain organic molecules, specific substituent's can have an influence on reaction rate in neighboring group participation. Increasing the **concentration** of a reactant increases the frequency of collisions between reactants and will, therefore, increase the **reaction rate**.

F) Pressure:-

Increasing the pressure in a gaseous reaction will increase the number of collisions between reactants, increasing the rate of reaction. This is because the activity of a gas is directly proportional to the partial pressure of the gas. This is similar to the effect of increasing the concentration of a solution.

In addition to this straightforward mass-action effect, the rate coefficients themselves can change due to pressure. The rate coefficients and products of

many high-temperature gas-phase reactions change if an inert gas is added to the mixture.

G) Absorption of light:-

The activation energy for a chemical reaction can be provided when one reactant molecule absorbs light of suitable wavelength and is promoted to an excited state. The study of reactions initiated by light is photochemistry, one prominent example being photosynthesis.

H) Effect of solvent :-

An increase in **solvent** polarity accelerates the **rates of reactions** where a charge is developed in the activated complex from neutral or slightly charged reactant. An increase in **solvent** polarity decreases the **rates of reactions** where there is less charge in the activated complex in comparison to the starting materials.

Zero order reaction :-

A zero-order reaction means that the rate of the reaction is *independent* of the concentration of reactants.

As such, increasing or decreasing the concentration of the reacting species will not speed up or slow down the reaction rate.

Example:- Nitrous oxide will decompose exothermically into nitrogen and oxygen, at a temperature of approximately 575 °C

$$2N_2O \xrightarrow{\Delta,Ni} 2N_2(g) + O_2(g)……………….(1)$$
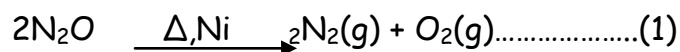
This reaction in the presence of a hot platinum wire (which acts as a catalyst) is zero-order, but it follows more conventional second order kinetics when carried out entirely in the gas phase.

$$2N_2O \rightarrow 2N_2 \, (g) + O_2 \, (g)\dots\dots\dots\dots\dots\dots(2)$$
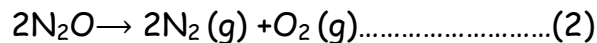
In this case, the N_2O molecules that react are limited to those that have attached themselves to the surface of the solid catalyst. Once all of the sites on the limited surface of the catalyst have been occupied, additional gas-phase molecules must wait until the decomposition of one of the adsorbed molecules frees up a surface site.

Consider a zero order reaction   A   Product

Initial conc.	a	0
Conc. at time t	(a-x)	x

According to law of mass action; Rate α Conc. of reactant

Rate = $-dA/dt = k[A]0 = k$

Where 'Rate' refers to the <u>rate of the reaction</u> and 'k' is the rate constant of the reaction.

This differential form can be rearranged and integrated on both sides to get the required **Integral** form as shown below.

Rate = $-d \, [A]^0 \, dt = k$

Multiplying both sides with '- dt', we get:

$d[A] = -k. \, dt$

Integrating on both sides, we get:

$\int [A]/[A]^0 d[A] = -\int^t_0 k.dt$

Where $[A]_0$ is the initial concentration of the reactant $[A]$ at time t=0 . Solving for $[A]$, we get: $[A] = [A0] - k.t$

This is the required integral form. This form enables us to calculate the population of the reactant at any given time posts the start of the reaction.

Characteristics of Zero order reaction:- 1. If x is plotted against time interval, we get a straight line passing through origin. The slope of line gives zero order constant.

2.The unit of zero order reaction concentration per time.

3.Half time:- It is time required for half the reactant to change into product. Let $t_{1/2}$ is the half-life period. At t = $t_{1/2}$ x = a/2 therefore $t_{1/2}$ = a/2Ko   **or** $t_{1/2}$ is directly proportional to a. thus half life for zero order reaction is proportional to initial concentration.
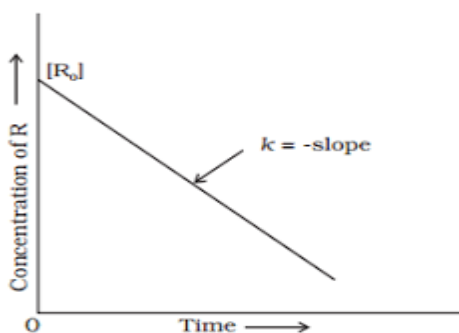
First order reaction:- It is a chemical **reaction** in which the rate of **reaction** is directly proportional to the concentration of the only one reacting substance. Examples are thermal decomposition of nitrous oxide, nitrogen pentaoxide,

acetone,propionic aldehyde,aliphatic ethers,azo compounds etc.

Consider a general reaction   A ————————→ Product

Initial conc.	a	0
Conc. at time t	(a-x)	x

Therefore, Rate law can be written as

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

$$\therefore \frac{dx}{dt} = K(a-x)$$

$$\therefore \frac{dx}{a-x} = K\,dt$$

Integrating within the limit if $x = 0$ to x and t is 0 to t.

$$\int_0^x \frac{dx}{a-x} = \int_0^t K\,dt$$

$$[ln(a-x)]_0^x = K[t]_0^t$$
$$[-ln(a-x) + ln\,a] = K(t-0)$$
$$Kt = ln\,a - ln(a-x)$$

$$K = \frac{1}{t} ln \frac{a}{a-x}$$

$$K = \frac{2.303}{t} log \frac{a}{a-x}$$

where K is the rate constant for first order reaction.

Characteristics of first order reaction:-

1) If log a/a-x against't' is plotted, a straight line passing through origin is obtained.

2) First order rate constant is expressed I terms of per time.

3) Half life period:- The time required to convert half of the reaction into its product is called half life period. Consider 'a' is the initial concentration, 'x' is the equilibrium concentration and t1/2 is the half-life period, then at t=$t_{1/2}$, x=a/$_2$ substituting in the rate expression for first order, K=2.303/t log a/a-x

= 2.303/$t_{1/2}$ log a/a-a/2 <u>or</u> $t_{1/2}$=2.303/K log a/a/2

= 2.303×log 2, therefore t1/2=0.693/K

As above expression does not contain initial concentration, half life period for first order reaction is independent of 'a'

Second order reaction:- Examples of second order reactions are,thermal dissociation of HI, nitrogen dioxide, ozone, chlorine monoxide, nitrosyl chloride, formaldehyde etc. The simplest kind of **second-order** reaction is one whose **rate** is proportional to the square of the concentration of one reactant. ... A **second** kind of **second-order** reaction has a reaction **rate** that is proportional to the product of the concentrations of two reactants.

Consider a general reaction A+B ————————→Product

Initial conc.	a	a	0
Conc. at time t	(a-x)	(a-x)	x

The rate law can be written as, dx/dt=K[A][B] , Therefore dx/dt= K(a-x)(a-x)

$$\frac{dx}{dt} = K (a-x)^2$$

$$\therefore \quad \frac{dx}{(a-x)^2} = K \, dt$$

Integrating above equation within the limit 0 to x and 0 to t

$$\int_0^x \frac{dx}{(a-x)^2} = K \int_0^t dt$$

$$\left[\frac{-1}{a-x}\right]_0^x = K \, [t]_0^t$$

$$\therefore \left(\frac{+1}{a-x}\right) - \left(\frac{+1}{a}\right) = K \, (t-0)$$

$$\frac{+1}{a-x} - \frac{1}{a} = K t$$

$$K t = \frac{-1}{a} + \frac{1}{a-x}$$

$$= \frac{a-(a-x)}{a\,(a-x)}$$

$$K t = \frac{a-a+x}{a\,(a-x)}$$

$$\therefore \quad K = \frac{1}{t} \frac{x}{a\,(a-x)}$$

Case II: - Consider a general reaction $\qquad$ A + B $\longrightarrow$ Product

Initial conc.	a	b	0
Conc. at time t	(a-x)	(b-x)	x

$$\therefore \frac{dx}{dt} = K\,(a-x)\,(b-x)$$

$$\frac{dx}{(a-x)\,(b-x)} = K\,dt$$

Spliting into partial fractions. we get

$$\frac{1}{(a-b)}\left[\frac{dx}{(b-x)} - \frac{dx}{(a-x)}\right] = K.dt$$

Integrating above equation

$$\int_0^x \frac{1}{(a-b)}\left[\frac{dx}{(b-x)} - \frac{dx}{(a-x)}\right] = \int_0^t K.dt$$

$$\therefore \frac{1}{a-b}\left[-\ln(b-x) + \ln(a-x)\right]_0^x = K\,[t]_0^t$$

$$\frac{1}{a-b}\left[-\ln(b-x) + \ln(a-x) + \ln b - \ln a\right] = K\,(t-o)$$

$$\frac{1}{a-b}\left[\ln \frac{b\,(a-x)}{a\,(b-x)}\right] = K\,t$$

$$\therefore K = \frac{2.303}{t(a-b)} \log \frac{b\,(a-x)}{a\,(b-x)}$$

Characteristics of second order reaction:-

1.Rate constant depends on concentration units.

2. Rate is expressed in $(time)^{-1} (Conc.)^{-1}$

3.Half life period is inversely proportional to the initial conc.of the reactants.

Pseudo order reaction: - If the molecularity and order of reaction is different, it is called Pseudo-molecular reaction. Consider a reaction of decomposition of carbonyl sulphide in water is bimolecular and it should be second order reaction but rate is dependent on conc.of carbonyl sulphide and it is first order reactions are called Pseudo molecular reaction.

$$COS + H_2O \longrightarrow CO_2 + H_2S$$
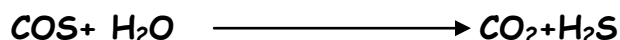
Consider a general reaction and suppose, $A + B \longrightarrow$ Product

Initial conc.	a	b	0
Conc. at time t	(a-x)	b	x

$$A + B \longrightarrow product$$

Initial concentration $\quad a \quad\quad b \quad\quad\quad 0$
conc. at time 't' $\quad\quad (a-x) \quad b \quad\quad\quad x$

Initially 'a' moles of A and 'b' moles of B is taken. After time 't', it is observed that x moles of product is formed. Imagine that the conc. of B remains unaffected during the course of reaction.

Therefore, Assuming the reaction second order, we can write

$$\frac{dx}{dt} = K[A][B]$$

$$\frac{dx}{dt} = K(a-x)b$$

$$\therefore \frac{dx}{(a-x)} = K.b.dt$$

Integrating between the limit 0 to x and 0 to t.

$$\int_0^x \frac{dx}{(a-x)} = \int_0^t Kb \, dt$$

$$[-\ln(a-x)]_0^x = K.b [t]_0^t$$

$$-\ln(a-x)] + \ln a = K.b (t-0)$$

$$\ln a - \ln(a-x) = K.b.t$$

$$\ln \frac{a}{a-x} = Kbt$$

$$K' = K.b = \frac{2.303}{t} \log \frac{a}{a-x}$$

**Effect of temperature on rate of reaction:** - When molecules collide, the kinetic energy of the molecules can be used to stretch, bend, and ultimately break bonds, leading to chemical reactions. If molecules move too slowly with little kinetic energy, or collide with improper orientation, they do not react and simply bounce off each other. However, if the molecules are moving fast enough with a proper collision orientation, such that the kinetic energy upon collision is greater than the minimum energy barrier, then a reaction occurs. The minimum energy requirement that must be met for a chemical reaction to occur is called the activation energy, Ea.

To get to the other end of the road; an object must roll with enough speed to completely roll over the hill of a certain height. The faster the object moves, the more kinetic energy it has. If the object moves too slowly, it does not have enough kinetic energy necessary to overcome the barrier; as a result, it eventually rolls back down.

In the same way, there is a minimum amount of energy needed in order for molecules to break existing bonds during a chemical reaction. If the kinetic energy of the molecules upon collision is greater than this minimum energy, then bond breaking and forming occur, forming a new product (provided that the molecules collide with the proper orientation).

Reaction: $HO^- + CH_3Br \rightarrow [HO\text{---}CH_3\text{---}Br]^{\ddagger} \rightarrow CH_3OH + Br^-$
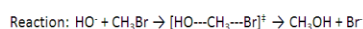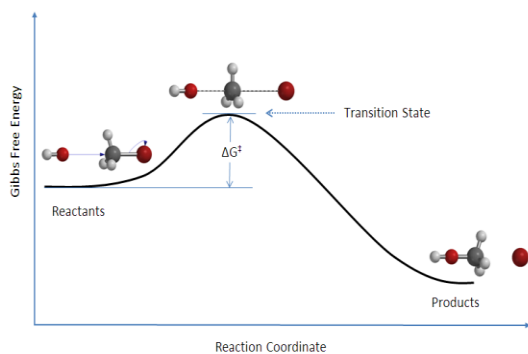
The activation energy (Ea), labeled ΔG‡ in Figure is the energy difference between the reactants and the activated complex, also known as transition state. In a chemical reaction, the transition state is defined as the highest-energy state of the system. If the molecules in the reactants collide with enough kinetic energy and this energy is higher than the transition state energy, then the reaction occurs and products form. In other words, the higher the activation energy, the harder it is for a reaction to occur and vice versa.

Overcoming the energy barrier from thermal energy involves addressing the fraction of the molecules that possess enough kinetic energy to react at a given temperature. According to kinetic molecular theory, a population of molecules at a given temperature is distributed over a variety of kinetic energies that is described by the Maxwell-Boltzman distribution law.

Arrhenius Equation:-

The equation was first proposed by Dutch chemist, J.H. Van't Hoff but Swedish chemist, Arrhenius provided its physical justification and interpretation. The Arrhenius equation is based on the Collision theory. It is not an equation that is born out of pure math that we can derive. It is an empirical equation that fits experimental data in most of the situations. The Arrhenius equation looks like this,

$$k = A\, e^{-E_a/RT} \dots\dots\dots\dots(I)$$

Where 'A 'is the Arrhenius factor or the frequency factor. It is also known as the pre-exponential factor. This constant is specific to a particular reaction. R is the gas constant and E_a is the activation energy which we measure in joules/mole.

According to the Arrhenius equation, a reaction can only take place when a molecule of one substance collides with the molecule of another to form an unstable intermediate. This intermediate exists for a very short time and then breaks up to form two molecules of the product. The energy required to form this intermediate is known as activation energy (E_a).

In a graph of potential energy vs reaction coordinate, the reaction coordinate represents the profile of energy change when reactants change into products. Some of the energy releases when the complex decomposes to form products. Therefore, the final enthalpy of the reactions depends only on the nature of the reactants and products.

Obviously, all the molecules do not have the same energy. The distribution of kinetic energy can be described by plotting the fraction of molecules with given kinetic energy vs kinetic energy. The peak of the curve in the graph corresponds to the most probable kinetic energy. When the temperature increases, the maximum of the curve moves to the higher energy value. Therefore, the curve broadens.
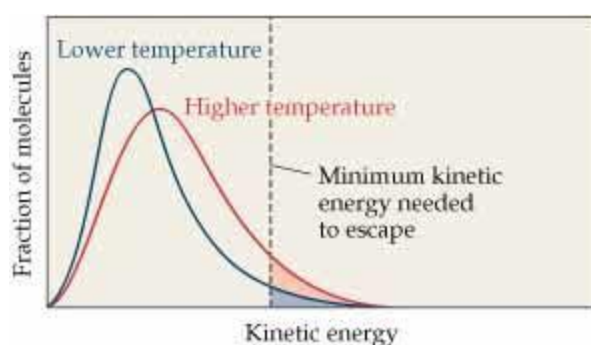
(Source: wps.prenhall.com)

Increasing the temperature increases the fraction of molecules, which collide with energies greater than the activation energy E_a.

Concept of Activation energy:- In chemistry, the minimum amount of energy that is required to activate atoms or molecules to a condition in which they can undergo chemical transformation or physical transport. In transition-state theory, the activation energy is the difference in energy content between atoms or molecules in an activated or transition-state configuration and the corresponding atoms and molecules in their initial configuration. The activation energy is usually represented by the symbol E_a in mathematical expressions for such quantities as the reaction rate constant,

$$k = Ae \times p\, (-E_a/RT), \quad \text{and the diffusion coefficient,}$$

$$D = D_o exp(-E_a/RT).$$ Activation energies are determined from experimental rate constants or diffusion coefficients that are measured at different temperatures.

Definition of Catalysis:- **Catalysis** is the process of increasing the rate of a chemical reaction by adding a substance known as a **catalyst**, which is not consumed in the catalyzed reaction and can continue to act repeatedly. Because of this, only very small amounts of catalyst are required to alter the reaction rate in principle.

Key Takeaways: What Is Catalysis?

- Catalysis is the process of increasing the rate of a chemical reaction by adding a catalyst to it.
- The catalyst is both a reactant and product in the reaction, so it is not consumed.
- Catalysis works by lowering the activation energy of the reaction, making it more thermodynamically favorable.

- Catalysis is important! About 90% of commercial chemicals are prepared using catalysts.

How Catalysis Works ?

A catalyst offers a different transition state for a chemical reaction, with lower activation energy. Collisions between reactant molecules are more likely to achieve the energy required to form products than without the presence of the catalyst. In some cases, one effect of catalysis is to lower the temperature at which a reaction will process. Catalysis does not change chemical equilibrium because it affects both the forward and reverse rate of reaction. It does not change the equilibrium constant. Similarly, the theoretical yield of a reaction is not affected.
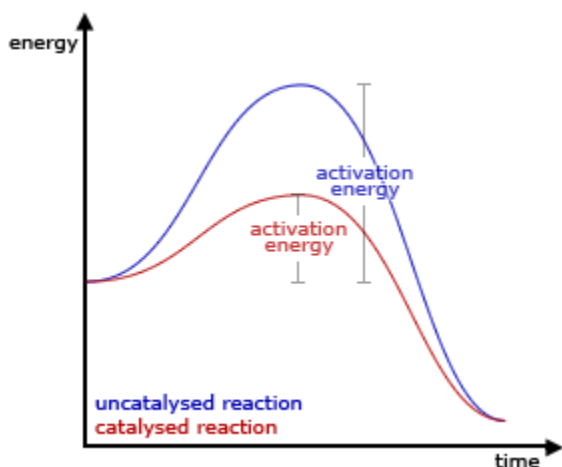

Types of catalysis:- There are several types of catalysts that can be used depending on the need or requirement of the chemical reaction.

1) Positive Catalysts:-

Catalysts which increase the rate of a chemical reaction are positive catalysts. It increases the rate of reaction by lowering the activation energy barriers such that a large number of reaction molecules are converted into products, thereby the percentage of yield of products increases.

Example: In the preparation of NH_3 by <u>Haber's process</u> Iron oxide acts as a positive catalyst and increases the yield of ammonia in spite of less reaction of Nitrogen. $N_2 + 3H_2 \longrightarrow 2NH_3$
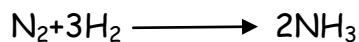
1)Negative Catalysts:- Catalysts which decrease the rate of reaction and negative catalyst. It decreases the rate of reaction by increasing the activation energy barrier which decreases the number of reactant molecules to transform into products and hence the rate of reaction decreases.

Example: Decomposition of Hydrogen peroxide into water and oxygen is retarded by using Acetanilide, these acts as a negative catalyst to decrease the rate of decomposition of hydrogen peroxide.

2)Auto catalyst:- If one of the product formed during a course of reaction acts as catalyst, it is called as auto catalyst. For example, during the oxidation o0f oxalic acid by $KMnO_4$, a small quantity of H_2SO_4 is required. The $MnSO_4$ formed as one of the products accelerates the reaction.

$$KMnO_4 + 5H_2C_2O_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 10CO_2$$

3) Promoter or Accelerators:-

A substance which increases the catalyst activity is known as Promoters or accelerators. **Example**: In Haber's process molybdenum or a mixture of potassium and Aluminium oxides act as Promoters.

4) Catalyst Poisons or Inhibitors:-

Substances which decrease the catalyst activity are known as catalyst poisons or inhibitors. **Example:** In the hydrogenation of alkyne to an alkene, catalyst palladium is poisoned with barium sulphate in quinolone solution and the reaction is stopped at alkene level. The catalyst is known as Lindler's catalyst.

5) Homogeneous Catalyst:-If catalyst and reactants are in same phase,that catalyst is called as homogeneous catalyst.Forexample,in the manfacture of sulphuric acid by lead,nitric oxide is used as catalyst. Hydrolysis of cane sugar is also example of this.

$$2SO_2 + O_2 \xrightarrow{\quad Na \quad} 2SO_3$$
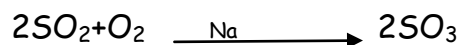
6) Heterogeneous Catalyst:- If catalyst and reactants are in different phase, that catalyst is called as heterogeneous catalyst. For example Manufacture of H_2SO_4, SO_2 is oxidized in presence of Platinum.

Characteristics of Catalyst:-

1.Catalyst remains chemically unaffected at the end of chemical reaction, although there may be change in its physical state such as the particle size or change in the color of the catalyst.

2. Small quantity of a catalyst is required.Eg.1 gm.ion of copper (II) In 10^6 liters can catalyze the oxidation of sodium sulphate by atmospheric oxygen.

3. A catalyst cannot start a chemical reaction.

4. Catalyst does not affect the state of equilibrium; irreversible reaction catalyst accelerates or retards the forward and backward reaction to the same extent. it provides only a alternate path.

5. A catalyst is specific in nature. A substance which acts as catalyst for one reaction may fail to catalyze other reactions.

6. Some catalysts are physically changed by an increase in temp. And hence their catalytic power may be decreased. Hence catalyst has an optimum temp.at which the action of catalyst is maximum.

7. A catalyst is poisoned by inhibitor or catalytic poison and rate may be enhanced by promoters or accelerators.

Enzyme Catalyst and its applications:-

A) Enzymes are the complex protein molecules, often called biocatalysts, which are produced by living cells.

B) They are highly specific and efficient both in the reactions that they catalyze and in their choice of reactants, which are known as substrates.

C) An enzyme typically catalyzes a single chemical reaction or a set of closely related reactions.

D) At optimum temp..rate of reaction for enzyme catalysis is maximum.

E) The rate of enzyme catalyzed reactions varies with PH(optimum PH)

F) Catalytic activity of enzyme can be reduced or destroyed by using other substances.

G) Metal ions Na, Mn etc. forms weak bond with enzymes and promotes catalytic activity, these are called activators.

Some examples of enzyme catalyst are,

1.Urease catalyses the hydrolysis of urea.

2. Pepsin acts as a catalyst for the hydrolysis of peptides.

3. Diastase is used to catalyze starch into maltose.