

CHEMICAL KINETICS

IMPORTANT ASPECTS OF CHEMICAL REACT

- (i) The feasibility of a chemical reaction which can be predicted by thermodynamics ($\Delta G = -ve$ at constant temperature and pressure is feasible)
- (ii) Extent to which a reaction will proceed can be determined from chemical equilibrium.
- (iii) the speed of the reaction, i.e., time taken by a reaction to take place (to reach equilibrium).

Chemical Kinetics: Branch of chemistry, which deals with the study of reaction rates and their mechanisms is called chemical kinetics.

* Thermodynamics tells only about the feasibility of reaction whereas chemical kinetics tells about the rate of reaction.

Factors affecting reaction rate:

Concentration, temperature, pressure and catalyst.

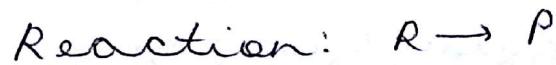
Rate of Chemical Reaction:

Some reactions such as ionic reactions occur very fast. E.g. Precipitation of $AgCl_{(s)}$ by mixing of aqueous solutions of $AgNO_3$ and $NaCl$.

Slow reactions: Rusting of iron in the presence of air and moisture.

Moderate speed reactions: Inversion of cane sugar, hydrolysis of starch

- Speed of the reaction or rate of the reaction is defined as the change in concentration of a reactant and product in unit time.
- It can be expressed in terms of :-
 - (i) the rate of decrease in the concentration of any one of the reactants, or
 - (ii) the rate of increase in the concentration of any one of the products.



At time t_1 : $[R]$, and $[P]$,

At time t_2 : $[R]_2$, and $[P]_2$

$\Delta t = t_2 - t_1$ [] : molar concentration

$$\Delta[R] = [R]_2 - [R]_1$$

$$\Delta[P] = [P]_2 - [P]_1$$

Rate of disappearance of R

$$= \frac{\text{Decrease in conc. of } R}{\text{Time taken}} = \frac{-\Delta[R]}{\Delta t}$$

Rate of appearance of P = $\frac{\text{Increase in conc. of } P}{\text{Time taken}}$

$$= \frac{\Delta[P]}{\Delta t}$$

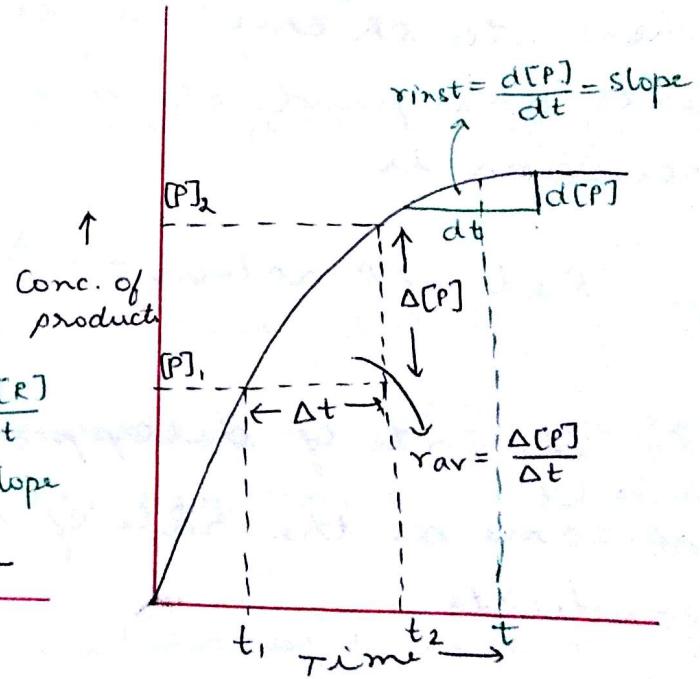
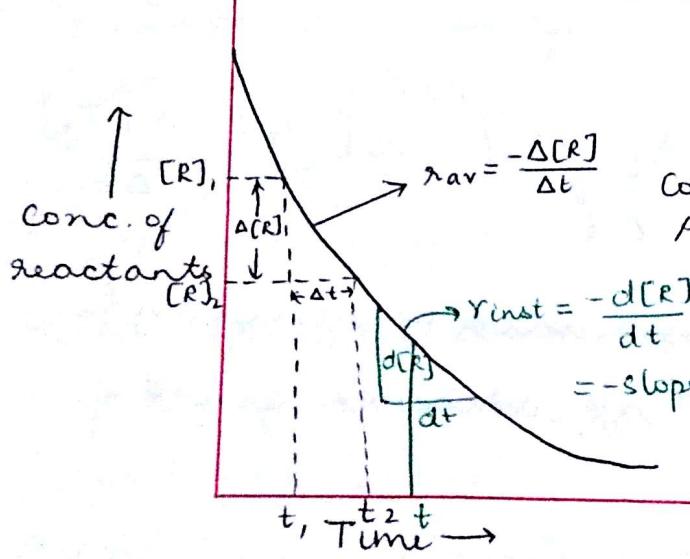
→ $\Delta[R]$ is a negative quantity as the concentration of reactants is decreasing, it is multiplied with -1 to make the reaction rate a positive quantity.

- Average rate depends upon the change in concentration of reactants or products and the time taken for that change to occur.

$$\textcircled{1} \quad r_{\text{av}} = -\frac{\Delta[R]}{\Delta t} = \frac{\Delta[P]}{\Delta t}$$

$$\textcircled{2} \quad r_{\text{inst}} = -\frac{d[R]}{dt} = \frac{d[P]}{dt}$$

INSTANTANEOUS AND AVERAGE RATE OF REACTION



Units of Rate of a Reaction:

- * concentration time^{-1}
- * mol L⁻¹ s⁻¹
- * with gaseous reactions, concentration of gases in terms of partial pressures
units are atm s⁻¹.

Instantaneous Rate:

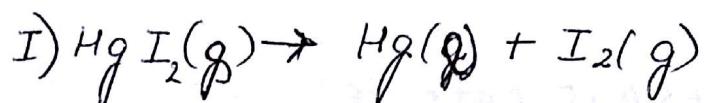
- * To express the rate at a particular moment of time.

For an infinitesimally small Δt instantaneous rate is given by

$$r_{\text{inst}} = -\frac{\Delta [R]}{\Delta t} = \frac{\Delta [P]}{\Delta t}$$

As $\boxed{\Delta t \rightarrow 0}$ or

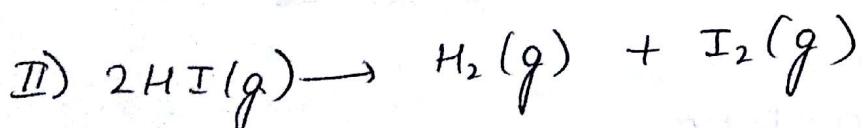
$$r_{\text{inst}} = -\frac{d[R]}{dt} = \frac{d[P]}{dt}$$



- Where stoichiometric coefficients of the reactants and products are the same rate of reaction is

$$\text{Rate of reaction} = -\frac{\Delta[HgI_2]}{\Delta t} = \frac{\Delta[Hg]}{\Delta t} = \frac{\Delta[I_2]}{\Delta t}$$

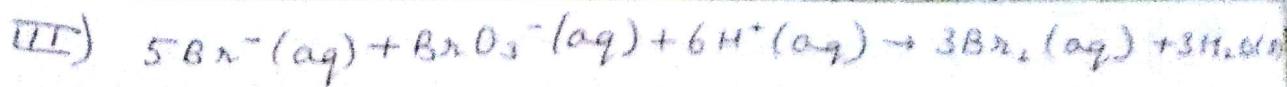
i.e., the rate of disappearance of reactants is same as the rate of appearance of the products.



- Where stoichiometric coefficients are different the rate of reaction is

$$\text{Rate of reaction} = -\frac{1}{2} \frac{\Delta[HI]}{\Delta t} = \frac{\Delta[H_2]}{\Delta t} = \frac{\Delta[I_2]}{\Delta t}$$

Divided by their stoichiometric coefficients.



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

- * For a gaseous reaction at constant temperature, concentration is directly proportional to the partial pressure of a species and hence, rate can also be expressed as rate of change of partial pressure of the reactant and/or the product.

Factors Influencing Rate of a Reaction:

Experimental conditions such as

- concentration of reactants (pressure in gases)
- temperature
- catalyst

1. Dependence of Rate on Concentration:

- The representation of rate of reaction in terms of concentration of the reactants is known as rate law.
- Also called rate equation or rate expression

2. Rate Expression and Rate Constant:

- The rate of reaction decreases with the passage of time as the concentration of the reactants decreases.
- Conversely, rates ↑ with ↑ in concentration of reactants. Rate of reaction depends upon its concentration of reactants.

General Equation:



a, b, c, d : stoichiometric coefficients

Rate Expression:

$$\text{Rate} \propto [A]^x [B]^y$$

x, y : may, may not be equal to the stoichiometric coefficients of reactants.

$$\text{Rate} \propto [A]^x [B]^y$$

$$\boxed{\text{Rate} = k[A]^x [B]^y}$$

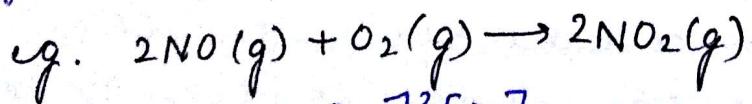
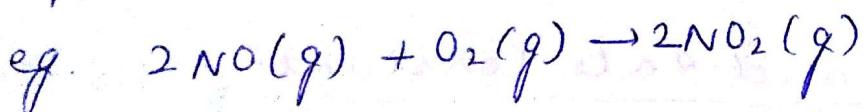
rate law or rate expression

$$\boxed{-\frac{d[R]}{dt} = k[A]^x [B]^y}$$

Differential Rate Equation

→ rate constant

RATE LAW: The expression in which reaction rate is given by 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.



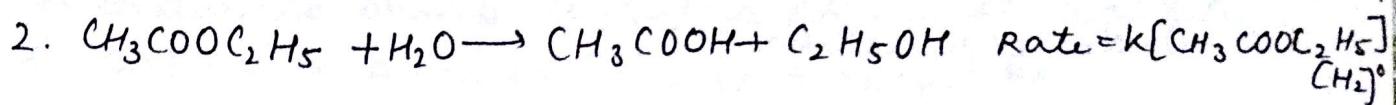
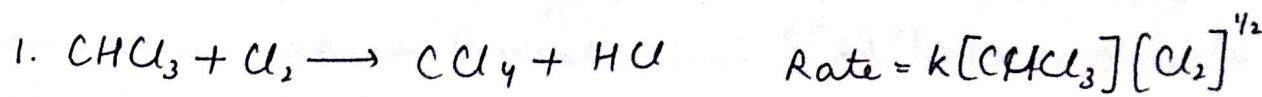
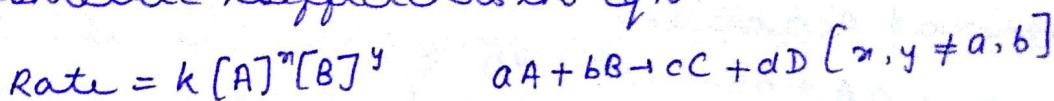
$$\text{Rate} = k[NO]^2 [O_2]$$

Differential form of equation:

$$-\frac{d[R]}{dt} = k[NO]^2 [O_2]$$

Ether Aads

Examples of reactions where x and y are ^{not} equal to stoichiometric coefficients in eqn:



* Rate law for any reaction cannot be predicted by merely looking at the balanced equation, i.e., theoretically but must be determined experimentally.

ORDER OF REACTION:

The sum of powers of the concentration of the reactants in the rate law expression is called the order of the chemical reaction.

- Order can be 0, 1, 2, 3 and even a fraction.
- Zero order reaction means that the rate of the reaction is independent of the concentration of the reactants.

Elementary Reactions: Taking place in one step.

Complex reactions: Sequence of elementary reactions (called mechanism) gives products.

e.g. Consecutive reactions like oxidation of ethane to CO_2 and H_2O passes through a series of intermediate steps in which alcohol, aldehyde and acid are formed), reverse reactions, side reactions like nitration of phenol yields σ -nitrophenol and p -nitrophenol.

UNITS OF RATE CONSTANT (k) :

General Reaction:



$$\text{Rate} = k[A]^x[B]^y$$

$$\text{Order of reaction} = x+y$$

$$k = \frac{\text{Rate}}{[A]^x[B]^y}$$

$$= \frac{\text{conc.}}{\text{time}} \times \frac{1}{(\text{conc.})^n} \quad (\text{where } [A]=[B])$$

$$= \frac{(\text{conc.})^{1-n}}{\text{time}}$$

$$\text{i.e.} = \left(\frac{\text{mol}}{\text{L}} \right)^{1-n} \text{sec}^{-1}$$

FOR '0' ORDER : $n=0$

$$k = (\text{conc})^{1-0} \text{ s}^{-1}$$

$$= \boxed{\text{mol L}^{-1} \text{s}^{-1}}$$

FOR '1' ORDER : $n=1$

$$k = (\text{mol L}^{-1})^0 \text{ s}^{-1} = \boxed{\text{s}^{-1}}$$

FOR '2' ORDER : $n=2$

$$k = (\text{mol L}^{-1})^{1-2} \text{ s}^{-1}$$

$$= \boxed{\text{L mol}^{-1} \text{s}^{-1}}$$

Q. (i) $k = 2.3 \times 10^{-5} \text{ L mol}^{-1} \text{s}^{-1}$ (2nd Order)

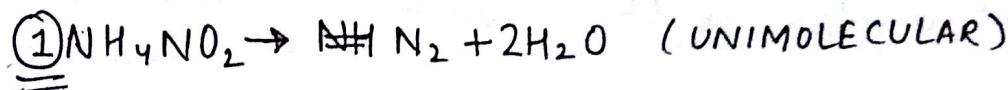
(ii) $k = 3 \times 10^{-4} \text{ s}^{-1}$ (1st ORDER)

MOLECULARITY OF A REACTION:

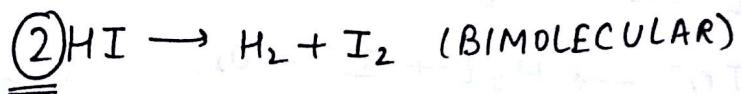
The number of reacting species (atoms, ions or molecules) taking part in an elementary reaction, which must collide simultaneously in order to bring about a chemical reaction is called molecularity of a reaction.

- The reaction is unimolecular when one reacting species is involved.

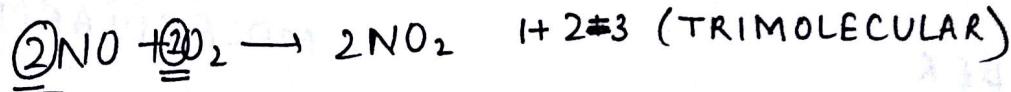
for eg., decomposition of ammonium nitrate.



- Bimolecular reactions involve simultaneous collision between two species.

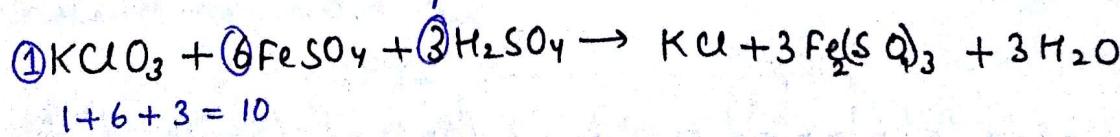


- Trimolecular / termolecular reactions involve simultaneous collision between three reacting species.



Probability of more than three molecules colliding and reacting simultaneously is very small.

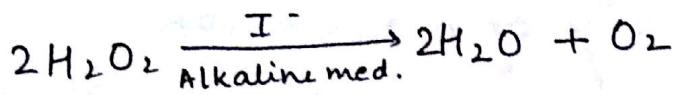
- Reactions with molecularity 3 are rare and slow to proceed.
- complex reactions involving more than 3 molecules in the stoichiometric equation take place in more than one step.



not 10th order but 2nd order reaction.

- Reaction takes place in several steps.
- Overall rate of the reaction is controlled by the slowest step in a reaction called the rate determining step.

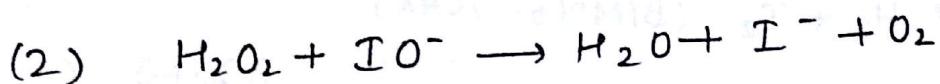
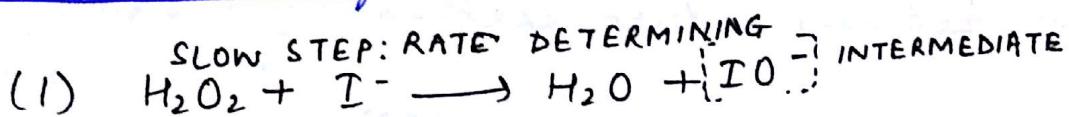
DECOMPOSITION of H_2O_2 (CATALYST USED: I^- ion) (IN ALK. MED.)



$$\text{Rate} = -\frac{d[H_2O_2]}{dt} = k[H_2O_2][I^-]$$

First order with respect to both I^- and H_2O_2 .

Mechanism of reaction: (IMP)



∴ Rate of formation of intermediate will determine the rate of this reaction.

ORDER

MOLECULARITY

- | | |
|---|--|
| 1. An experimental quantity. | 1. Molecularity cannot be zero or a non-integer. |
| Can be zero and even a fraction. | 2. Applicable only for elementary reactions for complex reactions it has no meaning. |
| 2. Applicable to elementary as well as complex reactions. | 3. Molecularity of the slowest step is same |
| 3. For complex reaction order is given by the slowest | |

step. as the overall reaction.

INTEGRATED RATE EQUATIONS:

Cone. dependence of rate is called differential rate equation.

Instantaneous rate is measured by determination of slope of the tangent at point 't' in cone. v/s time plot. Relation between directly measured experimental data i.e. cone. at different times and rate constant -

ZERO ORDER REACTIONS:

Rate of reaction proportional to zero power of the concentration of reactants.



$$\text{Rate} = k[R]^0 = -\frac{d[R]}{dt} \quad [:\text{'0' order}]$$

$$\Rightarrow -\frac{d[R]}{dt} = k(1)$$

$$\Rightarrow d[R] = -k dt$$

Integrating both sides

$$\Rightarrow \int d[R] = - \int k dt$$

$$\Rightarrow [R] = -kt + I \quad (I : \text{constant of integration})$$

At $t=0$ $R = [R]_0$ where $[R]_0$ is initial concentration of the reactant.

$$\Rightarrow [R]_0 = I \quad \text{---} ②$$

Substituting ② in ①

$$\Rightarrow [R] = -kt + [R]_0$$

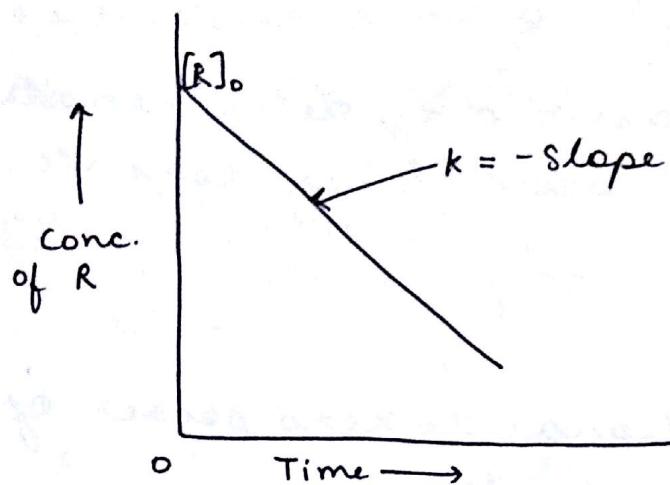
$$\Rightarrow [R]_0 - [R] = kt \Rightarrow$$

$$k = \frac{[R]_0 - [R]}{t}$$

$$[R]_t = -kt + [R]_0 \quad [R] = [R]_0 + kt$$

$$y = mx + c$$

$$\Rightarrow y = [R]_t ; m = +k ; x = t ; c = [R]_0$$



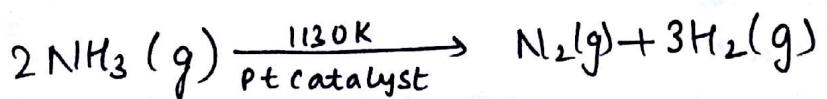
VARIATION IN CONC. VS TIME PLOT FOR A ZERO ORDER REACTION

→ Zero order reactions are relatively uncommon but they occur under special conditions.

Examples of zero order reactions :

- * Some enzyme catalysed reactions and reactions which occur on metal surfaces.

I. Decomposition of gaseous ammonia on a hot platinum surface (0 order at high pressure)



$$\boxed{\text{rate} = k[\text{NH}_3]^0 = k}$$

In this reaction, Pt metal acts as a catalyst. At high pressure the metal surface gets saturated with gas molecules.

So a further change in reaction conditions is unable to alter the amount of ammonia on the surface of the catalyst making the reaction independent of its concentration.

II. Thermal decomposition of HI on gold surface.

FIRST ORDER REACTIONS:

Reaction proportional to the first power of the concentration of the reactant R.

e.g.



$$\text{Rate} = -\frac{d[R]}{dt} = k[R]$$

$$\frac{d[R]}{[R]} = -k dt$$

Integrating,

$$\int \frac{d[R]}{[R]} = -k \int dt$$

$$\log [R] = -kt + I$$

or

$$\ln [R] = -kt + I \quad \textcircled{1}$$

At time $t=0$ when $R=[R]_0$

$$\Rightarrow \ln [R]_0 = I \quad \textcircled{2}$$

Substituting $\textcircled{2}$ in $\textcircled{1}$

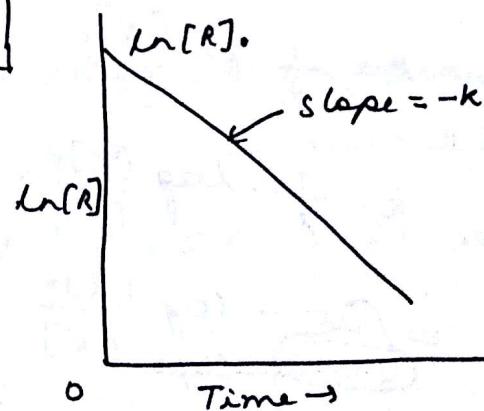
$$\Rightarrow \boxed{\ln [R] = -kt + \ln [R]_0}$$

$$\Rightarrow \ln [R] - \ln [R]_0 = -kt$$

$$\Rightarrow \frac{\ln [R]_0}{\ln [R]} = kt$$

$$\Rightarrow \frac{\ln [R]_0}{[R]} = kt$$

$$\Rightarrow \boxed{\frac{1}{t} \ln \left(\frac{[R]_0}{[R]} \right) = k}$$



$\ln [R]$ and t PLOT
FOR 1st ORDER RXN.

At time t , from equation $\ln[R] = -kt + I$

$$\ln[R]_1 = -kt_1 + \ln[R]_0 \quad \text{--- (3)}$$

At time t_2

$$\ln[R]_2 = -kt_2 + \ln[R]_0 \quad \text{--- (4)}$$

$[R]_1$ and $[R]_2$ are concentrations of reactants at time t_1 and t_2 .

$$(3) - (4)$$

$$\ln[R]_2 - \ln[R]_1 = -kt_2 + kt_1$$

$$\ln\left(\frac{[R]_1}{[R]_2}\right) = k(t_2 - t_1)$$

$$k = \ln\left(\frac{[R]_1}{[R]_2}\right) \cdot \frac{1}{(t_2 - t_1)}$$

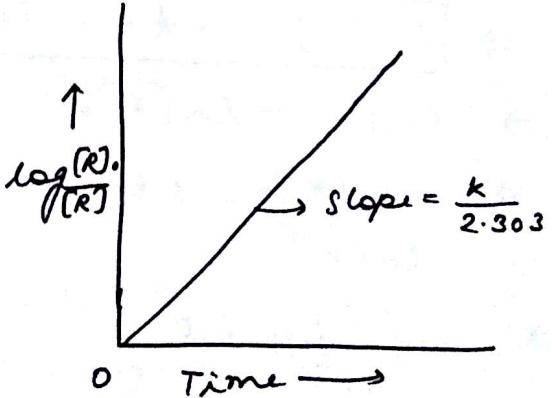
$$\ln\left(\frac{[R]}{[R]_0}\right) = -kt$$

$$[R] = [R]_0 e^{-kt}$$

$$\text{from } k = \frac{1}{t} \ln\left(\frac{[R]_0}{[R]}\right)$$

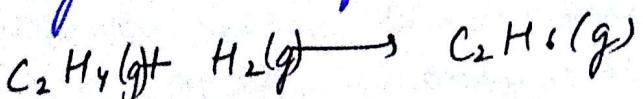
$$k = \frac{1}{t} \cdot \log\left(\frac{[R]_0}{[R]}\right) \times 2.303$$

$$\Rightarrow \frac{k}{2.303} t = \log\left(\frac{[R]_0}{[R]}\right)$$



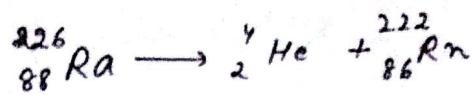
Examples of FIRST order reactions:

i. Hydrogenation of ethene.



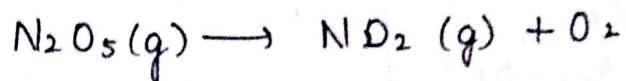
$$\text{Rate} = k[C_2H_4]$$

II) All natural and artificial radioactive decay of unstable nuclei take place by first order kinetics.

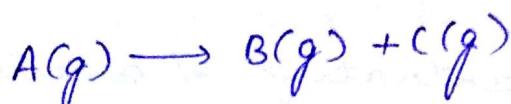


$$\text{Rate} = k[\text{Ra}]$$

III) Decomposition of N_2O_5 and N_2O are some exgs. of first order reactions.



FIRST ORDER REACTION IN GAS PHASE:



p_i : initial pressure of A

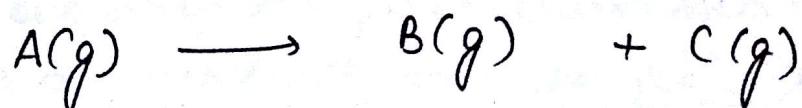
p_t : total pressure of gas at time t

Derivation of integrated rate equation:

Total pressure $= p_t = p_A + p_B + p_C$ (pressure units)

p_A , p_B and p_C are partial pressures of A, B and C.

At time t, x atm is decreased in pressure A and one mole each of B and C is formed, the increase in pressure of B and C will also be x atm each.



At $t=0$ p_i atm 0 atm 0 atm

At time t $(p_i - x)$ atm x atm x atm

$$p_t = (p_i - x) + x + x$$

$$p_t = p_i + x \Rightarrow x = p_t - p_i$$

where $P_A = p_i - x$

$$= p_i - p_t + p_i$$

$$\boxed{P_A = 2p_i - p_t}$$

$$k = \frac{2.303}{t} \left(\log \frac{p_i}{(P_A)} \right)$$

$$\boxed{k = \left(\frac{2.303}{t} \right) \log \left(\frac{p_i}{2p_i - p_t} \right)}$$

HALF-LIFE OF A REACTION:

Time in which the concentration of a reactant is reduced to one half of its original/initial concentration.

Representation: $t_{1/2}$

FOR ZERO ORDER REACTION,

$$k = \frac{[R]_0 - [R]}{t}$$

$$\text{At } t = t_{1/2}, [R] = \frac{[R]_0}{2}$$

The rate constant at $t_{1/2}$ is

$$k = \frac{[R]_0 - [R]_0/2}{t_{1/2}}$$

$$k = \frac{[R]_0}{2 \times t_{1/2}}$$

$$\Rightarrow \boxed{t_{1/2} = \frac{[R]_0}{2k}}$$

$t_{1/2}$ is directly proportional to the initial conc. of the reactants and inversely proportional to the rate const. k .

FOR FIRST ORDER REACTION:

$$k = \frac{2.303}{t} \log \frac{[R]_0}{[R]}$$

$$t = t_{1/2} \text{ and } [R] = [R]_0/2$$

$$k = \frac{2.303}{t_{1/2}} \log \left(\frac{[R]_0 \times 2}{[R]_0} \right)$$

$$t_{1/2} = \frac{2.303}{k} \cdot \log 2$$

$$= \frac{2.303 \times 0.301}{k} = \frac{0.693}{k}$$

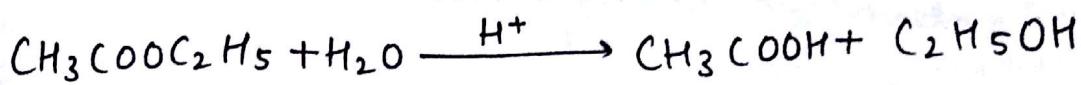
$$\Rightarrow t_{1/2} = \frac{0.693}{k}$$

$t_{1/2}$ is constant. It is independent of initial concentration of the reacting species.

PSEUDO FIRST ORDER REACTION:

order sometimes altered by conditions

Hydrolysis of $\text{CH}_3\text{COOC}_2\text{H}_5$ (Acetate) :-



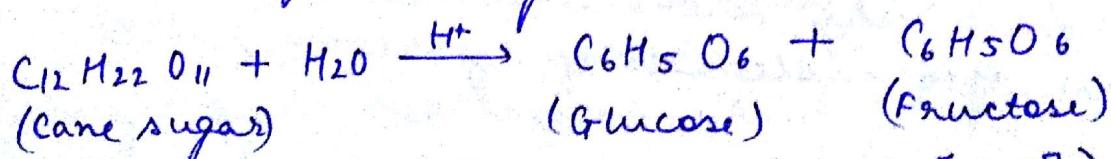
Concentration of H_2O not altered much during course of reaction.

$$\text{Rate} = k' [\text{CH}_3\text{COOC}_2\text{H}_5] [\text{H}_2\text{O}]$$

$$\text{Rate} = k [\text{CH}_3\text{COOC}_2\text{H}_5] \quad (k = k' [\text{H}_2\text{O}])$$

Reaction behaves as first order reaction. Such reactions are called pseudo first order reaction.

Inversion of Cane sugar :-



$$D_{\text{inverted}} = k [\text{C}_{12}\text{H}_{22}\text{O}_{11}] \quad (k = k' [\text{H}_2\text{O}])$$

TEMPERATURE DEPENDENCE OF THE RATE OF A REACTION:

Chemical reactions accelerated by increase in temperature.

e.g. → Decomposition of N_2O_5 takes place at faster rate when temperature is increased.

→ In a mixture of KMnO_4 and $\text{C}_2\text{H}_5\text{COOH}$, KMnO_4 gets decolourised faster at a higher temp. than at a lower temperature.

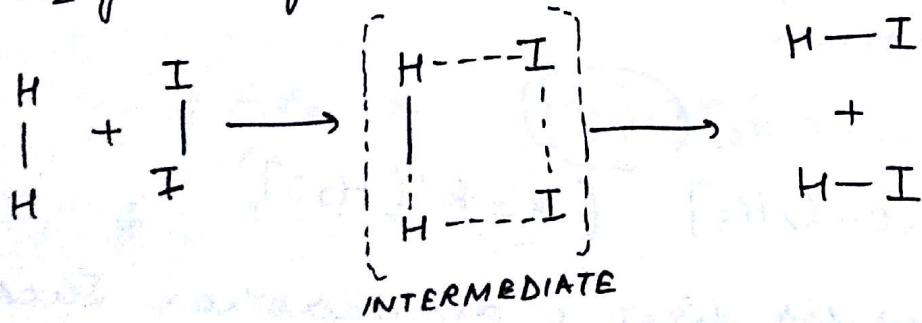
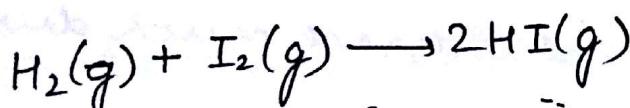
- For a chemical reaction with rise of in temperature by 10° the rate constant is nearly doubled.
- Temp. dependence of rate of chemical equation accurately explained by Arrhenius equation.

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

A : Arrhenius factor / frequency factor / pre-exponential factor
(constant specific to a particular reaction)

R : Gas constant

E_a : Activation energy (in J/mol)



Reaction can take place only when a molecule of hydrogen and a molecule of iodine collide to form an unstable intermediate. It exists for a very short time and then breaks up to form two molecules of hydrogen iodide.

ACTIVATED COMPLEX: The intermediate is also called activated complex.

ACTIVATION ENERGY: Energy required to form this intermediate/activated complex is known as activation energy (E_a).

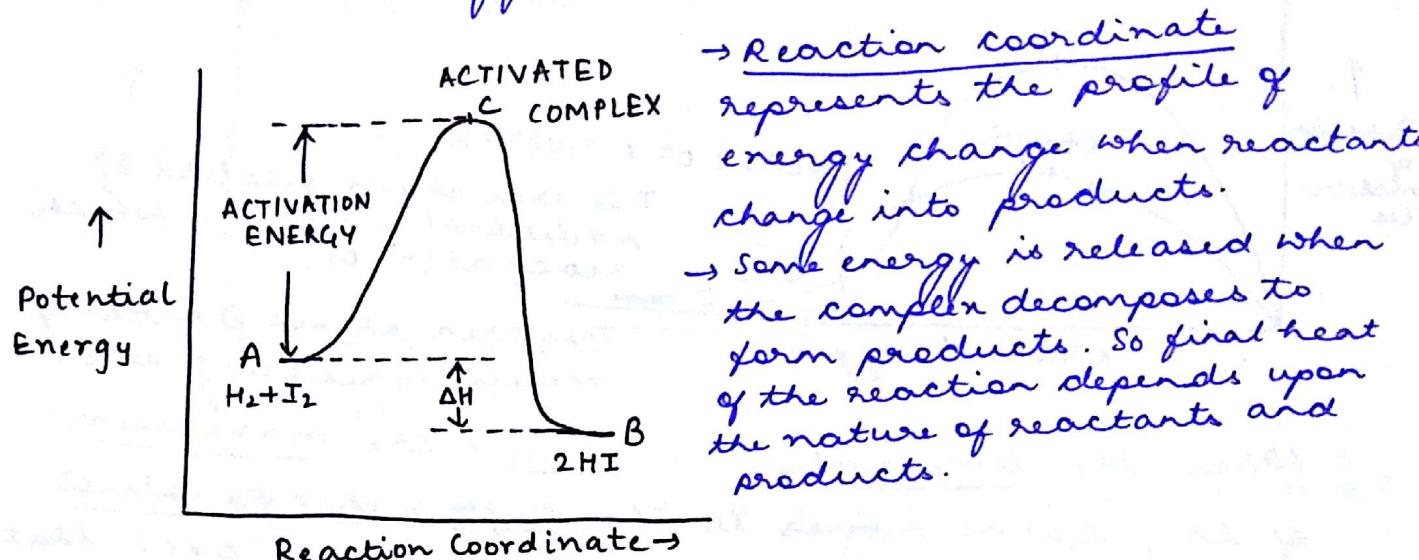
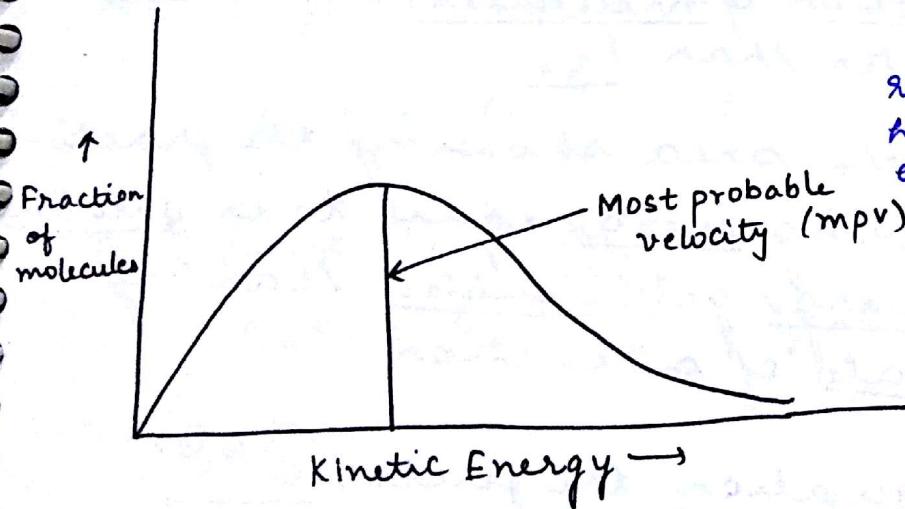


DIAGRAM SHOWING PLOT OF POTENTIAL ENERGY VS REACTION COORDINATE.

Boltzmann and Maxwell Curve:



ENERGIES AMONG GASEOUS MOLECULES

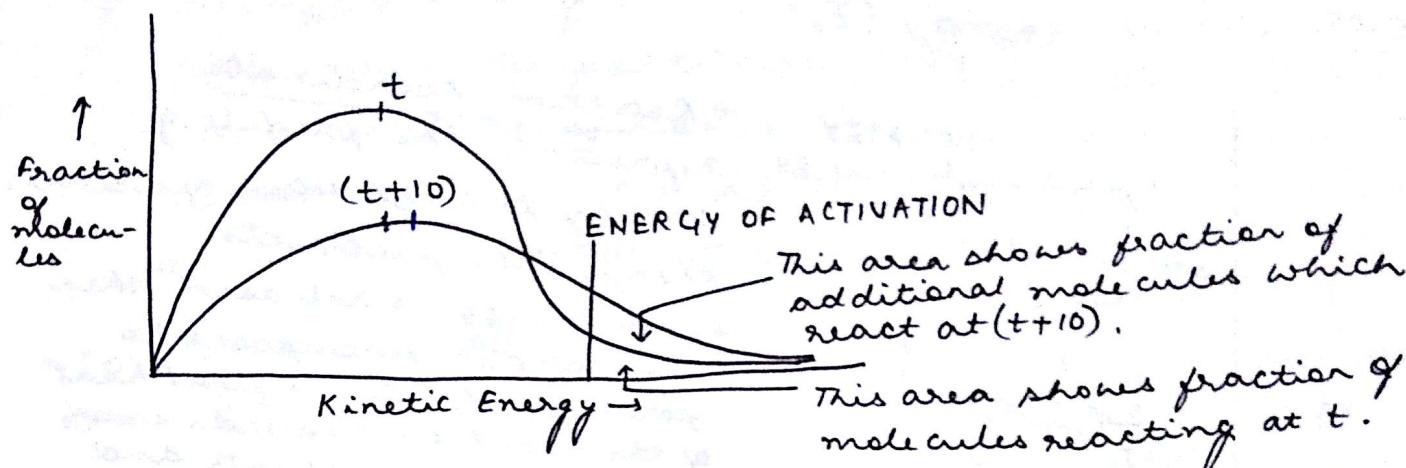
- * All molecules in the reacting species do not have the same kinetic energy.
- * Difficult to predict behaviour of any one molecule with precision.
- * According to Boltzmann and Maxwell, the distribution of K.E. may be described by plotting the fraction of molecules (N_E/N_T) with a given K.E. (E) vs K.E. - .

* Here N_E : no. of molecules with energy E .
 N_T : total no. of molecules.

* Peak of curve: most probable K.E., i.e., K.E. of maximum fraction of molecules.

- * Decreasing number of molecules with energies higher or lower than this value.

Temperature dependence curves:



- * When the temperature is raised, the maximum of the curve moves to the higher energy value and the curve spreads to the right such that there is a greater proportion of molecules with much higher energies.
- * Area under the curve must be constant since total probability must be one at all times.
- Increasing the ^{temp of substance} fraction of molecules, which collide with energies greater than E_a .
- In the curve at (t+10), the area showing the fraction of molecules having energy equal to or greater than activation energy gets doubled leading to doubling the rate of a reaction.

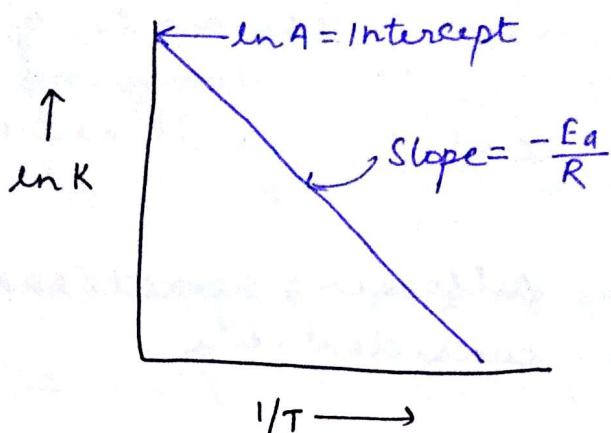
In the Arrhenius equation the factor $e^{-E_a/RT}$ corresponds to the fraction of molecules having ^{kinetic} activation energy equal to or greater than the activation energy E_a .

Taking natural log on both sides of
 $k = A e^{-E_a/RT}$

$$\ln K = \ln(A \cdot e^{-E_a/RT})$$

$$\Rightarrow \ln K = \ln A + \ln e^{-E_a/RT}$$

$$\Rightarrow \boxed{\ln K = \ln A + \frac{-E_a}{RT}}$$



Thus it has been found from Arrhenius equation that increasing the temperature or decreasing or decreasing the activation energy (E_a) will result in an increase in the rate of the reaction and an exponential increase in the rate constant.

At temp. T_1 , equation ① is

$$\ln k_1 = \ln A - \frac{E_a}{RT_1} \quad \text{--- } ③$$

At temp T_2 it is

$$\ln k_2 = \ln A - \frac{E_a}{RT_2} \quad \text{--- } ④$$

$$④ - ③$$

$$\ln k_2 - \ln k_1 = \ln A - \frac{E_a}{RT_2} - (\ln A + \frac{E_a}{RT_1})$$

$$\ln \left(\frac{k_2}{k_1} \right) = \frac{E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

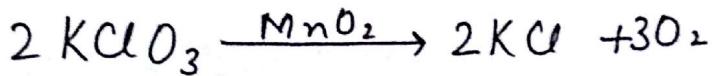
$$\log \left(\frac{k_2}{k_1} \right) = \frac{E_a}{2.303R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$\log\left(\frac{K_2}{K_1}\right) = \frac{E_a}{2.303R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$

EFFECT OF CATALYST:

A substance which increases the rate of the reaction without itself undergoing any permanent chemical change is known as a catalyst.

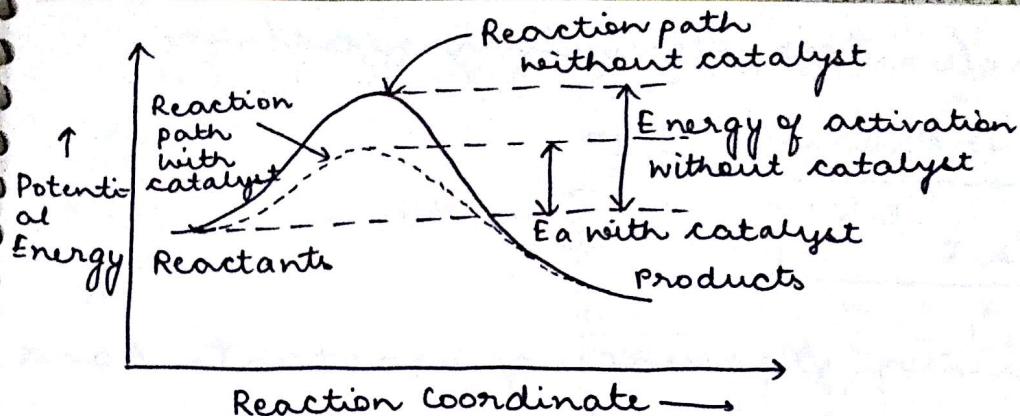
e.g. MnO_2 catalyses the following reaction and increases its rate considerably.



Inhibitors are substances which are added to reduce the rate of the reaction.

Intermediate Complex Theory:

- According to this theory, a catalyst participates in a chemical reaction by forming temporary bonds with the reactants resulting in an intermediate complex. This has a transitory existence and decomposes to yield products and the catalyst.
- The catalyst provides an alternate pathway or reaction mechanism by reducing the activation energy between the reactants and products and hence lowering the potential energy barrier.
- From Arrhenius eqn, lower the value of ΔE_a faster will be the rate of the reaction.



Effect of catalyst on activation energy

CHARACTERISTICS OF A CATALYST:

1. Does not alter Gibbs energy, ΔG of a reaction
2. Catalyses the spontaneous reactions but does not catalyse non-spontaneous reactions
3. Does not change the equilibrium constant of a reaction rather, it helps in attaining the equilibrium faster, ie, it catalyses the forward and the backward reactions to the same extent so that the equilibrium state remains same but is reached earlier.

COLLISION THEORY OF CHEMICAL REACTIONS:

(By Trautz and Lewis)

Based on Kinetic Theory of Gases :

According to this theory, the reactant molecules are assumed to be hard spheres and the reaction is postulated to occur when molecules collide with each other.

Collision frequency (Z): The number of collisions per second per unit volume of the reaction mixture is known as collision frequency.

For a bimolecular elementary reaction



$$\boxed{\text{Rate} = Z_{AB} e^{-E_a/RT}} \quad - \quad \textcircled{I}$$

- Z_{AB} : collision frequency of reactants A and B.
- $e^{-E_a/RT}$: fraction of molecules with energies equal to or greater than E_a .
- A is related to Z_{AB} (collision frequency).

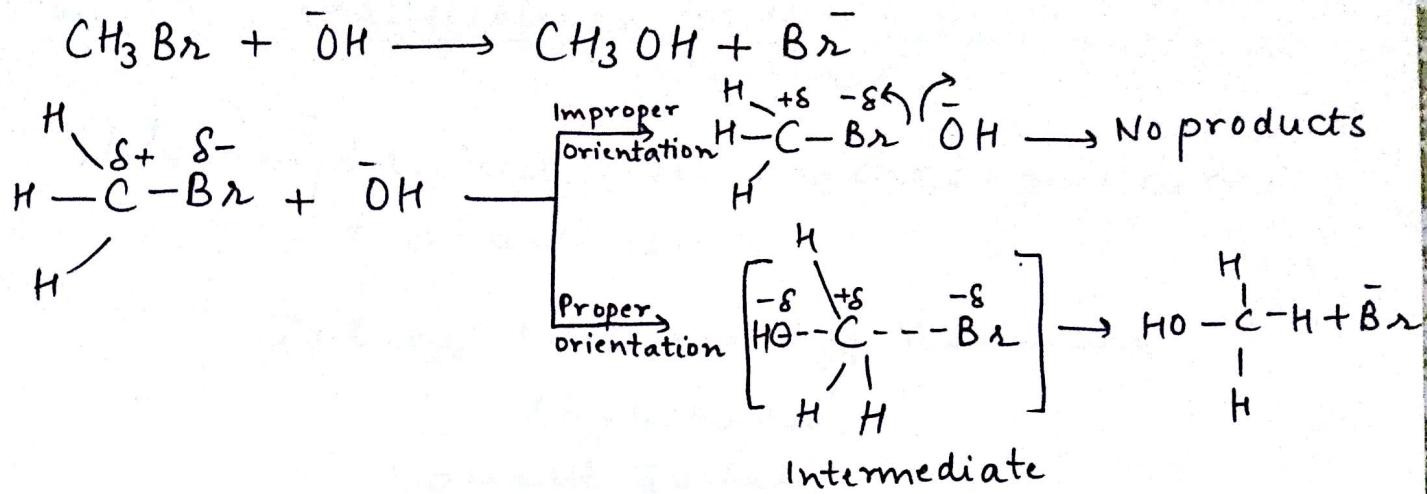
Equation \textcircled{I} predicts the value of rate constants fairly accurately for the reactions involving atomic species or simple molecules but for complex molecules significant deviations are observed.

Reason: All collisions do not lead to the formation of products.

Effective Collisions:

The collisions in which molecules collide with sufficient kinetic energy (threshold energy) and proper orientation, so as to facilitate the formation of products by breaking of bonds between reacting species and formation of new bonds are called as effective collisions.

e.g. formation of methanol from C_2H_5Br depends upon orientation of reactant molecules.



The proper orientation of reactant molecules lead to bond formation whereas improper orientation makes them simply bounce back and no products are formed.

To account for effective collisions, another factor P , called the probability or steric factor is introduced. Takes into account the fact that in a collision, molecules must be properly oriented, i.e.,

$$\text{Rate} = P Z_{AB} e^{-E_a/RT}$$

In collision theory, ① activation energy and ② proper orientation of the molecules together determine the criteria for an effective collision and hence the rate of the chemical reaction.

Drawbacks:

Considers atoms/molecules to be hard spheres and ignores their structural aspect.