# CHAPTER 9
# CHEMICAL KINETICS

## RATE OF REACTION

Rate of reaction is the change of the concentration of reactant or product in unit time.

$$Rate = \frac{change\ in\ concentration\ of\ substance}{Time\ taken\ for\ change}$$

The rate of reaction is not a constant quantity but changes with the concentration of reactant molecules present. Initially, when the concentration of reactant is high, the rate is correspondingly high. The rate gradually decreases, and eventually becomes zero when all of the reactants have been consumed completely.

## RATE EXPRESSION OR RATE LAW

$$Rate = k[A]^m[B]^n$$

The rate equation gives the dependence of the rate of a reaction on the concentration of the reactants. It states that the rate of chemical reaction is proportional to the product of molar concentration of the reacting substances raised to appropriate power (the value of which is determined experimentally)

$$\text{Rate} = k[A]^m[B]^n$$

m: order w.r.t A

n: order w.r.t B

Overall order : m+n

The proportionality constant 'k' is called rate constant or velocity constant.

'm' and 'n' may be either whole numbers or fractions or zero.

'k' has a fixed value for a reaction under given conditions of pressure and temperature.

Rate constant is independent of concentration and time.

# ORDER OF REACTION

$$Order = m + n$$

Order of reaction expresses the effect of concentration on the rate of reaction.

## 1. ZERO ORDER REACTIONS

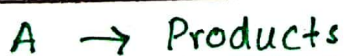A reaction that is independent of reactant molecules is called zero order. e.g

$$2NH_3 \rightarrow N_2 + 3H_2$$

$$Rate = k [NH_3]^0$$

The combination of $H_2$ and $Cl_2$ in presence of sunlight is also a zero order reaction.
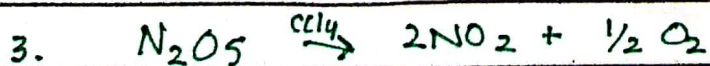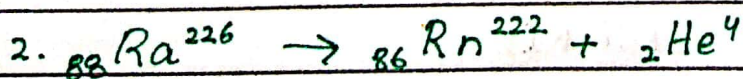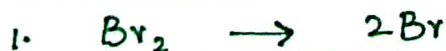
The reactions catalyzed by enzymes also follow zero order kinetics.

## 2. FIRST ORDER REACTIONS

When rate depend only on concentration of one reactant.

$$A \rightarrow Products$$

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1. $Br_2 \rightarrow 2Br$

2. $_{88}Ra^{226} \rightarrow \, _{86}Rn^{222} + \, _2He^4$

3. $N_2O_5 \xrightarrow{CCl_4} 2NO_2 + \frac{1}{2}O_2$

4. $NH_4NO_2 \rightarrow N_2 + 2H_2O$

## ✱ SECOND ORDER REACTIONS

$$Rate = k[A^o]^2$$

or $$Rate = k[A][B]$$

1. Thermal Decomposition of Nitrogen dioxide

$$2NO_2 \rightarrow N_2 + 2O_2 \qquad Rate = k[NO_2]^2$$

2. Thermal Decomposition of Hydrogen Iodide

$$2HI \rightarrow H_2 + I_2$$

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

3. Formation of urea in Solution phase

$$NH_4^+ + CNO^- \rightarrow (NH_2)_2CO$$
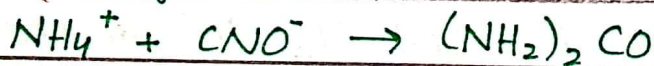
$$Rate = k[NH_4^+][CNO^-]$$

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## ✱ THIRD ORDER REACTIONS

$$Rate = k[A]^3$$

$$Rate = k[A]^2[B]$$

$$Rate = k[A][B][C]$$

1. $$2NO + H_2 \rightarrow N_2O + H_2O$$

$$Rate = k[NO]^2[H_2]^1$$

2. $$2FeCl_3 + 6KI \rightarrow FeI_2 + 6KCl + I_2$$
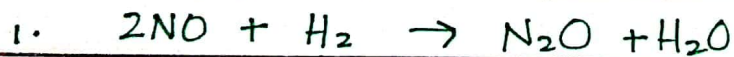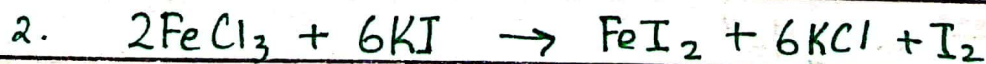
$$Rate = k[FeCl_3]^1[KI]^2$$

3. $$2NO + O_2 \rightarrow 2NO_2$$
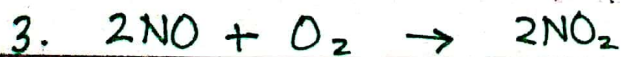
$$Rate = k[NO]^2[O_2]$$

# * FRACTIONAL ORDER REACTIONS

1. $H_2 + Br_2 \rightarrow 2HBr$

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

2. $CHCl_3 + Cl_2 \rightarrow CCl_4 + HCl$
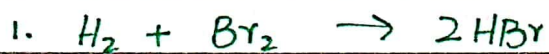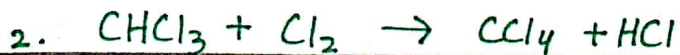
   $Rate = k[CHCl_3][Cl_2]^{1/2}$

# * NEGATIVE ORDER REACTION

$2O_3 \rightarrow 3O_2$
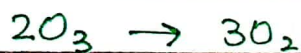
$Rate = k[O_3]^2[O_2]^{-1}$

When the concentration of oxygen doubles, the rate becomes half.

Note:

The order of a reaction for a particular species cannot be predicted by looking at the balanced chemical equation. It can be determined only by experiment.

→ In a first order reaction the rate constant has only the unit of time

→ The radioactive decay is always a first order reaction.

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# EXPERIMENTAL DETERMINATION OF ORDER OF REACTION

In order to determine the order of a reaction the first step is to measure the rate of the reaction. As the rate of the reaction is change in concentration of reactants or products per unit time. The concentration of any species can be monitered by chemical or physical method such as volumetric, gravimetric, spectrophotometric, pressure measurement, conductometric, pH metric methods etc.

The dependence of rate on the concentration of the reactants gives clue to the order of the reaction.

For a reaction involving only one reactant, if the rate doubles, when the concentration of the reactant doubles, then the reaction is ~~four~~ first order.

If the rate increases four times when the concentration doubles, the reaction is second order w.r.t reactant

## * ISOLATION METHOD

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

# FACTORS AFFECTING RATE OF REACTION

## 1. NATURE OF REACTANT

→ More active reactants give fast rate of reaction
→ No. of electrons present in innermost shell affects the reactivity of reactant.
→ Elements of IA are more reactive than IIA
→ Neutralization reactions and decomposition reactions are very fast
→ Oxidation reduction reactions are slower
→ Ionic reactions are faster than covalent reactions

## 2. CONCENTRATION OF REACTANT

→ Reaction is due to effective collision of reactant molecules.
→ Greater concentration of reactants, more effective collisions, thus rate of reaction will be high
→ If gaseous mixture or solution is concentrated it contains many active particles per unit volume and reaction is faster than a dilute mixture.
→ Rate of reaction is directly proportional to concentration of reaction.
→ Sometimes concentration of reactant become double and rate of reaction increase four times.
→ A piece of wood burns much more rapidly in pure oxygen (high conc., 100% oxygen) then it does in ordinary air.

## 3. PARTICLE SIZE OF SOLID REACTING WITH GASES

→ Heterogeneous reactions occur only at surface.

→ Greater the surface area, greater will be chance of contact of molecules

→ Greater surface area of molecules, greater will be rate of reaction.

→ Lumps of soft coal, which doesnot burn readily in air, burns explosively when ground to powder.

→ Marble chips (calcium carbonate) react with HCl giving off $CO_2$ along with other products. By grinding the chips to powder, the surface area in contact with acid is greatly increased and hence the rate of reaction increases.

## 4. TEMPERATURE

→ By increasing temperature, the number of collisions of molecule increases

→ Rate of reaction increases by increase in temperature

→ On increasing temperature by 10K, the rate of reaction becomes doubled.

→ By increasing temperature, number of molecules attaining activation energy increases hence the rate of reaction increases.

# 5. CATALYST

→ Rate of reaction may increase or decrease in the presence of catalyst

→ The conversion of potassium chlorate into potassium chloride and oxygen by heating become faster in the presence of $MnO_2$ as a catalyst.

$$2KClO_3 \xrightarrow[MnO_2]{\Delta} 2KCl + 3O_2$$

# ACTIVATION COMPLEX

"The minimum amount of energy in addition to the average kinetic energy which the particles must have for effective collision is called activation energy"

→ Reactants go into transition state before going into product called activated complex.

→ Energy of activated complex is higher than reactants and products.

→ Amount of energy to form transition state is called energy of activation.

→ When the energy of product is less than reactants, the reaction is exothermic.

→ When the energy of products is higher than reactants, the reaction is endothermic.

→ Energy of activation for forward reaction

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# Collision Theory Of Reaction Rate

1) For a chemical reaction to occur, particles must collide. In the resulting collisions, atoms are rearranged. Bonds are broken and formed, leading to the production of new substances.

2) Reaction between the colliding particles can only take place if upon collision they possess a certain minimum amount of energy, the activation energy.

3) Not every collision between molecules having the required energy of activation lead to reaction. Only those collisions are effective which take place with proper orientation or arrangement of the colliding molecules.

→ The number of colliding molecules of different gases calculated from kinetic theory of gases is of the order of magnitude of $10^{32}$ molecules per litre per second at standard conditions.

→ The activation energy depends upon the nature of the reactants (bond energy) and is therefore a characteristic value for each.

→ The combination of two H atoms to form $H_2$ require no specific orientation.

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* In the reaction.

$$CO + NO_2 \rightarrow CO_2 + NO$$
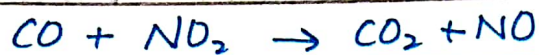
The probability of this reaction increases when carbon atom of CO happens to collide with one of oxygen atoms of $NO_2$.

# TRANSITION STATE THEORY

"During reactions, the bonds of reactants weaken and bond length increases while new bonds may start to form, finally the reacting molecules form some kind of hypothetical structure known as transition state "

→ Transition state theory is modification of collision theory.

→ Transition state doesnot represent a real molecule

→ It is impossible to isolate transition state.

→ It is possess properties common to real molecule such as molecular weight, intermediate distance, definite enthalpy and definite composition.

→ It loses structure and the ability to rotate and vibrate.

→ The transition state may either return to the initial reactant or it proceeds to form products.

→ Transition state is cluster of molecules or atoms.

→ In transition state, old bonds are in the process of breaking and new bonds are in the process of making

→ Transition state is at highest point of reaction energy diagram

# CATALYST

"A substance which alters the rate of a chemical reaction but remains chemically unchanged at the end of the reaction is called catalyst"

# TYPES OF CATALYSIS

## 1. HOMOGENEOUS CATALYSIS

In this type of catalysis, the catalyst and the reactants are in the same phase and the reacting system is homogeneous throughout.
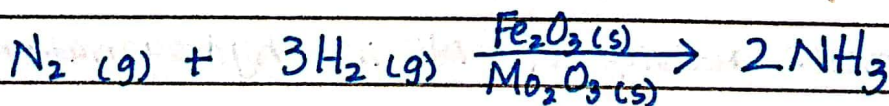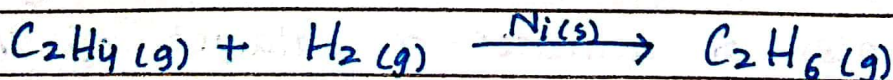
e.g

$$CH_3COOC_2H_5 + H_2O \xrightarrow{H_3O^+} CH_3COOH + C_2H_5OH$$

$$2SO_2 + O_2 \xrightarrow{NO+NO_2} 2SO_3$$
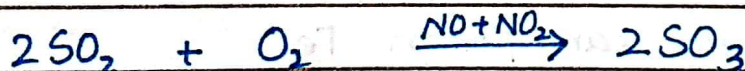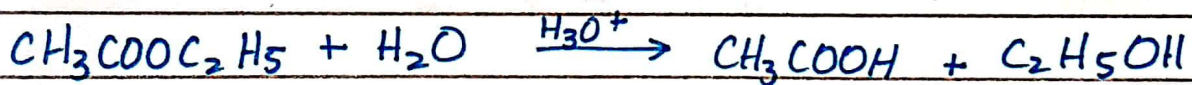
## 2. HETEROGENEOUS CATALYSIS

When the phase of catalyst differ from the phase of reactant.

e.g

$$C_2H_4 \, (g) + H_2 \, (g) \xrightarrow{Ni(s)} C_2H_6 \, (g)$$

$$N_2 \, (g) + 3H_2 \, (g) \xrightarrow[Mo_2O_3 \, (s)]{Fe_2O_3 \, (s)} 2NH_3$$

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# CHARACTERISTICS OF A CATALYST

→ Catalyst remains chemically unchanged
→ Catalyst is more effective when it is in finely divided powder form.
→ Catalyst should not affect chemical equilibrium state of reaction.
→ Catalyst cannot start a reaction; it only lowers the energy of activation
→ Catalysts are specific in their nature.
→ Catalytic poisoning occurs when any foreign particle affect the activity of catalyst.
→ Addition of impurity in catalyst is called poisoning of catalyst. It may be temporary or permanent.

e.g

* HCl can poison $MnO_2$ in decomposition of $H_2O_2$
* CO in Haber's process can poison Fe

# TYPES OF CATALYST

## 1. PROMOTER

Substance that increases the activity of catalyst is called promoter or activator or catalyst of the catalyst.
e.g
Cu promotes activity of Ni in hydrogenation of oil

## 2. INHIBITOR

When a substance reduces the rate of reaction then it is called inhibitor or negative catalyst. e.g

Tetraethyl lead is added to petrol which acts as inhibitor

## 3. AUTO - CATALYST

In some reactions, products formed act as catalyst called auto-catalyst.

e.g

* Hydrolysis of ester give acetic acid which act as auto-catalyst

* The reaction of oxalic acid with $KMnO_4$, $MnSO_4$ is produced. $Mn^{+2}$ ions act as auto catalyst

→ A well-known industrial process is catalytic cracking of crude oil, in which large hydrocarbon molecules are broken down into simpler and more useful products in the presence of catalyst 'Fe'

## * ENZYME CATALYSIS

1. Ptyalin : Present in saliva and accelerates the conversion of starch into sugar

2. Pepsin : Present in gastric juice and breaks down protein into simpler molecules.