

WHAT IS RATE OF CHEMICAL REACTION?

The chemical change taking place per unit time is called rate of reaction. mathematically it can be written as

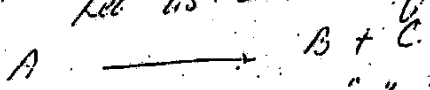
$$\text{Rate of reaction} = \frac{\Delta C}{\Delta t}$$

ΔC = change in concentration, Δt = total time taken for change.

The rate of reaction can be expressed in terms of reactants or in terms of products. The concentration of reactants decreases with passage of time and concentration of products increases.

Thus rate can be defined as: "The decrease in concentration of reactants per unit time" or "The increase in concentration of products per unit time"

Let us consider following general reaction



Let concentration of "A" at time t_1 is $= [A_1]$

concentration of "A" at time t_2 is $= [A_2]$

change in concentration of "A" $= [A_2] - [A_1]$

Time taken for change $= t_2 - t_1$

Thus rate of reaction $= \frac{[A_2] - [A_1]}{t_2 - t_1}$

$$\text{Rate} = - \frac{\Delta [A]}{\Delta t} \text{ moles/l sec}$$

The negative sign shows that concentration of reactants decreases with passage of time.

Rate of the same reaction can be expressed in terms of products "C" & "B"

$$\text{Rate} = \frac{[B_2] - [B_1]}{t_2 - t_1} = \frac{\Delta [B]}{\Delta t}$$

$$\text{Rate} = \frac{[C_2] - [C_1]}{t_2 - t_1} = \frac{\Delta [C]}{\Delta t}$$

In fact $-\frac{\Delta [A]}{\Delta t} = \frac{\Delta [B]}{\Delta t} = \frac{\Delta [C]}{\Delta t}$

The rate of reaction determined between two time intervals t_1 & t_2 is called Average Rate.

INSTANTANEOUS RATES :- The rate of reaction at a specific time is called INSTANTANEOUS RATE.

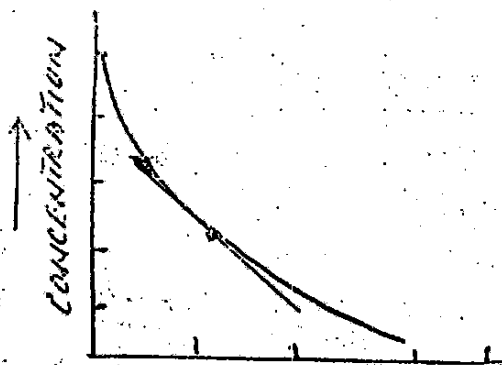
It is generally written as $\frac{dx}{dt}$ or $\frac{dc}{dt}$.
"dx" is very small amount of products produced in very short interval of time "dt". Instantaneous rates are generally expressed by graphic method.

DISCUSS VARIOUS METHODS OF DETERMINING RATES OF REACTION.

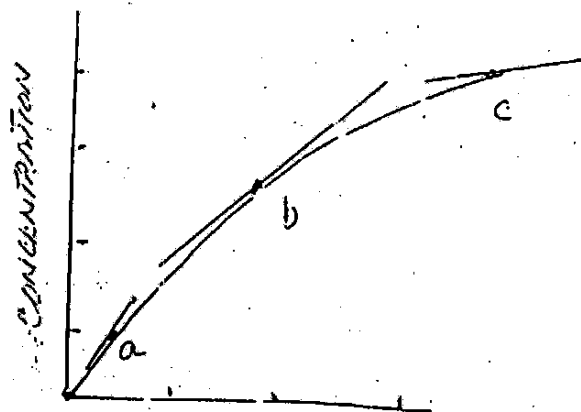
There are several methods for determining rates of reaction. Some commonly used methods are given below.

GRAPHIC METHOD :- (BY CHEMICAL ANALYSIS).

In this method small amounts of reaction mixture is removed from reactor after definite intervals of time. The reaction mixture is analyzed and amount of products and reactants is determined. A graph is plotted between concentration and "t".



CONC. OF REACTANT vs time



CONC. OF PRODUCTS vs time

The rate of reaction at a specific time is determined by drawing a tangent at point of interest.

The slope (dy/dx) of tangent gives the instantaneous rate of reaction.

It is clear from graph that rate is higher in the beginning "part a" and it decreases with passage of time as shown by part "b" and "c". Thus rate of reaction is a constantly changing.

SPECTROSCOPIC METHODS: - These are modern techniques to determine rate of reaction. The names of these techniques are given below.

- (i) ULTRAVIOLET SPECTROSCOPY - "U.V."
- (ii) INFRARED SPECTROSCOPY - "I.R."
- (iii) NUCLEAR MAGNETIC SPECTROSCOPY - "N.M.R."
- (iv) MASS SPECTROSCOPY - "MASS"

CONDUCTIVITY MEASUREMENTS: - When there is change in number of ions going from reactants to products, there is change in conductivity as reaction proceeds. The change in conductivity per unit time also gives the rate of reaction.

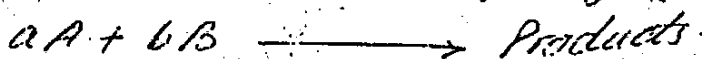
DILATOMETRIC MEASUREMENTS: - When there is change in volume going from reactants to products, the change in volume per unit time also gives rate of reaction. It is called DILATOMETRY.

REFRACTOMETRIC MEASUREMENT: - The change in refractive index ("n") per unit time also gives rates of reaction if there is change in refractive index going from reactants to products.

WHAT IS MEANT BY RATE EXPRESSION? DEFINE RATE CONSTANT OF A REACTION.

An equation which relates rate of reaction with molar concentration of reactants is called RATE EXPRESSION. It actually shows effect of change in concentration of reactants on rate of reaction in a mathematical form.

Let us consider following general reaction:



The rate of reaction is given by law of mass action.

$$\frac{dx}{dt} \propto [A]^m [B]^n$$

$$\frac{dx}{dt} = k[A]^m [B]^n \text{ --- (1)}$$

The equation (1) is called rate expression. "k" is called RATE CONSTANT or VELOCITY CONSTANT.

"m" & "n" may or may not be equal to "a" & "b" respectively. The sum of "m" and "n" is called order of reaction. Rate expression is experimentally

Rate constant: - The rate constant is defined as rate of reaction when molar concentration of reactants is unity. From eq (1)

$$\frac{dx}{dt} [A]^m [B]^n = k$$

If [A]=1 & [B]=1 then $\frac{dx}{dt} = k$

The rate of reaction decreases with passage of time but value of rate constant remains the same throughout the course of reaction.

WHAT IS MEANT BY ORDER OF REACTION? DEFINE FIRST ORDER, SECOND ORDER REACTION.

The order of reaction is defined as "The sum of powers of molar concentration terms involved in rate expression" is called order of reaction.

Let us consider following general reaction $aA + bB \rightarrow \text{Products}$

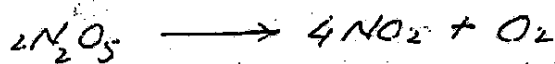
$$\frac{dx}{dt} = k[A]^m [B]^n$$

The equation is called Rate expression. And order of this reaction is = m+n

The "m" & "n" may or may not be equal to "a" & "b" respectively. Let us consider some examples.

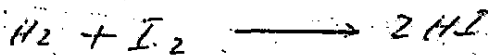
FIRST ORDER REACTION: If rate expression involves one reactant raise to power "1" then

It is first order reaction



$$\text{Rate} = k[\text{N}_2\text{O}_5]$$

SECOND ORDER REACTION: - If sum of powers of molar concentration terms is "2" then it is second order. e.g.



$$\text{Rate} = k[\text{H}_2][\text{I}_2]$$

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

THIRD ORDER REACTION: - If sum of powers of molar concentration terms involved in rate expression is "3" then it is third order reaction. e.g.



$$\text{Rate} = k[\text{NO}]^2[\text{O}_2]$$

$$\text{ORDER} = 2 + 1 = 3$$

HOW TO DETERMINE ORDER & RATE EXPRESSION.

The rate expression and order of reaction is always experimentally determined.

(The reaction whose rate expression and order is to be determined, is started with known concentrations of reactant. The rate of reaction is determined by suitable method (discussed earlier).

Then reaction is carried out again with double amount of reactants and again rate is determined.

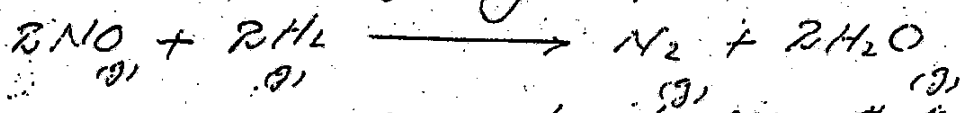
(i) If rate of reaction is doubled by doubling concentration and becomes three times by tripling conc. then reaction is first order w.r. to that reactant.

(ii) If rate of reaction is increased 4-times by doubling concentration, and becomes "9" times by tripling concentration then reaction is second order w.r. to that reactant.

(iii) If rate of reaction increases cube times the change in concentration then it is third order, w.r. to that reaction.

(iv) If there is no change in rate of reaction by change in concentration the reaction is zero order.

EXAMPLE:- Consider following example



From balanced chemical equation it seems that reaction is "FOURTH ORDER" but actually it is THIRD ORDER as shown below.

(i) Rate of reaction is doubled by doubling conc. of Hydrogen and becomes three times by increasing concentration three times. Hence reaction is first order w.r to Hydrogen
Rate $\propto [\text{H}_2]^1$

(ii) Reaction rate becomes four times by doubling conc. of [NO] hence it is second order w.r to [NO]
Rate $\propto [\text{NO}]^2$

Overall rate expression

$$\text{Rate} \propto [\text{H}_2]^1 [\text{NO}]^2$$

$$\text{Rate} = k[\text{H}_2]^1 [\text{NO}]^2$$

ORDER OF REACTION = 1 + 2 = 3

WHAT IS ENERGY OF ACTIVATION?

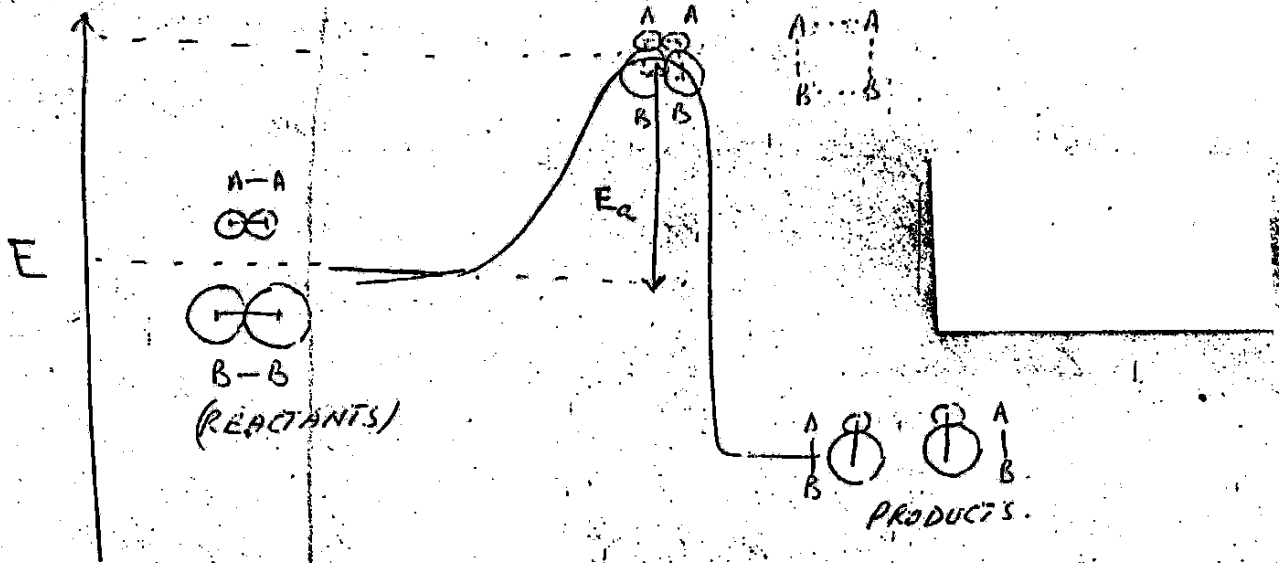
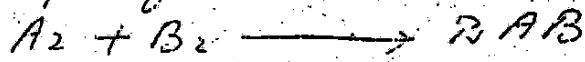
The minimum amount of energy required in addition to average energy of reactants to convert them into product is called Energy of Activation.

For a reaction to take place reactant molecules must collide with one another. But it has been found that collision number is quite high but rate of reaction is quite low. Thus Arrhenius proposed an idea of Activated complex in the form of collision theory.

According to this theory:-

- (i) The reactant molecules must collide with one another for a reaction to take place.
- (ii) All collisions are not fruitful. Only those molecules are converted into products after collision which possess sufficient energy to form activated complex.
- (iii) The molecules must be suitably oriented at the time of collision.

The amount of energy required to form this activated complex is called energy of activation. It is shown by following graph for a reaction

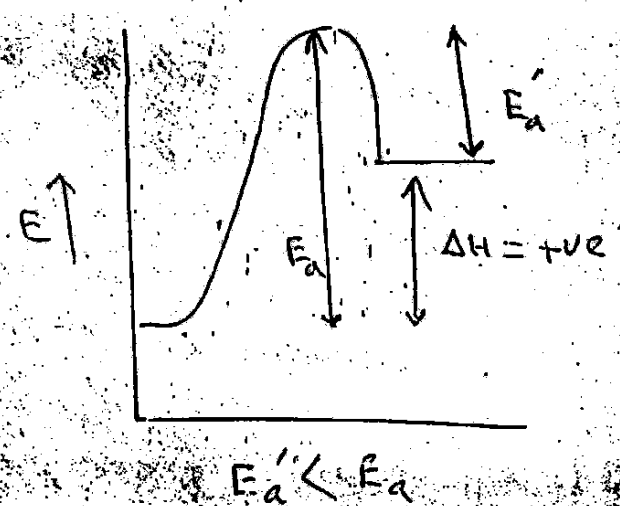
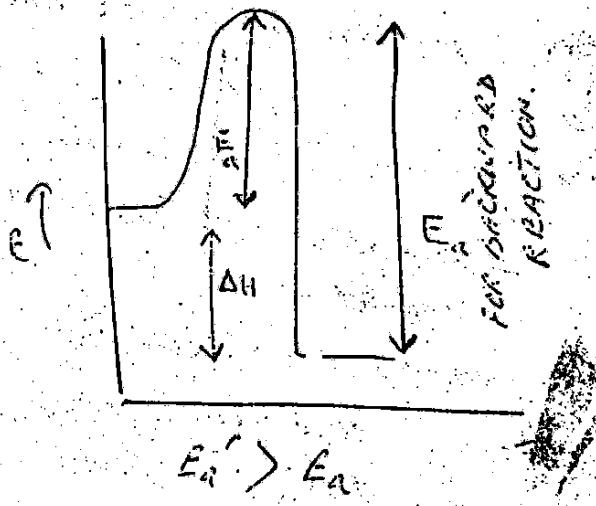


ENERGY OF ACTIVATION & THERMODYNAMICS OF REACTION.

Thermodynamically reactions are divided into two main categories viz Endothermic & Exothermic. These can be explained in terms of Energy of Activation.

EXOTHERMIC REACTION
 In these reactions heat is liberated.
 Energy of activation for forward reaction is less than that for backward reaction in these reactions.

ENDOTHERMIC REACTION
 In these reactions heat is absorbed.
 Energy of activation for forward reaction is greater than that for reverse reaction in these reactions.



The reactions which have high energy of activation proceed at low rate and vice versa. (The reactions having low activation energy proceed at room temp. because reactant molecules acquire energy of activation just by collision with one another. The reactions having high energy of activation proceed on heating)

DISCUSS EFFECT OF TEMPERATURE IN RATE OF CHEMICAL REACTION.

Rate of chemical reaction increases by increasing temperature. Generally rate of reaction is doubled by increasing temperature through 10°C . However increase in rate of reaction by increasing temperature is different in different reactions.

The increase in rate of reaction due to increase in temperature can be explained as follows:

The increase in temperature increases average K.E. of molecules. The increase in K.E. may be responsible for increase in rate of reaction. But increase in K.E. for every 10°C is 4%. Thus only this factor cannot explain such a high increase in rate of reaction.

The second possibility is that increase in temp. increase number of collisions between gas molecules. The increase in collision number is only 2%. So only this factor cannot explain increase in rate of reaction by increasing temperature.

In fact reaction takes place only if colliding molecules possess sufficient energy so that they can surmount energy barrier between reactants and products. If they don't possess this much energy, they just rebound on collision & no product is formed.

On increasing temperature, more and more molecules possess sufficient energy so that they can form products. Thus

number of fruitful collisions are increased on increasing temperature.

The effect of temperature on rate of reaction is given by mathematical equation called ARHENIUS EQ.

$$k = A e^{-E_a/RT}$$

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

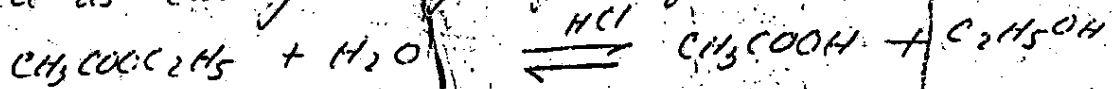
The equation shows that rate constant increases with increase in temp. but it decreases with increase in energy of activation.

WHAT IS CATALYST? DISCUSS ITS TWO TYPES?

EXPLAIN FUNCTION, POISONING & LIMITS OF CATALYST.

CATALYST: A chemical substance which speeds up the rate of reaction but is recovered after completion of reaction is called catalyst. However catalyst may undergo a change in physical change during the reaction.

For example an inorganic acid "HCl" is used as catalyst in hydrolysis of ester.



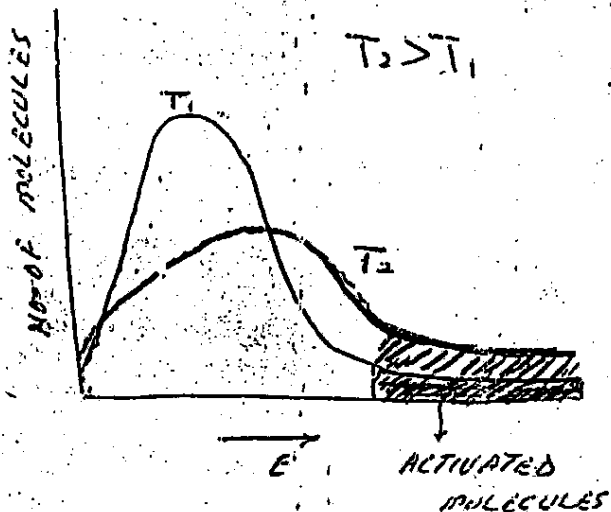
Without catalyst, equilibrium is established in a week but with "HCl" as catalyst the reaction is completed in a few hours.

The process of speeding up a chemical reaction with the help of a catalyst is called CATALYSIS.

TYPES OF CATALYST:-

There are two main types of catalysts.

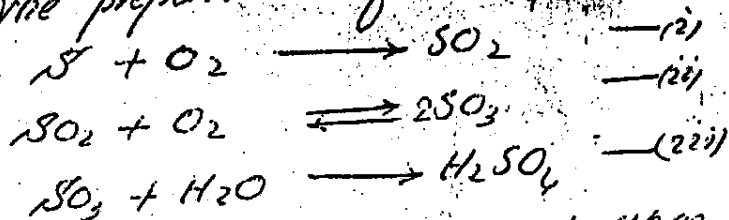
- (i) Homogenous catalyst
- (ii) Heterogenous Catalyst.



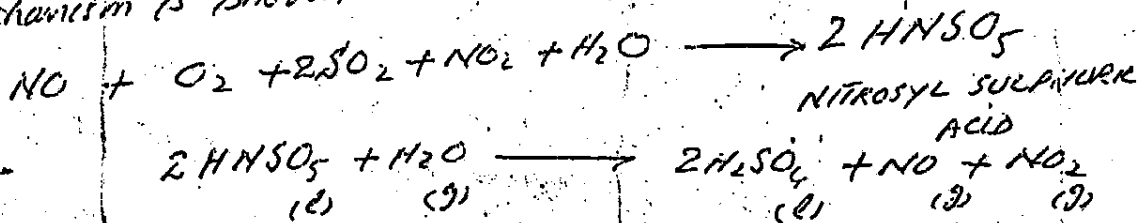
10

HOMOGENEOUS CATALYST: When catalyst has same physical state as that of reactants and products it is called Homogeneous catalyst. For example consider preparation of sulphuric acid by lead chamber acid.

The preparation of H_2SO_4 involves following steps



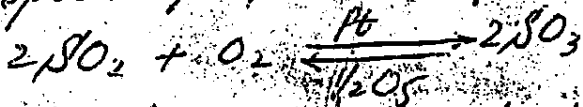
The rate of production of H_2SO_4 depends upon second step. In lead chamber process NO, NO_2 gases are used as catalyst to speed up ii step. The exact mechanism of reaction is not known. The probable mechanism is shown below.



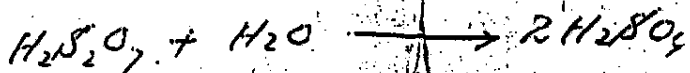
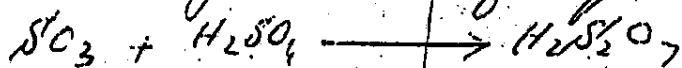
NO, NO_2 being catalyst are recovered.

HETEROGENEOUS CATALYST: The catalyst which has different physical state from that of reactant and product is called HETEROGENEOUS CATALYST.

In CONTACT PROCESS " Pt " or " V_2O_5 " is used as catalyst to speed up second step.

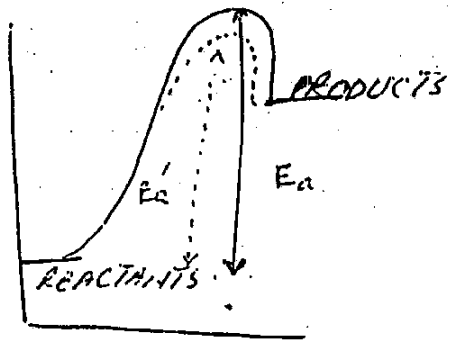


The SO_3 produced is not absorbed in " H_2O " but it is absorbed in H_2SO_4 to produce "oleum". This is diluted to get H_2SO_4 of required conc.



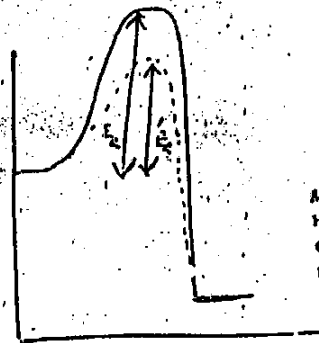
FUNCTION OF CATALYST: The catalyst speeds up the rate of reaction by decreasing energy of activation. The energy of activation is defined as minimum amount of energy required in addition to average energy of reactants to convert

them in to products (the catalyst speeds up rate of endothermic as well as exothermic reactions as shown below.)



ENDO THERMIC REACTION

$$E'_a < E_a$$



EXOTHERMIC REACTION

$$E'_a < E_a$$

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" E_a " is energy of activation without catalyst and " E'_a " is energy of activation in presence of catalyst. The catalyst speeds up both forward and reverse reaction. The catalyst has some specific positions on its surface called Active sites. At active sites the reactant molecules get attached to catalyst and are converted into products. The exact mechanism is different for different catalysts. Many transition elements are used as catalysts because transition elements have free valencies on its free surface which act as active sites.

POISONING OF CATALYST: - The deactivation of catalyst due to presence of small amount of impurity in it is called poisoning of catalyst. For example if small amount of Arsenic is present in Pt, it would destroy catalytic ability of Platinum. The impurity (arsenic) gets attached to active sites of catalyst and form platinum Arsenide.

INHIBITORS: The chemical substances which slow down a reaction are called inhibitors. For example amount of organic substances like (Pyridine, quinoline) retards rancidity of butter and oils.

LIMITS OF CATALYST: - The catalyst has no effect on total thermodynamics of reaction (the catalyst cannot be used to carry out reaction which is thermodynamically not possible). It only reduces energy of activation. It cannot change non spontaneous reaction into spontaneous reaction.

EXPLAIN THE FOLLOWING TERMS.

12

(i) **CHEMICAL KINETICS:** - The branch of chemistry which deals with rates of chemical reactions is called chemical kinetics. It also includes the study of mechanisms of reaction and factors affecting rates of reactions. In this branch of chemistry we are mainly concerned with reaction rates and various factors affecting reaction rates.

The reaction rate is defined as the amount of change taking place in unit time is called rate of chemical reaction. It is denoted by rate = $\frac{dx}{dt}$. It is also called average rate.

The reactions are divided into three categories on the basis of rates of reactions.

(ii) **VERY FAST REACTIONS:** These are reactions which are completed in a fraction of second. Their rates cannot be measured easily. $\text{AgNO}_3 + \text{NaCl} \longrightarrow \text{NaNO}_3 + \text{AgCl}$

(iii) **VERY SLOW REACTIONS:** These are reactions which are very much slow and their rates are difficult to determine. For example rusting of iron.

MODERATELY SLOW REACTIONS: These are reactions which proceed at a moderate rate. These are neither very slow nor very fast.

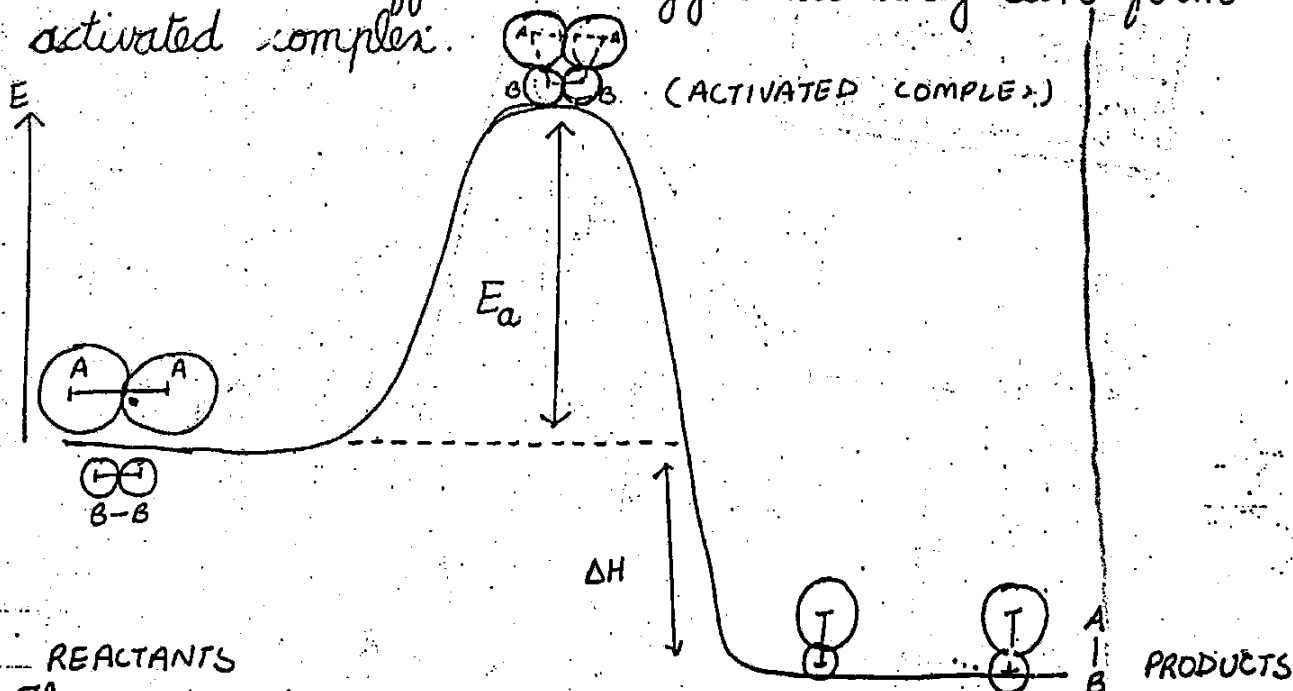
In chemical kinetics we are mainly concerned with such moderate reactions.

COLLISION THEORY: - The collision theory was proposed to explain how do the chemical reactions take place and why do the rate of chemical reaction decrease by increasing temperature by 10°C. An extension of this theory is called transition state theory. This theory is based upon following postulation.

- (1) For a chemical reaction to take place reactant molecules must collide with one another.
- (2) All collisions do not lead to products i.e. all collisions are not fruitful. A small number of molecules are converted into products after collision.
- (3) The molecules must be suitably oriented at the time of collision.

Let us consider details of this theory. According to kinetic molecular theory, molecules are continuously moving in random directions. Due to their motion they collide with one another and with walls of container. But each collision between the reactant molecules do not lead to products.

Only those molecules are converted into products after collision which possess sufficient energy E_a that they can form activated complex.

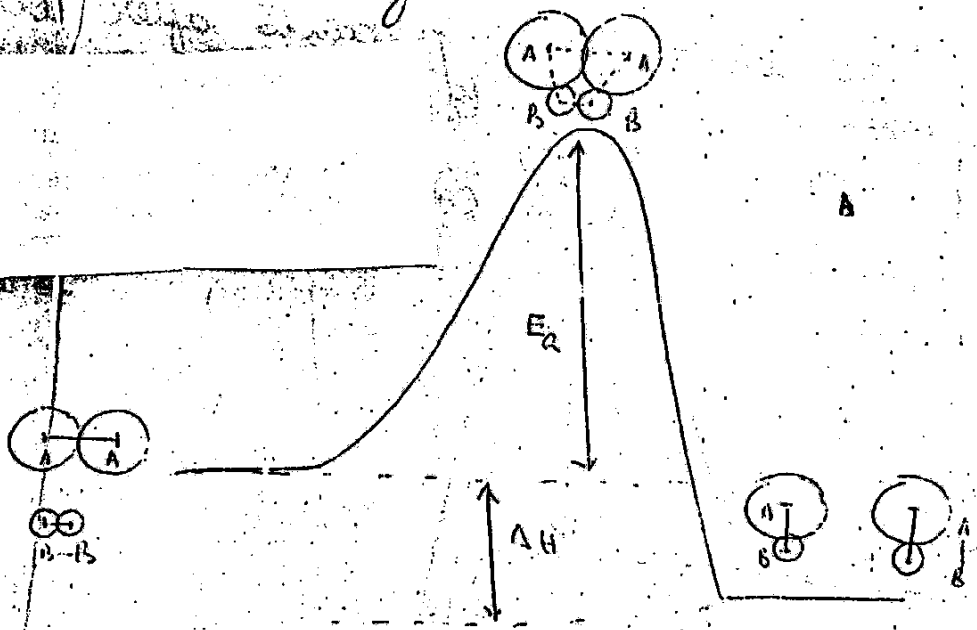


The amount of energy required in addition to average energy of reactants to convert them into products is called energy of Activation. The minimum amount of

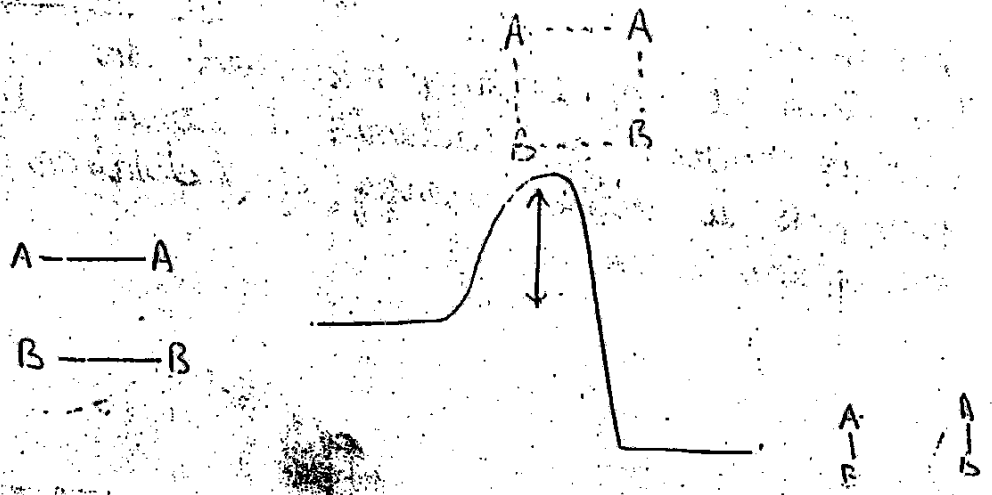
energy required to form activated complex is called "ENERGY OF ACTIVATION". Only those molecules are converted into products on collision which possess as much energy as collision.

ACTIVATED COMPLEX: The high energy complex formed by collision of molecules is called **ACTIVATED COMPLEX**. It has high energy as compared to energy of reactant or products. It is an intermediate state between reactants and products. No bond is completely broken or completely formed in intermediate complex. It is also called **TRANSITION STATE**.

At transition state old bonds are being broken and new bonds being formed. For a reversible reaction reactants the intermediate state is same for forward reaction as well as reverse reaction. It can be shown as follows



It can also be shown as follows



(15)

Only those molecules are converted into products which have ability to form transition state or activated complex. For this purpose they must be suitably oriented, and must possess sufficient energy. Since all molecules do not have sufficient energy and are not suitably oriented at the time of collision so all collisions do not lead to products.

ARRHENIUS EQUATION:- It is a mathematical eq. which indicates effect of temperature on rates of chemical reaction. It can be written as

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

Where k is called rate constant
 A is Arrhenius constant
 E_a is called energy of activation
 R is general gas constant
 T is absolute temperature.

It is an exponential equation. It can be written as

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

The equation shows that rate constant has higher value at high temperature and vice versa.

Further equation shows that reactions which have high activation energy proceed at lower rate and vice versa.

If a graph is plotted between $\log k$ (along y-axis) and $1/T$ along x-axis a straight line is obtained. The slope of line gives rate of reaction.

18

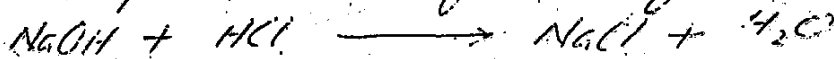
WHAT ARE VARIOUS FACTORS EFFECTING RATE OF A CHEMICAL REACTION?

Ans:- The rate of reaction is defined as, chemical change taking place per unit time is called Rate of reaction. The average rate is written as $\frac{\Delta c}{\Delta t}$ where " Δc " change in conc. of reactants or products and Δt is time taken for change. The instantaneous rate is usually written as $\frac{dx}{dt}$ where " dx " is very small amount of products (change in conc.) in very small interval of time dt .

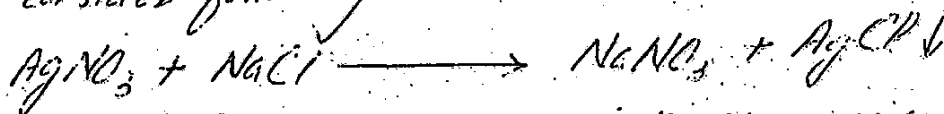
The rate of reaction depends upon a number of factors. These are

- (i) The nature of reactants
- (ii) The concentration of reactants
- (iii) The temperature of reacting system
- (iv) The presence of catalyst

THE NATURE OF REACTANTS: - The rate of reaction mainly depends upon nature of reactants. For example ionic reactions take place at a very fast rate. Consider an acid base reaction (Neutralization reaction) which is completed in a fraction of second.



Similarly consider following reaction



MOLECULAR REACTIONS are however quite slow as compared to ionic reactions. For example consider following reaction

$$\text{CH}_3\text{COOH} + \text{HOCH}_3 \rightleftharpoons \text{CH}_3\text{COOCH}_3 + \text{H}_2\text{O}$$

Similarly reaction of metals with acids is relatively faster than reaction of non metals with acids. Some metals like Na, K react with water at much faster rate than some other metals like Ca, Fe, etc.

THE EFFECT OF CONCENTRATION: - According to law of mass action, the rate of reaction depends upon molar concentration of reactants. However effect of

change in molar concentration cannot be determined from balanced chemical equation. The rate of reaction may increase decrease or may not be effected by change in initial conc. of reactants. This is determined experimentally.

(i) If rate of reaction is doubled by doubling conc. of reactant and becomes three time by increasing conc. 3 times then reaction is first order w.r to that reactant.

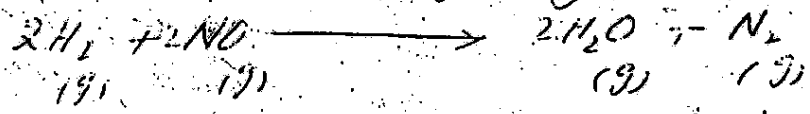
(ii) If rate of reaction increases square times the increase in molar conc. of reactant then reaction is second order w.r to that reactant. $\text{Rate} \propto [A]^2$

(iii) If rate of reaction increases cube times the change increase conc then reaction is 3rd order w.r to that reactants. $\text{Rate} \propto [A]^3$

(iv) If rate of reaction remains unchanged by increase or decrease in conc then reaction is zero order w.r to that reactant.

(v) In a very very few reactions rate of reaction may be inc. decreased by an increase in conc. then reaction is said to be zero or negative order w.r to that particular reactant. This is experimentally determined.

Consider following reaction.



Following six experiments has been performed on this reaction.

Exp	Initial conc [NO]	Initial conc [H ₂]	Initial rate
1	0.006	0.001	0.025
2	0.006	0.002	0.050
3	0.006	0.003	0.075
4	0.001	0.009	0.0063
5	0.002	0.009	0.0025
6	0.003	0.009	0.057

It is clear from above table that rate of reaction is doubled by doubling conc. of $[H_2]$ and becomes three times by tripling conc. Thus reaction is first order w.r to $[H_2]$

Rate of reaction $\propto [H_2]$ — (i)

Further if all other factors kept const, then rate of reaction increases square times the change in conc. of $[NO]$. i.e becomes 4-times by doubling conc. of $[NO]$. Thus reaction is second order w.r to $[NO]$

Rate of reaction $\propto [NO]^2$ — (ii)

Combining eq (i), and (ii) Rate $\propto [H_2][NO]^2$

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

Thus it is third order reaction.

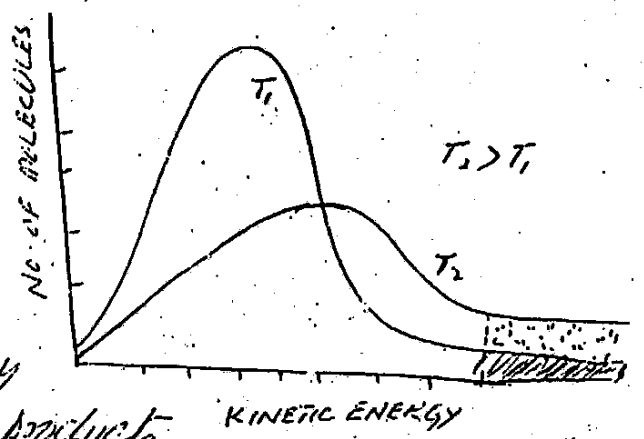
NOTE:- Order of reaction is defined as sum of powers of molec. conc. terms involved in rate expression of a chemical reaction.

EFFECT OF TEMPERATURE:-

The rate of reaction increases by increasing temperature. In most of reactions, rate is doubled by approximately 10°C rise in temperature. However in different reaction the increase in rate per degree rise of temp. is different.

The increase in rate by increasing temperature is due to the fact that more and more molecules possess sufficient energy that they can be converted into products by surmounting energy barriers between reactants and products. This energy barrier is called energy of activation. Further at higher temp. no. of molecules is increased and collision frequency is also increased.

However main factor is that number of fruitful collisions is increased i.e more and more molecules possess sufficient energy that they can be converted into products as shown by R.H.S. of graph.



The effect of temperature on reaction rate can be explained by Arrhenius equation. It is exponential eq- written as

$$k = A e^{-E_a/RT}$$

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

where k = Rate constant

E_a = Energy of Activation

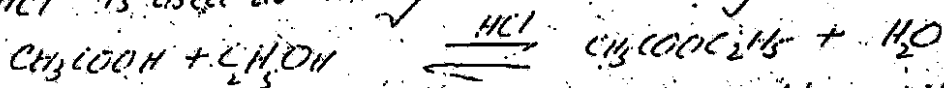
A = Arrhenius constant depend upon nature of gas.

T = Absolute temperature

The equation shows that rate of reaction increases on by increasing temperature and decreases by increasing energy of activation.

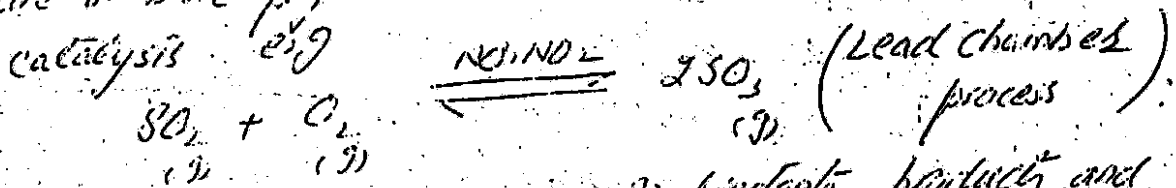
EFFECT OF CATALYST: Catalyst is defined as "The substance which increases rate of chemical reaction but does not change itself during or after the chemical reaction. In other words catalyst is recovered after completion of reaction. However catalyst may undergo change in physical state during a chemical reaction.

For example during esterification reaction "HCl" is used as catalyst. Without catalyst this reaction completes

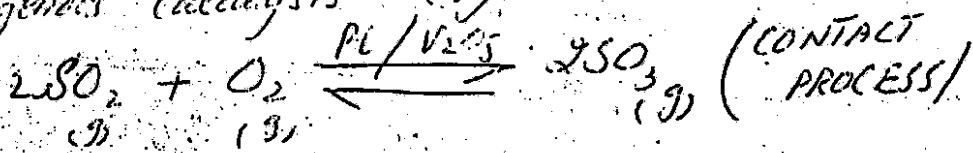


in less than eight days but by adding HCl it is completed in three to four hours

HOMOGENOUS CATALYST: If reactants, products and catalyst are in same physical state, it is called Homogenous catalysis



HETEROGENOUS CATALYSIS: If reactants, products and catalyst have different physical states it is called heterogenous catalysis



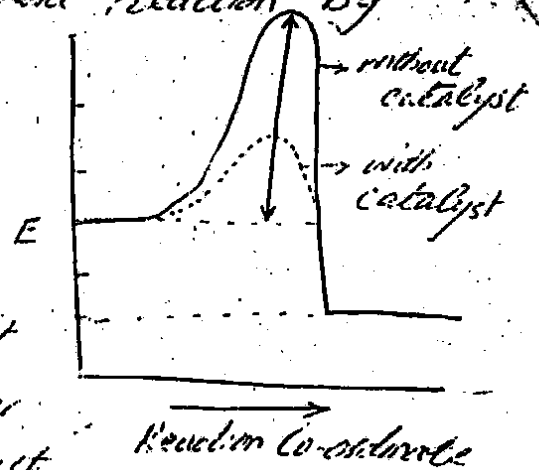
FUNCTION OF CATALYST The catalyst speeds up rate of forward as well as backward reaction by decreasing energy of activation.

The catalyst have free valences

(Active sites) on its surface. The reactant molecules get attached

on these active sites. The reactant molecules react with each other while still attached with ~~reverse~~ catalyst.

The products get free from catalyst. The exact mechanism is unknown.



LIMITS OF CATALYSIS: The catalyst can speed up a chemical reaction but cannot total thermodynamics of reaction. It cannot change an endothermic reaction into exothermic reaction and vice versa. It cannot bring about a reaction which is not thermodynamically possible.

POISONING OF CATALYST: The decrease in activity of catalyst due to some impurity is called poisoning of catalyst.

FILL IN THE BLANKS BY SUITABLE WORDS.

- 1) Concentration of reactants DECREASES but those of products INCREASES with passage of time in a reaction.
- 2) The time for completion of first order reaction DOES NOT DEPEND on conc. of reactants.
- 3) Instantaneous rate is expressed as $\frac{d(\text{conc})}{d(\text{time})}$
- 4) The rate of reaction is -ve rate of change of conc. of reactants with respect to time.
- 5) The units of first order rate constant are Sec^{-1} .
- 6) Increase in temperature INCREASES rate of reaction.
- 7) The heat contents of products are less than reactants for EXOTHERMIC reactions but reverse is true for ENDOTHERMIC reactions.

WHAT IS ORDER OF REACTION? GIVE EXAMPLES.

Ans - The sum of powers of molar conc terms involved in rate expression is called order of reaction. Or it may also be defined as number of reacting molecules whose concentration change as a result of chemical change.

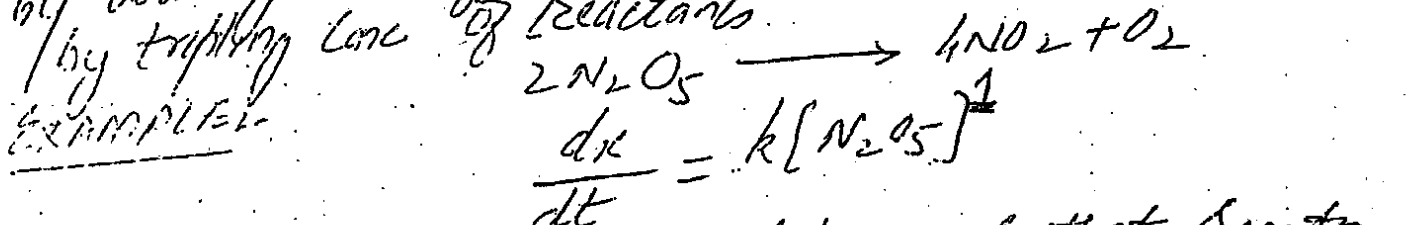
EXPLANATION | Let us consider following general reaction
 $aA + bB \rightarrow cC + dD$

The rate expression for this reaction is $\text{Rate} = k[A]^a[B]^b$
The reaction has "a" order w.r. to "A" and "b" order w.r. to "B". The overall order is $= a+b$

It must be kept in mind that order of reaction is always determined experimentally. The powers of molar conc terms may or may not be equal to coefficients of balanced chemical equation. The reaction may be first order, second order, third order, zero order or even neg. order. The order of reaction gives useful information about mechanism of reaction.

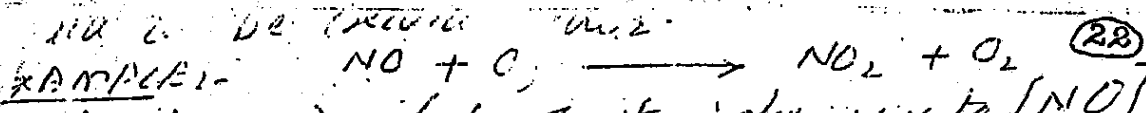
FIRST ORDER REACTION | The reaction in which sum of powers of molar conc terms involved in rate expression is 1 is called first order reaction
 $A \rightarrow \text{Product}$

In first order reaction rate of reaction is doubled by doubling conc of reactant's and becomes three times by tripling conc of reactant's.



It has been experimentally determined that reaction is first order although co-efficient of balanced eq is 2.

SECOND ORDER REACTION | If sum of powers of molar conc terms involved in rate expression is two the reaction

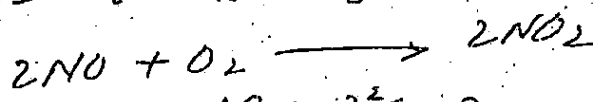


The reaction is found to be first order w.r. to [NO] and first order w.r. to [O₃] (The overall order is 2).

$$\frac{dx}{dt} \propto [NO][O_3]$$

$$\frac{dx}{dt} = k[NO][O_3]$$

THIRD ORDER



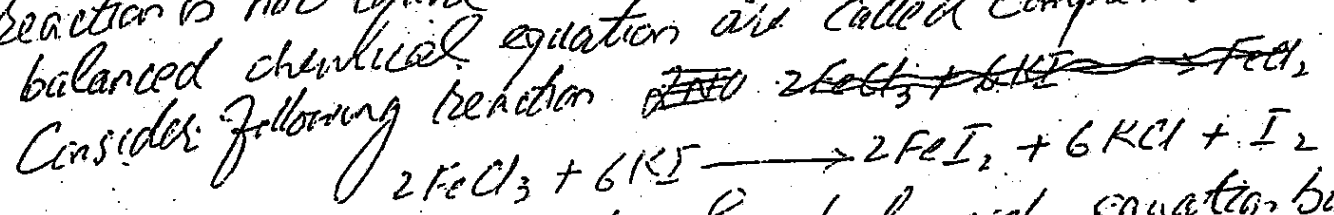
$$\frac{dx}{dt} = k[NO]^2[O_2]$$

The reaction is second order w.r. to NO and first order w.r. to oxygen. Overall order is 3.

First ZERO ORDER REACTION The reaction in which rate of reaction is independent of initial conc. of reactants are called zero order reactions.

EXAMPLE: Photochemical reactions are usually zero order reaction. If a reactant is present in v. large excess as compared to other reactants, the rate of reaction becomes zero order w.r. to that reactant.

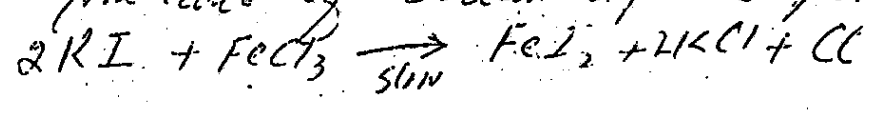
COMPLEX REACTION The reactions in which order of reaction is not equal to sum of co-efficients of balanced chemical equation are called complex reactions.

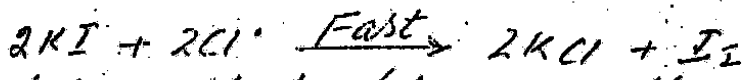


It seems to be 8th order from balanced equation but it has been found to be third order experimentally.

$$\frac{dx}{dt} = k[FeCl_3][KI]^2$$

It suggests that reaction may be taking place in more than one steps. The rate of reaction depends upon slow step:





The first step is rate determining step. Therefore rate expression is $\frac{dx}{dt} = k[FeCl_3][KI]^2$

FRACTIONAL ORDER REACTION

The order of reaction may be fractional. For example consider reaction of chloroform with chlorine

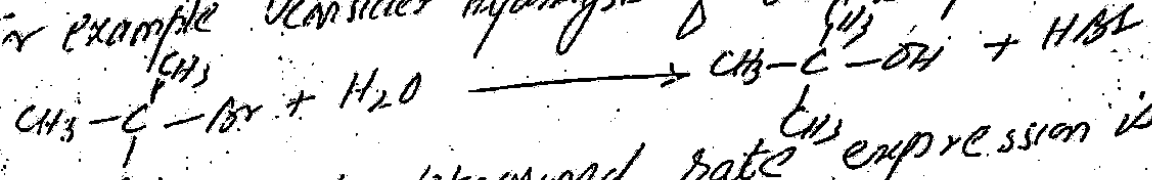


$$\text{Rate} = k[CHCl_3][Cl_2]^{\frac{1}{2}}$$

The order of reaction is $1 + 0.5 = 1.5$

PSEUDO FIRST ORDER REACTION

A second order reaction which behaves like a first order reaction due to presence of one reactant in large excess is called Pseudo first order reaction. For example consider hydrolysis of ter-butyl bromide



The experimentally determined rate expression is $\frac{dx}{dt} = k[(CH_3)_3CBr]$

Since water is in large excess, so rate of reaction is independent of conc. of water. Thus it behaves like a first order reaction.

HALF LIFE:

Q:- WHAT IS HALF LIFE PERIOD? HOW TO DETERMINE ORDER OF REACTION BY HALF LIFE METHOD.

Ans:- The period of time in which 50% of reactants are converted into products is called half life.

EXAMPLE NO. 1:- Half life of N_2O_5 is 24 minutes. It means if we 0.1 mole/dm³ of N_2O_5 , after 24 minutes it will be 0.05 mole/dm³ left behind. And after 48 minutes its amount will become 0.025 mole/dm³. (25% of initial concentration)

EXAMPLE NO. 2:- The half life of $^{235}_{92}\text{U}$ is 710 million years.

If we take 1 kg of $^{235}_{92}\text{U}$, after 710 million year 0.5 kg will be left over and 0.5 kg will change into daughter elements. In the next 710 years, 50% of 0.5 kg i.e. 0.25 kg will change into daughter elements.

Thus half life of nuclear disintegration process is independent of initial concentration of radioactive material.

RELATIONSHIP BETWEEN HALF LIFE AND ORDER OF REACTION.

The half life period of any reaction is inversally proportional to initial conc. of reactants raised to power one less than order of that reaction.

It means $t_{0.5} \propto \frac{1}{a^{n-1}}$ where $n = \text{order of reaction}$

For first order reaction $[t_{0.5}] \propto \frac{1}{a^{1-1}}$

$[t_{0.5}] \propto \frac{1}{a^0}$ or $[t_{0.5}] = \frac{0.693}{k}$

Thus half life of first order reaction is independent of conc.

The half life of second order reaction is

$$[t_{0.5}]_2 \propto \frac{1}{a^{2-1}} \quad \text{or} \quad [t_{0.5}]_2 = \frac{1}{ka}$$

Thus half life of second order reaction is inversely prop. to initial conc. of reactant.

Half life of third order reaction $[t_{0.5}]_3 \propto \frac{1}{a^{3-1}}$

$$[t_{0.5}]_3 \propto \frac{1}{a^2} \quad \text{or} \quad [t_{0.5}]_3 = \frac{1.5}{ka^2}$$

GENERAL FORMULA $t_{0.5} \propto \frac{1}{a^{n-1}}$

Thus if we know half life period and initial conc. of reactants then order of reaction can be determined.

DETERMINATION OF ORDER OF REACTION BY HALF LIFE METHOD: The reaction whose order is to be determined is performed with two different initial concentrations. Let a_1 and a_2 and half life periods t_1 and t_2 are determined. Since $t_{0.5} \propto \frac{1}{a^{n-1}}$

$$t_1 \propto \frac{1}{a_1^{n-1}}$$

$$\text{and } t_2 \propto \frac{1}{a_2^{n-1}}$$

$t_1 =$ first half life for conc. a_1
 $t_2 =$ half life for conc. a_2

Dividing (1) by eq (2)

$$\frac{t_1}{t_2} = \frac{a_2^{n-1}}{a_1^{n-1}}$$

Taking log of both sides

$$\log \frac{t_1}{t_2} = \log \left(\frac{a_2}{a_1} \right)^{n-1}$$

$$\log \frac{t_1}{t_2} = (n-1) \log \frac{a_2}{a_1}$$

$$\frac{\log \frac{t_1}{t_2}}{\log \frac{a_2}{a_1}} + 1 = n$$

$$\log \frac{a_2}{a_1}$$

Thus if we know two half lives for two different initial conc. we can determine order of reaction "n".

HOW TO DETERMINE ORDER OF REACTION BY

LARGE EXCESS METHOD: - In this method one reactant is taken in small amount and other reactants in large excess. The reaction is zero order w.r. to those reactants which are present in large excess.

The concentration of reactant which is in limited amount is doubled and rate of reaction is determined. The concentration of reactant is increased three times and rate is determined again.

(i) If rate of reaction is doubled by doubling conc. and becomes three times by tripling conc. the reaction is said to be first order w.r. to that reactant.

(ii) If rate of reaction increases square times the conc. reaction is said to be second order w.r. to that reactant.

(iii) If rate of reaction increases cube times the conc. the reaction is said to be third order w.r. to that reactant.

(iv) If there is no effect of conc. on rate of reaction the reaction is zero order w.r. to that reactant.

The same process is repeated with all reactants one by one. The order of reaction w.r. to each reactant is determined.

EXAMPLE: - $2\text{NO} + 2\text{H}_2 \longrightarrow \text{N}_2 + 2\text{H}_2\text{O}$
It has been determined by large excess method that by doubling conc. of H_2 , rate of reaction is doubled when NO is present in large excess. Thus reaction is first order w.r. to H_2 $\frac{d[\text{H}_2]}{dt} \propto [\text{H}_2]^1$

The rate of reaction increases square times by changing conc. of NO by keeping H_2 in large excess. Thus

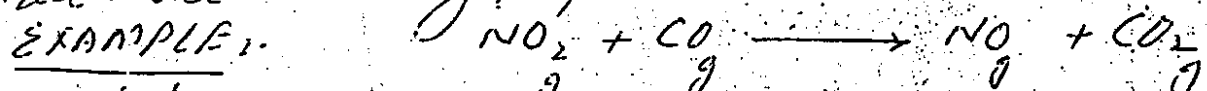
which is second order w.r to NO.

The overall order is 3rd order $\therefore \frac{dx}{dt} \propto [NO]^2$ (7)

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

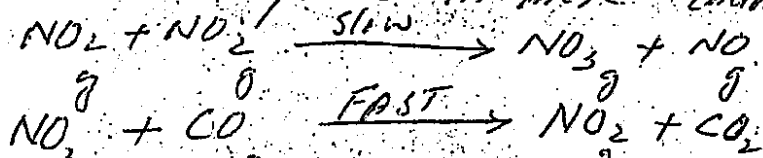
WHAT IS RATE DETERMINING STEP? EXPLAIN REACTION INTERMEDIATE WITH SUITABLE EXAMPLE?

If a reaction takes place in several steps, the rate of reaction will depend upon the slowest step. It is called RATE DETERMINING STEP. The number of molecules taking part in rate determining step will appear in rate expression. The order of reaction will depend upon rate determining step.



The rate expression for this reaction is $\frac{dx}{dt} = k [NO_2]^2$

This type of reactions are called complex reactions. The rate of reaction is independent of conc of CO. It indicates reaction must take place in more than one steps. These are



Thus first step is determining step $\frac{dx}{dt} \propto [NO_2][NO_2]$. CO is not involved in this step thus overall rate of reaction will not depend upon [CO].

REACTION INTERMEDIATE The unstable molecule or ion or radical which appears during reaction but does not appear in balanced chem. eq. is called REACTION INTERMEDIATE. It is unstable as compared to reactants and products. It may be stable enough to be isolated and identified under special conditions.

This reaction also shows that balanced chemical eq. may not give any information about the way the reaction actually takes place.

EFFECT OF TEMPERATURE

Temperature affects rate of catalyst. Some catalysts are affected by change in temp. Thus catalytic ability is changed.

EXAMPLE: Colloidal Platinum may coagulate with rise in temperature.

POISONING OF CATALYST

The decrease in catalytic ability of catalyst due to some impurities is called poisoning of catalyst. These substances are called poisons. The poisoning of catalyst may be temporary or permanent. In permanent poisoning the poison reacts chemically with catalyst. The compounds of "S" or "As" are poisons for many metallic catalysts.

WINKLER PROCESS

Presence of "CO" impurity decrease catalytic ability in synthesis of NH_3 .

(ii) Arsenic oxides deactivates Pt in contact process for manufacture of H_2SO_4 .

WRITE BRIEF NOTES ON FOLLOWING:-

1. ACTIVATION OF CATALYST:- "Catalyst of Catalyst"

The substances which promote catalytic ability of catalyst are called PROMOTER or ACTIVATORS.

(i) The catalytic ability of Nickel is increased by small amount of Te or Cu. in hydrogenation of oils.

(ii) Small amount of high melting oxides (Al_2O_3 , Cr_2O_3) increase catalytic ability of Iron in Haber process.

2. NEGATIVE CATALYSIS

The substances which retard or slow down rate of reaction are called Negative catalyst or Inhibitor. For example tetraethyl lead saves petrol from preignition.

REMAINS UNCHANGED. The chemical composition of catalyst remains unchanged during reaction. However physical state of catalyst may change during reaction. $2KClO_3 \xrightarrow[MnO_2]{\Delta} 2KCl + 3O_2$

EXAMPLE. MnO_2 is used in the form of granules but changes into fine powder. If hard catalysts are used they may become dull at the completion of reaction.

TRACE AMOUNT / catalyst is required in very small amount

EXAMPLE. 1 mg of fine Pt powder can change 2.5 dm³ of H_2 and 1.25 dm³ of O_2 into water $2H_2 + O_2 \xrightarrow{Pt} 2H_2O$

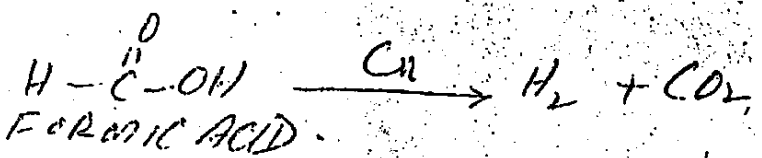
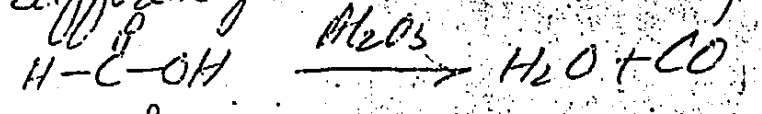
1g of colloidal Pt can convert thousands of H_2O_2 into products. Traces of moisture can make NH_3 and HCl react to form NH_4Cl .

FINELY DIVIDED. A catalyst is more effective in finely divided form. A powdered Pt is more effective than a lump of it. Nickel is used in finely divided form in hydrogenation.

EQUILIBRIUM STATE - Catalyst does not change concn of reactants and products but decreases the time required to reach equilibrium state.

LIMITATION / A catalyst cannot start a reaction which is not thermodynamically not feasible. It is now considered that catalyst can initiate a reaction. The mechanism of catalyzed reaction is different than uncatalyzed reaction.

SPECIFIC IN ACTION / A catalyst is specific in its action. A catalyst for one reaction may not work for another reaction. Different catalysts acting on same reactants can give different products. Consider following examples



FORMIC ACID.