Chemical Kinetics

Chemical Kinetics is the branch of chemistry that deals with

    a) Rates of reactions

    b) Factors influencing the rates of reaction

    c) Reaction mechanism

Rate of reaction

The rate of a reaction is defined as the change in molar concentration of a reactant or a product per unit time. To be more specific, rate can be expressed as the rate of decrease in concentration of a reactant or the rate of increase in concentration of a product.

Let us consider a hypothetical reaction, where one mole of reactant 'R' is converted to one mole of product 'P' assuming that the volume of the system remains constant. If the concentrations of reactant and product at time t_1, are $[R]_1$ and $[P]_1$, respectively and at time t_2, the concentrations are $[R]_2$ and $[P]_2$, then

Change in time, $\Delta t = t_2 - t_1 =$ time taken

Change in the concentration of reactant, $\Delta[R] = [R]_2 - [R]_1$

Change in the concentration of product, $\Delta[P] = [P]_2 - [P]_1$

Here, the square brackets are used to express molar concentrations. Molar concentration of a solution is also termed as active mass.

Rate of disappearance of R $= \dfrac{decrease\ in\ concentration\ of\ R}{time\ taken} = \dfrac{\Delta[R]}{\Delta t}$

Rate of appearance of P $= \dfrac{increase\ in\ concentration\ of\ P}{time\ taken} = \dfrac{\Delta[P]}{\Delta t}$

Rate of a reaction is mathematically given as, $Average\ Rate = \dfrac{\Delta C}{\Delta t} = \dfrac{-\Delta[R]}{\Delta t} = \dfrac{+\Delta[P]}{\Delta t}$

Negative sign is to denote that the reactant concentration decreases and positive sign is to denote that the product concentration increases in the reaction.

Instant rate

The rate of a reaction is not maintained constant throughout the reaction. The rates obtained over an interval of time are called average rates of the reaction. Average rate depends upon the change in concentration of a substance and time taken for that change to occur.

The rate of a reaction at a specified time is called instant rate. It is also called instantaneous rate. The rate of a chemical reaction at any instant is the decrease in the concentration of reactant or increase in the concentration of product at that specified time during the process of the reaction. Average and instant rates of a reaction are shown graphically

The rate of the reaction varies exponentially with time of the reaction.

The concentration of the reactants in a reaction varies exponentially with time.

No reaction takes place with uniform rate throughout the course of the reaction.

The rates of chemical reactions differ from one another, since the number and the nature of the bonds are different in the different substances (reactants or products or both)

The units of rate are: concentration time^{-1}. If concentration is in mol L^{-1} and the time is given in seconds, the units of rate are mol L^{-1} s^{-1} or mol dm^{-3} s^{-1}. The units of rate are also given as g L^{-1}s^{-1} or in SI system as kg m^{-3} s^{-1}.

Expressing the rate with respect to Reactants & Products

    i. For the reaction   A $\rightarrow$ B

$$\text{Rate} = -\frac{d[A]}{dt} = +\frac{d[B]}{dt}$$

    ii.   For the reaction $N_2 + O_2 \rightarrow 2NO$

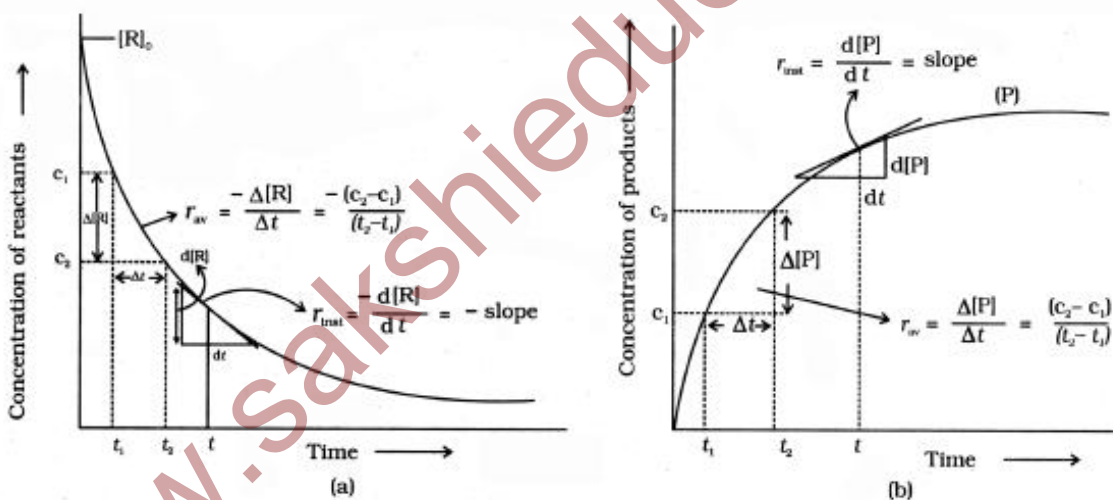$$Rate = -\frac{d[N_2]}{dt} = -\frac{d[O_2]}{dt} = +\frac{1}{2}\frac{d[NO]}{dt}$$

(Or)

$$Rate = -\frac{2d[N_2]}{dt} = -\frac{2d[O_2]}{dt} = +\frac{d[NO]}{dt}$$

iii.   For the reaction $pP + qQ \rightarrow rR + sS$

Rate = $-\frac{1}{p}\frac{d[P]}{dt} = -\frac{1}{q}\frac{d[Q]}{dt} = +\frac{1}{r}\frac{d[R]}{dt} = +\frac{1}{s}\frac{d[S]}{dt}$

iv.   For the reaction. $5Br^-(aq) + BrO_3^-(aq) + 6H^+(aq) \rightarrow 3Br_2(aq) + 3H_2O(1)$

$$Rate = -\frac{1}{5}\frac{\Delta[Br^-]}{\Delta t} = -\frac{\Delta[BrO_3^-]}{\Delta t} = -\frac{1}{6}\frac{\Delta[H^+]}{\Delta t} = \frac{1}{3}\frac{\Delta[Br_2]}{\Delta t} = \frac{1}{3}\frac{\Delta[H_2O]}{\Delta t}$$
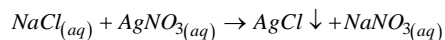

Types of Reactions: Depending upon the rate of reaction, the reactions can be classified into following types

i) Very fast (or) Instantaneous reactions: Fast reactions are those in which the time required for the completion of the reaction is very less. Reactions between ionic substances are fast and are called instantaneous. It is not possible to determine the rates of very fast reactions.
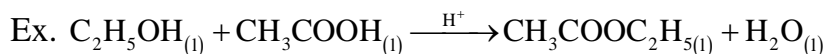
a) Acid - base reactions

$$HCl_{(aq)} + NaOH_{(aq)} \rightarrow NaCl_{(aq)} + H_2O_{(l)}$$
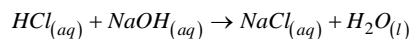
b) Precipitation reactions:

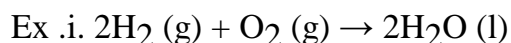$$NaCl_{(aq)} + AgNO_{3(aq)} \rightarrow AgCl \downarrow + NaNO_{3(aq)}$$

c) Explosive reactions: Explosion of T.N.T

ii) Reactions with Moderate speed: These reactions require certain time for completion.Thus their rate can be determined.

Ex. $C_2H_5OH_{(l)} + CH_3COOH_{(l)} \xrightarrow{H^+} CH_3COOC_2H_{5(l)} + H_2O_{(l)}$

iii. Very slow reactions: These reactions require a lot of time for completion.Thus their rate can't be determined.

Ex .i. $2H_2$ (g) + O_2 (g) $\rightarrow 2H_2O$ (l)

   ii. Rusting of IRON.

*Generally reactions between covalent substances are slow and time consuming.

Factors influencing reaction rates

I.**Nature of reactants**: Rate of reaction mainly depends on the nature reaction as the number and nature of bonds vary from one reaction to another.

   Reactions between ionic substances are instantaneous as the forces operate between the oppositely charged ions are strong electrostatic attractions. A white precipitate of silver chloride is obtained immediately by mixing solutions of sodium chloride and silver nitrate.

$$NaCl_{(aq)} + AgNO_{3(aq)} \rightarrow AgCl_{(s)} + NaNO_{3(aq)}$$
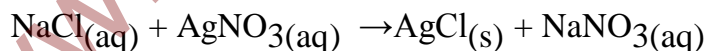
Reactants between covalent substances are slow and time consuming. These reactions involve bond breaking and bond making. The more the number of bonds transformed, the more is the time required. Formation of ammonia between the elements nitrogen and hydrogen is very slow.

eg.1 . $N_2 + 3H_2 \rightarrow 2NH_3$

   2. $C_2H_5OH + CH_3 – COOH \rightarrow CH_3– COOC_2H_5 + H_2O$
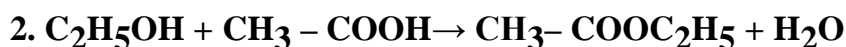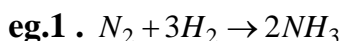
II. Concentration of reactants: At a given temperature, the rate of reaction depends on the concentration of the reactants. The effect of concentration on the rate of the reaction is known from the law of mass action. "The rate of a reaction at any instant of time is directly proportional to the concentration of reactants taking part in the reaction at that instant".

In case of gaseous reactions, partial pressures are measured for the substances. The rate of the reaction is proportional to the partial pressure each of the reactants involved in the reaction.

Eg: - When zinc pieces are added to dilute HCl, chemical reaction takes place slowly liberating H_2 gas. But the same reaction is rapid by taking concentrated HCl.

III.Temperature: **The rate of reaction increases with an increase in the temperature of the reaction.**

Eg. Acidified $K_2Cr_2O_7$ solution is decolourised by OXALLIC acid slowly at ordinary temperature while quickly when heated to 80 to90^{0}C.

The temperature dependence of the rate of a chemical reaction is explained by Arrhenius equation, $k = A\,e^{-E_a/RT}$

Here A is the Arrhenius factor, also called frequency factor or pre-exponential factor. It is a constant for a given reaction. K is the rate constant, R is the molar gas constant and E_a is the energy of activation. Taking logarithms on both side of the Arrhenius equation, we get

$$\ln k = -\frac{E_a}{RT} + \ln A \textbf{ (Or) } \log k = -\frac{E_a}{2.303\,RT} + \log A$$

A plot of ln k versus T^{-1} is a straight line as shown in the following with a negative slope. The slope is given as $-E_a/R$.

A plot of log k versus T^{-1} is a straight line as shown in the following with a negative slope. The slope is given as $-E_a/2.303R$.
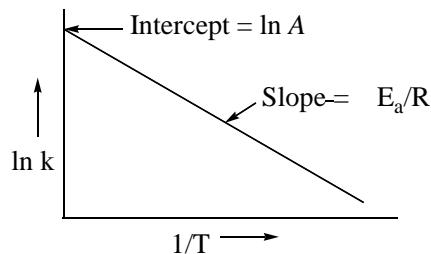
In general the specific rate is approximately doubled for every 10^OC rise of temperature for many reactions. The ratio of two specific rates measured at temperatures that differ by 10^OC is called the temperature coefficient of the reaction. The temperature coefficient is normally 2(3 in some reactions).

$$\text{Temperature coefficient} = \frac{k_{(t+10)^oC}}{k_{t^oC}} = \frac{k_{35^oC}}{k_{25^oC}} = 2 \text{ or } 3$$

#when temperature increases from T_1 to T_2, the final and initial rates are related as

Final rate= Initial rate (Temperature coefficient)^n, where n= $(T_2 - T_1)/10$

If k_1 and k_2 are the rate constants of a given chemical reaction at two different temperatures, T_1 and T_2 and assuming the free exponential factors are same at different temperatures. $\ln \frac{k_2}{k_1} = \frac{E_a}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$ **(or)** $\log \frac{k_2}{k_1} = \frac{E_a}{2.303R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$ ***If $T_2 = \infty$, then $k_1 = k_2$**

iv. Catalyst: **A catalyst is a substance which alters the rate of a reaction without itself undergoing any permanent change. Catalyst increases the rate of reaction by**

providing a new path of lower activation energy. Catalyst has no effect on

Reaction coordinate
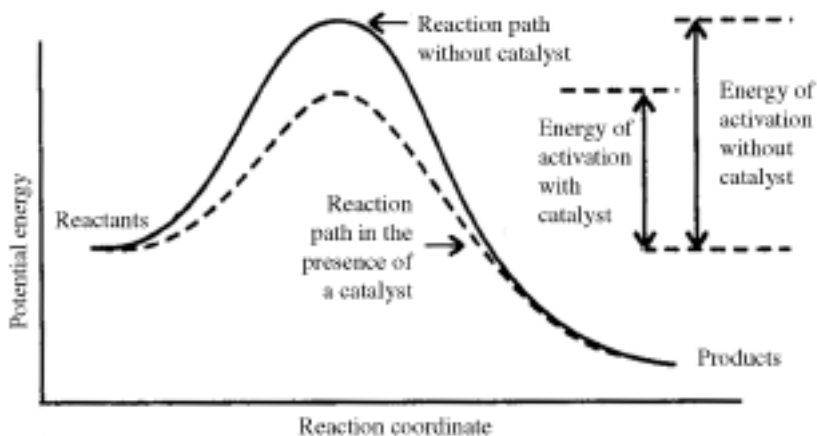
* Pressure of the gases, volume of the vessel, state of the substance, p^H etc also influence the rate of some reactions.

Rate Law and Rate Constant

I. The equation which relates the rate of the reaction and the concentration of the reactants is known as rate equation or rate law (or) Rate law is the expression in which reaction rate is given in terms of molar concentration of reactants with each term raised to some power, which may or may not be same as the stoichiometric coefficient of the reacting species in a balanced chemical equation.
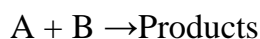
For example: $2NO_{(g)} + O_{2(g)} \rightarrow 2NO_{2(g)}$
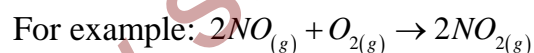
Rate equation for this reaction will be. Rate $= k[NO]^2[O_2]$

II. Rate equation is obtained experimentally. "Isolation" methods are usually followed to study rate of the reaction.

A + B → Products
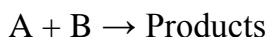
If the initial concentration of B is taken in large excess than A then rate depends on A only.
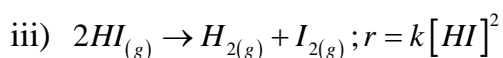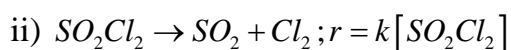
A + B →Products

Let rate $r \alpha [A]^n [B]^m$ (or) rate $= K[A]^n [B]^m$

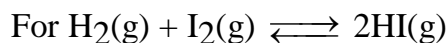'K' is called rate constant or specific rate or rate per unit concentrations of the reactants.

$$K = \frac{V}{(\text{reac tan ts})^n}$$

Units of $K = \text{mole}^{1-n} \, L^{n-1} \sec^{-1}$

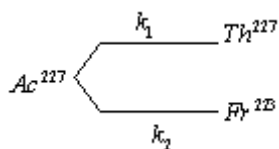i) $2NO + Cl_2 \rightarrow 2NOCl ; v = k[NO]^2 [Cl_2]$

ii) $SO_2Cl_2 \rightarrow SO_2 + Cl_2 ; r = k[SO_2Cl_2]$

iii) $2HI_{(g)} \rightarrow H_{2(g)} + I_{2(g)} ; r = k[HI]^2$

III. Rate law equation for reversible reaction

Rate $= [\text{Rate of forwardreaction}] - [\text{Rate of backwardreaction}]$

For $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

Rate $= \frac{1}{2} \frac{d[HI]}{dt} = k_1 [H_2][I_2] - k_2 [HI]^2$

Rate law equation involving side reactions

Rate of formation of $Th^{227} = k_1 [Ac^{227}]$

Rate of formation of $Fr^{223} = k_2 [Ac^{227}]$

Rate $= (k_1 + k_2)[Ac^{227}]$

Rate law and units of rate constant of some chemical reactions		
Chemical reaction	**Experiment rate law**	**Units of rate constant**

$SO_2Cl_2 \rightarrow SO_2 + Cl_2$	Rate = k[SO_2Cl_2]	S^{-1}
$2H_2O_2 \rightarrow 2H_2O + O_2$	Rate = k[H_2O_2]	s^{-1}
$2NO + O_2 \rightarrow 2NO_2$	Rate = k[NO]^2 [O_2]	L^2 mol^{-2} s^{-1}
$H_2 + Cl_2 \xrightarrow{h\upsilon} 2HCl$	RATE= K	mol L^{-1} s^{-1}
$H_2 + I_2 \rightarrow 2HI$	Rate = k [H_2] [I_2]	L mol^{-1} s^{-1}
$CHCl_3 + Cl_2 \rightarrow CCl_4 + HCl$	Rate = k [$CHCl_3$] [Cl_2]$^{1/2}$	$L^{1/2}$ mol$^{-1/2}$ s^{-1}
$CH_3COOC_2H_5 + H_2O \rightarrow CH_3COOH + C_2H_5OH$	Rate = k [$CH_3COOC_2H_5$]	s^{-1}

Rate constant

1. Rate constant is proportionality constant

2. It is equal to the reaction rate at unit concentration of reactants

3. It is independent on concentration of reactants

4. It is also dependent on the reaction temperatureand catalyst

5. Units of rate constant are: mol^{1-n} L^{n-1} S^{-1} where n is the order of reaction

Molecular collision theory of reaction rates:

It was developed by Trautz and Lewis. It is based on kinetic theory of gases.

The main points of collision theory are

1. For a reaction to take place reacting molecules must collide.

2. All collisions do not give products.

3. Collisions possessing threshold energy and proper orientation are called effective

collisions. These are also called fruitful or productive collisions.

4. Threshold energy: The minimum amount of energy required by colloiding molecules to change into products is called threshold energy. Only those collisions give rise to products in which the molecules acquire energy greater than or equal to threshold energy.

5. Collisions among molecules possessing energy less than threshold energy do not result in the formation of products. They are called normal collisions. They are to be provided with excess energy.

6. The additional energy required by reacting molecules to attain threshold energy is called activation energy. Activation Energy = Threshold Energy - Normal Energy

7. Collision between activated molecules is activated collisions

$$A + A \rightarrow A^* + A \quad (A^* = \text{activated molecule})$$

8. The number of collisions per sec per unit volume of the reaction mixture is generally high and is known as collision frequency. The fraction of activated collisions among the total collisions is very much small. The fraction of frutiful collisions is given

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

9. If P is the orientation factor, $k = PZ\, e^{-Ea/RT}$.

Z is the collision factor. $Z = \pi \sigma_{AB}^2 \sqrt{8kT/\pi\mu}\ n_A . n_B$

For a molecule of AB, σ is collision diameter and μ is reduced mass. k is the Boltzmann constant and T is the temperature in kelvin.

10) As temperature increases the no of effective collisions and hence rate of reaction increases.
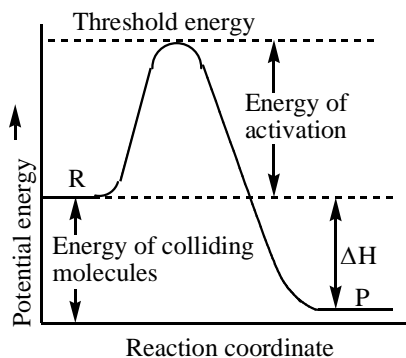
Concept of Activation Energy

Energy of activation is a factor characteristic of reactants. It is independent of concentration and pressure, but to the first approximation, independent of temperature also. If activation energy of forward reaction (Ea$_f$) is less than that of the backward reaction (Ea$_b$), the reaction is exothermic.
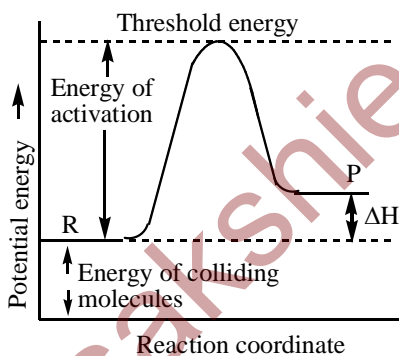
The heat of the reaction, $\Delta H = Ea_f - Ea_b$

Reactions with lower activation energy are fast and with higher activation energy are slow.

Energy Profile Diagram

Exothermic reaction, ΔH is -ve

Endothermic reaction, ΔH is +ve

For an Exothermic reaction Activation energy of forward (E_F)< Activation energy of forward(E_b)

For an Endothermic reaction Activation energy of forward (E_F)> Activation energy of forward (E_b)

Enthalpy of reaction= Activation energy of forward (E_F) - Activation energy of forward (E_b)