CHEMICAL KINETICS

Dr. Suman Adhikari

Department of Chemistry,

Govt. Degree college, Dharmanagar

Email: sumanadhi@gmail.com

Phone no.: 9774354025

“Chemical Kinetics helps us to understand how chemical reactions occur”

The branch of chemistry, which deals with the study of reaction rates and their mechanisms, called **chemical kinetics**.

The rate of a reaction can be defined as the change in concentration of a reactant or product in unit time. To be more specific, it can be expressed in terms of:

(i) the rate of decrease in concentration of any one of the reactants, or

(ii) the rate of increase in concentration of any one of the products.

Rate of reaction

For a reaction,

$$A + B \rightarrow D$$

The rate may be expressed as

$$\frac{-d[A]}{dt} \quad \text{or} \quad -\frac{d[B]}{dt} \quad \text{or} \quad \frac{d[D]}{dt}$$

$$\text{Rate of reaction} = \frac{\text{Change in the concentration of species}}{\text{Time interval}}$$

$$\text{Unit of rate of reaction} = \text{mol}L^{-1}\,s^{-1}$$

Rate of reaction

For general reaction

$$aA + bB \longrightarrow cC + dD$$

Rate of reaction

$$= \frac{-1}{a}\frac{d(A)}{dt} = \frac{-1}{b}\frac{d(B)}{dt} = \frac{1}{c}\frac{d(C)}{dt} = \frac{1}{d}\frac{d(D)}{dt}$$

According to law of mass action

$$\text{Rate} = k[A]^a[B]^b$$

Where k is rate constant.

Rate constant

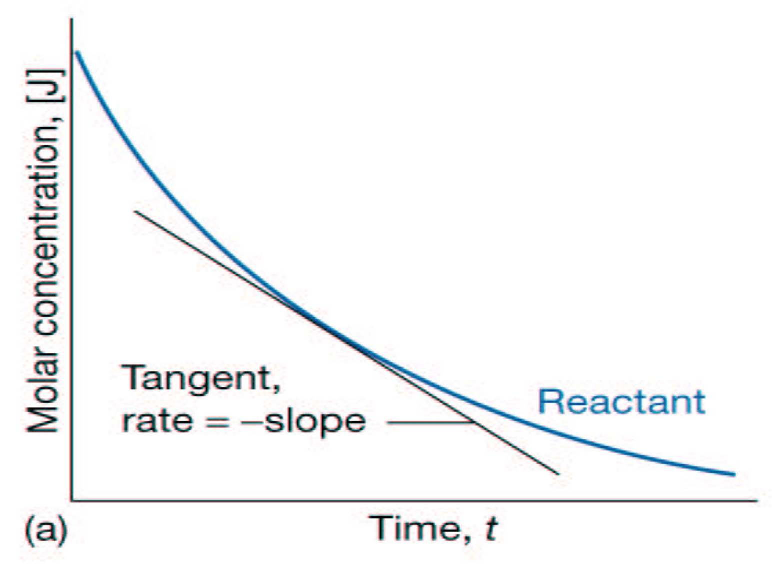
Measure of rate of reaction

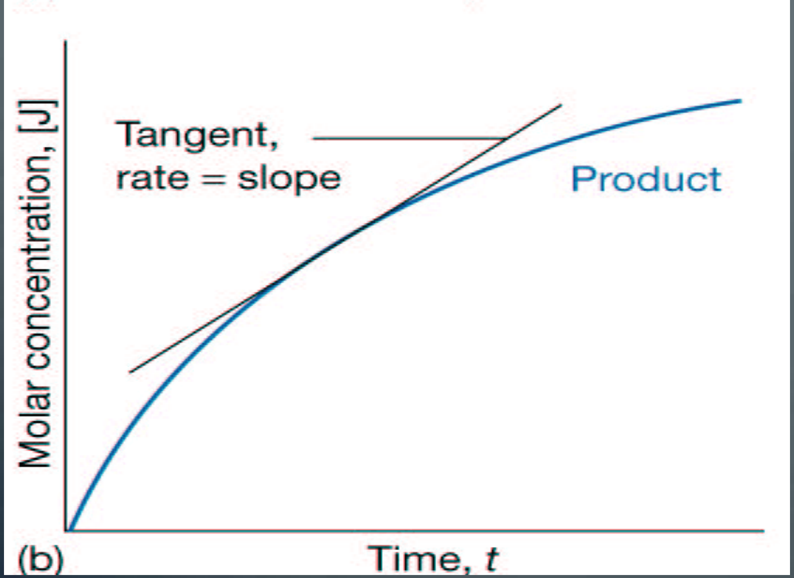
Different for different reactions

Independent of concentration of reactants

Depends on the temperature

Graphical representation of rate





- The slope of graph at any instant gives us the rate of reaction at that moment and is called instantaneous rate of the reaction.

- The average of these slopes over a period gives us rate of the reaction which is called as average rate of the reaction.

Rate law

It is a mathematical expression that gives the true rate of reaction in terms of concentration of the reactants which actually influence the rate.

Rate expression is experimentally determined.

Consider a general reaction

$$\boxed{CH_3CHO(g) \xrightarrow{\Delta} CH_4(g) + CO(g)}$$

$$\frac{d[CH_4]}{dt} = k[CH_3CHO]^{3/2}$$

Molecularity

For an elementary reaction, molecularity is the total number of molecules taking part in reaction.

It has no significance for complex reaction

Order of reaction

The number of molecules which actually react and undergo a change in concentration is known as **order of reaction**.

For example,the dissociation of N_2O_5 is a first order reaction

$$2N_2O_5 \longrightarrow 4NO_2 + O_2$$

There can be a reaction of fractional order

Consider a general reaction

$$aA + bB \longrightarrow cC + dD$$

The rate law

$$\frac{dx}{dt} = k[A]^a[B]^b$$

$$\text{overall order} = a + b$$

Molecularity vs. Order

Molecularity of Reaction	Order of Reaction
It is the number of atoms, ions or molecules that must collide with one another simultaneously so as to result into a chemical reaction.	It is the sum of the power of concentration terms on which the rate of reaction actually depends or it is the sum of powers of the concentration terms in the rate law equation.
Molecularity of reaction Cannot be zero.	Order of reaction can be zero.
It is a theoretical concept.	It is determined experimentally.
It is always a whole number.	It can even have fractional values.
The overall molecularity of complex reaction has no significance. Individual step has its own molecularity.	Order of reaction is for overall reaction.

ZERO ORDER REACTION

$A \longrightarrow \text{Product}$

Rate of reaction $\frac{d[A]}{dt} = -k[A]^0$

where k = rate constant for zero order reaction

$\int d[A] = -k \quad dt$

$[A] = -kt + C$ where C = Integration Constant.

When $t = 0$, then $[A] = A_0$ hence $C = A_0$

$kt = [A]_0 - [A]$

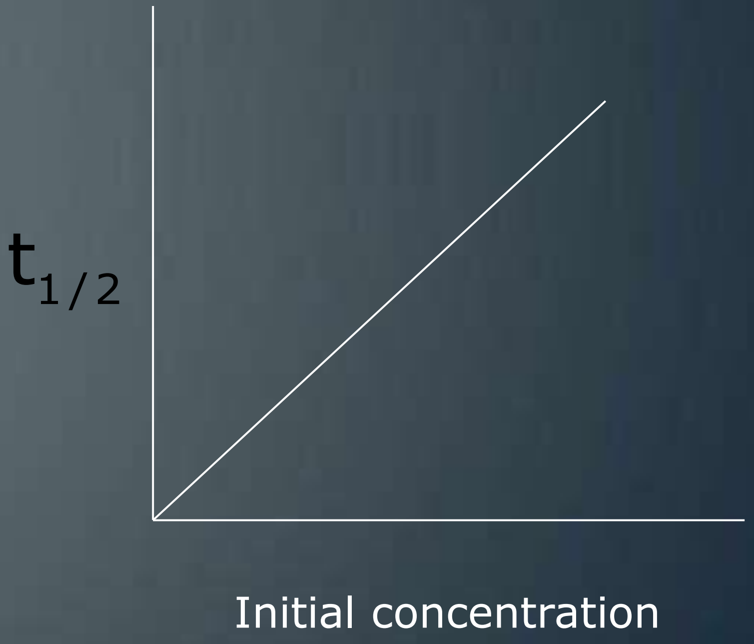
Zero order reaction

Half life of a reaction :- Time taken for the reactant concentration to decrease to one half of its initial value

$$[A] = \frac{Ao}{2}$$

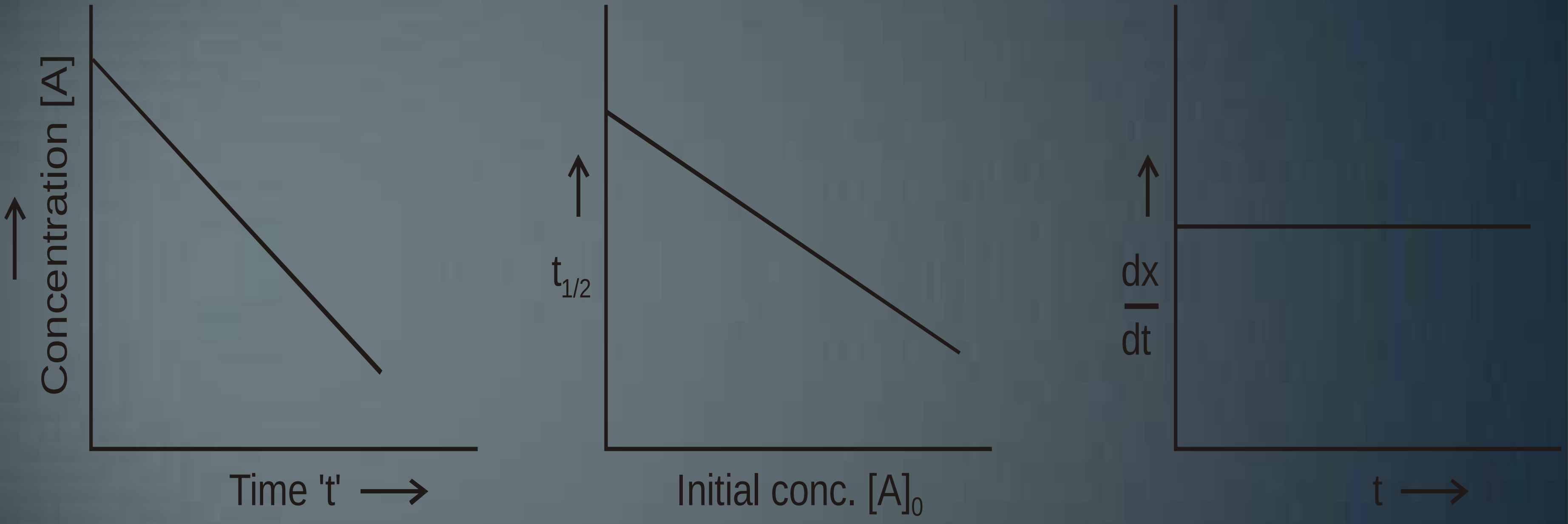
$$k_{t_{1/2}} = (Ao) - \frac{(Ao)}{2} = \frac{Ao}{2}$$

$$t_{1/2} = \frac{(Ao)}{2k}$$



Half life α initial concentration

Zero order reaction



Graphical representation for zero order reaction on the basis of $x = kt + C$

First order reaction

$$A \longrightarrow \text{Product}$$

initial conc.	a	0
at time t	$(a - x)$	x

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

$$-\int_{a}^{a-x} \frac{d[A]}{dt} = k\int_{0}^{t} \frac{d[A]}{dt}$$

$$\ln[A]_{a-x}^{a} = kt$$

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

Unit of rate constant is time^{-1}

$$k = \frac{2.303}{t} \log_{10} \frac{a}{(a-x)}$$

$(mol/lit)^{1-n} time^{-1}$ $\quad$ n = order of reaction

First order reaction

$$\log(a-x) = \frac{-kt}{2.303} + \log a$$

Plot of $(a-x)$ vs t is a straight line

with slope $= \dfrac{-k}{2.303}$

When $t = t_{1/2}$

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

Half life of first order reaction does not depend upon initial concentration

Amount of substance left after n half lives $= \dfrac{Ao}{2^n}$

First order reaction

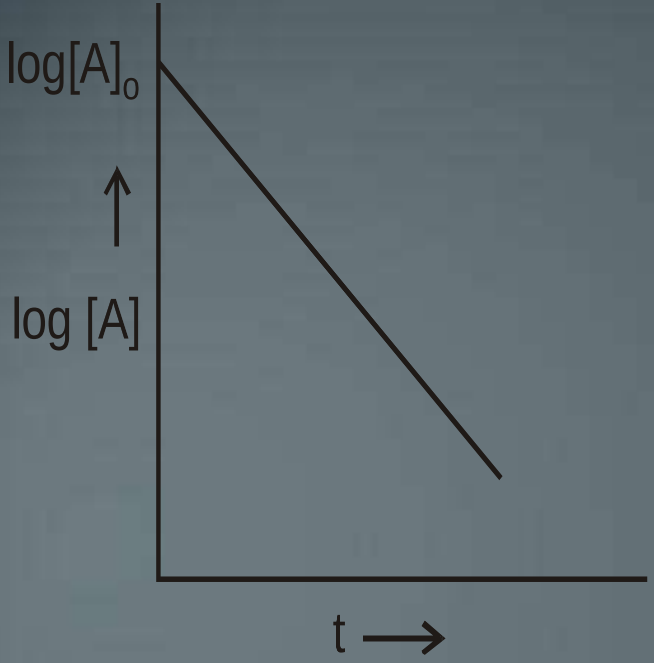
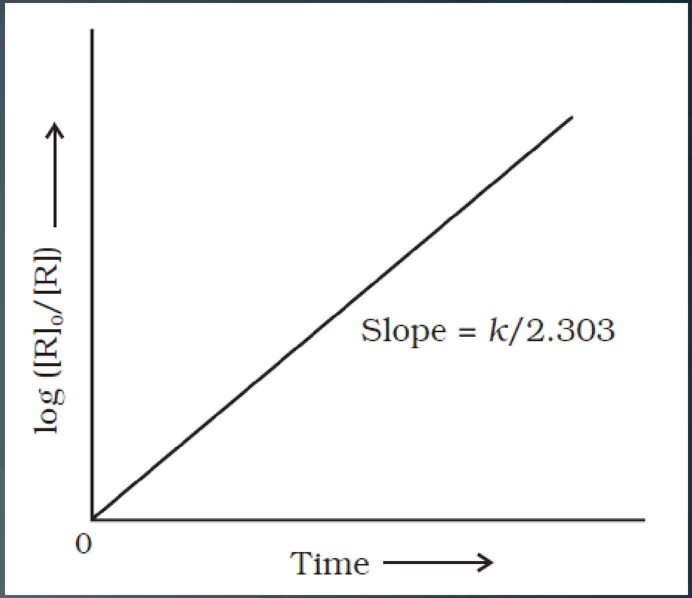


Fig: Graphical representation for first order reaction



Plot of log [R]0/[R] vs time for a firstorder reaction

$$\text{Slope of line} = -\frac{k}{2.303}$$

Pseudo - first order reaction

Reactions which are not truly of the first order but under certain conditions reactions become that of first order are called pseudo unimolecular reaction.

For example: Hydrolysis of ester in presence of acid

$$CH_3COOC_2H_5 + H_2O \rightarrow CH_3COOH + C_2H_5OH$$

From this reaction, the rate expression should be

$$r = k\,[\text{ester}]\,[H_2O]$$

Since, hydrolysis takes place in the excess of H_2O and concentration change of H_2O is negligible practically.

therefore, $r = k'\,[\text{ester}]$

Where $k' = k[H_2O]$.

Methods of determining the order of a reaction

Integrated method

The equation which gives a constant value of k decides the order of reaction

Graphical method

The data are plotted acc. to different integrated rate equations so as to yield a straight line .Slope gives the value of rate constant

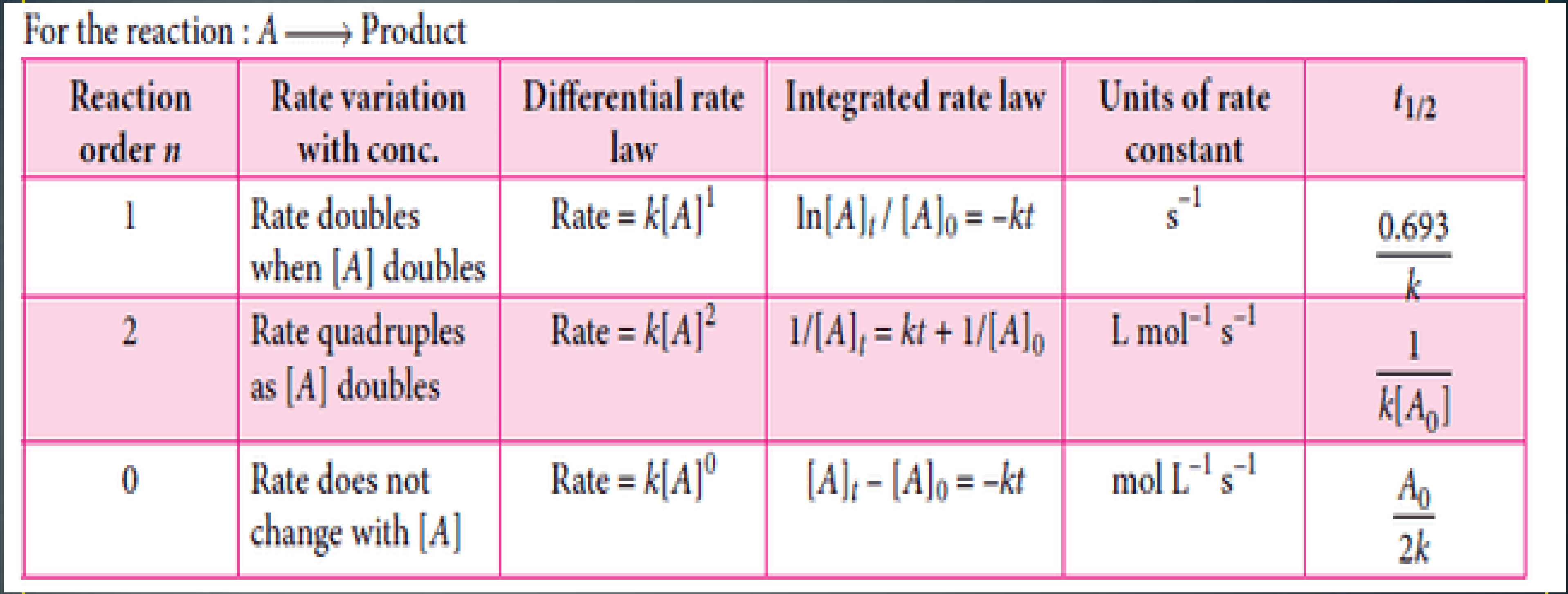
Initial rate method

Concentration of one of the reactant is varied

Half life method

In this method we plot half life of the reactant versus concentration of the reactant.

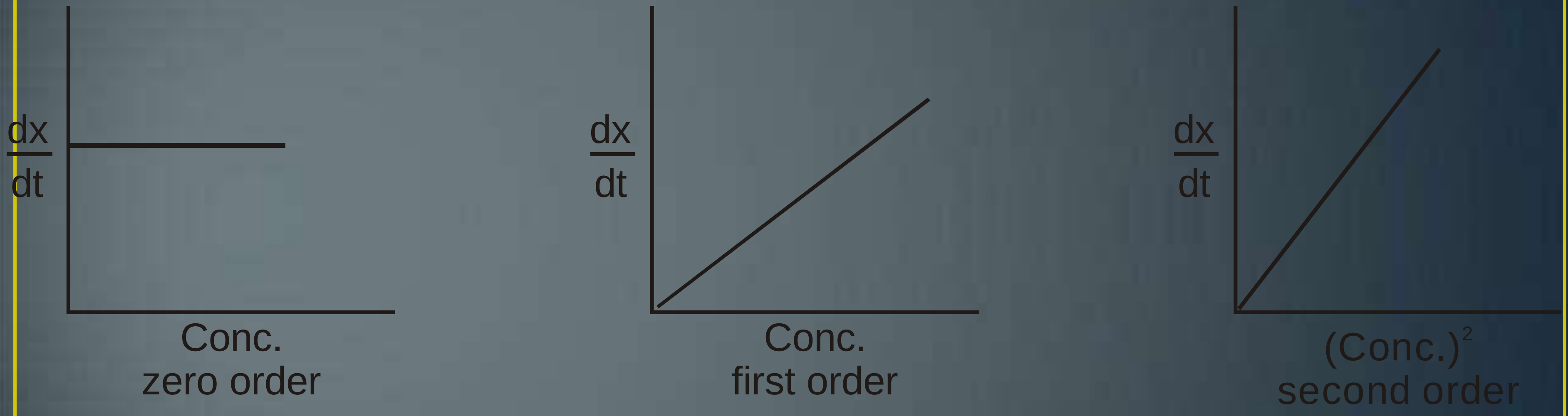
RATE LAW EXPRESSION FOR DIFFERENT ORDER REACTIONS



For the reaction : $A \longrightarrow \text{Product}$

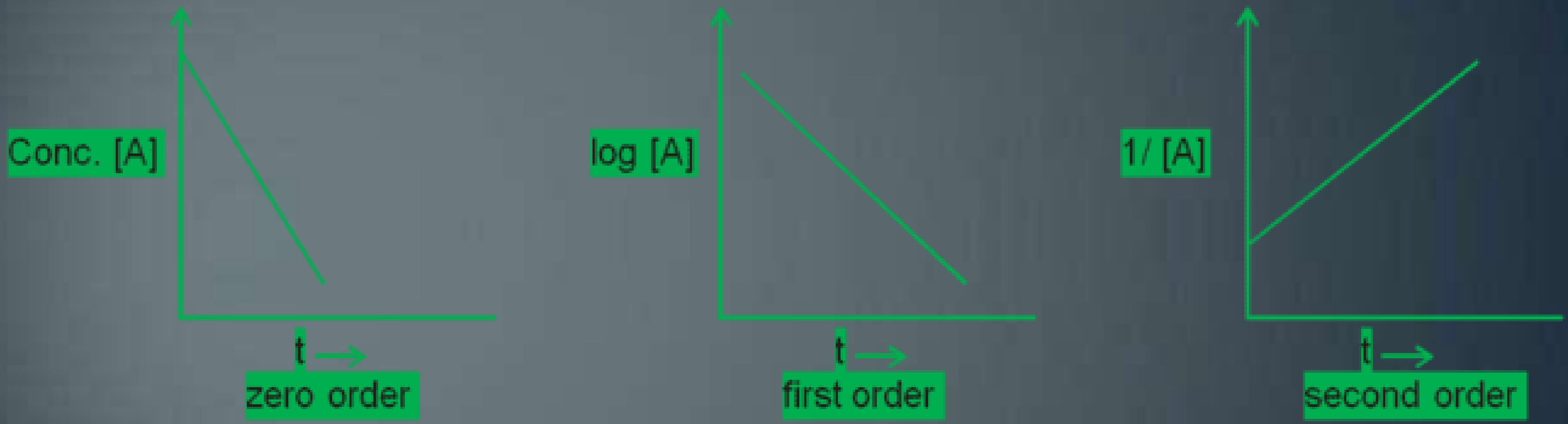
Reaction order *n*	Rate variation with conc.	Differential rate law	Integrated rate law	Units of rate constant	$t_{1/2}$
1	Rate doubles when [*A*] doubles	$\text{Rate} = k[A]^1$	$\ln[A]_t / [A]_0 = -kt$	s^{-1}	$\frac{0.693}{k}$
2	Rate quadruples as [*A*] doubles	$\text{Rate} = k[A]^2$	$1/[A]_t = kt + 1/[A]_0$	$L\ mol^{-1}\ s^{-1}$	$\frac{1}{k[A_0]}$
0	Rate does not change with [*A*]	$\text{Rate} = k[A]^0$	$[A]_t - [A]_0 = -kt$	$mol\ L^{-1}\ s^{-1}$	$\frac{A_0}{2k}$

Graphical Representation



Graphical representation of rate versus concentrations

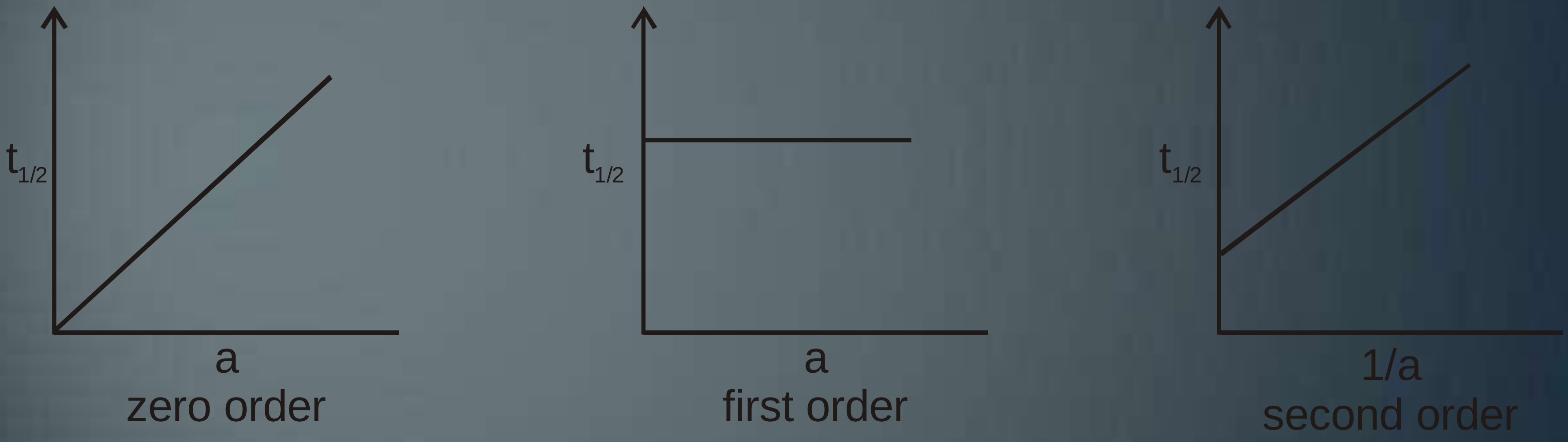
Graphical Representation



Graphical representation for concentration of integrated rate equation versus time

Half life method

$$t_{1/2} \quad \alpha \quad \frac{1}{[A]_0^{n-1}}$$



zero order

first order

second order

Graphical representation for half lives versus concentration

Theories of chemical kinetics

1. Collision theory
2. Transition state theory

Collision theory

Reaction occurs when reacting species have sufficient energy to collide and proper orientation in space.

Energy barrier:

The minimum energy which the colliding particles possess in order to bring about the chemical reaction is called threshold energy(activation energy).

Orientation barrier:

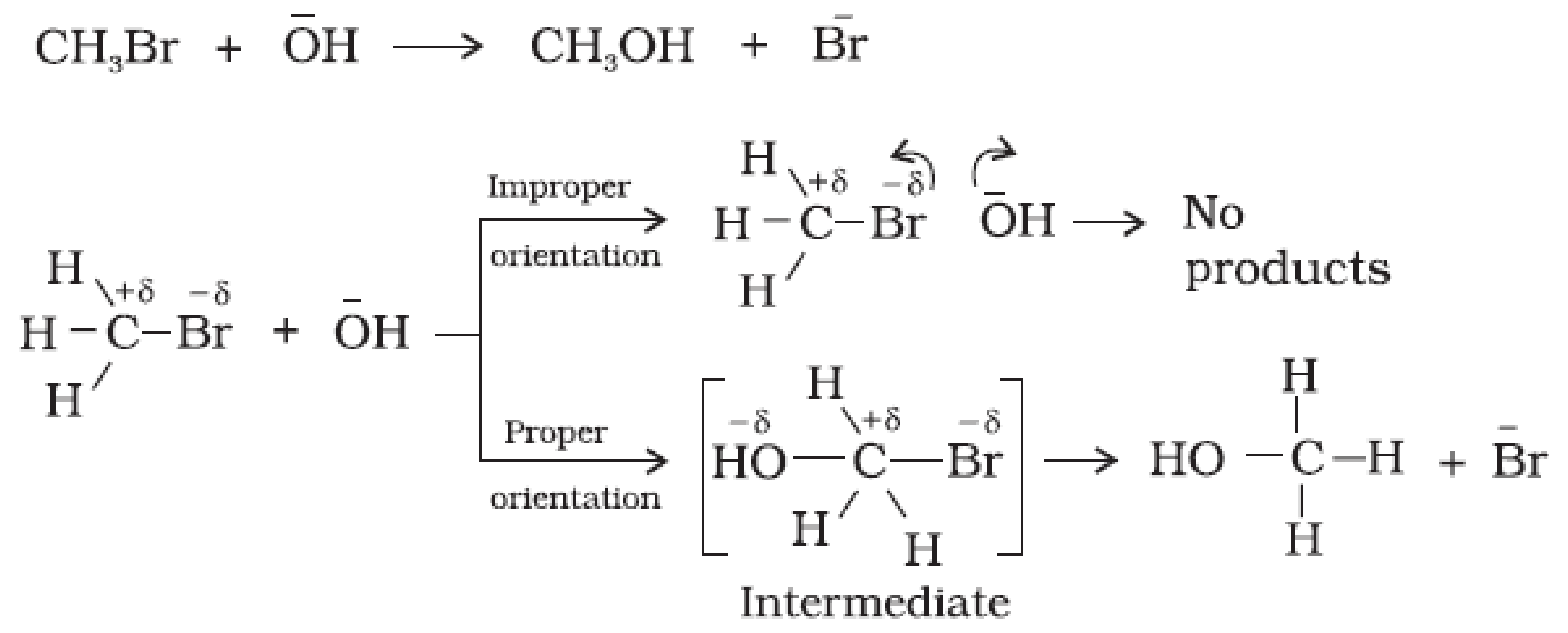
Colliding molecules should be in their proper orientation at the time of collision.

Collision frequency (Z):

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

Proper orientation

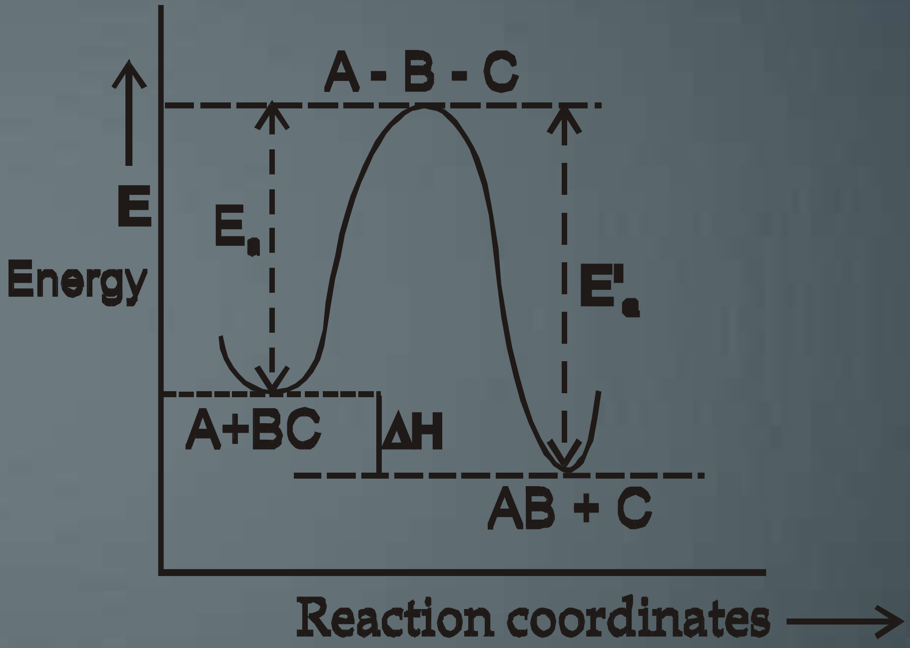
The proper orientation of reactant molecules lead to bond formation whereas improper orientation makes them simply bounce back and no products are formed.



$CH_3Br + \bar{O}H \longrightarrow CH_3OH + \bar{Br}$

Transition State Theory

In the **activated complex theory**, we consider two reactants approaching and their potential energy rising and reaching a maximum.



$\Delta H = E_a - E_a`$

Activation energy - the energy needed to start a chemical reaction. It is very low for some reactions and very high for others.

Some Points about E_a

1. E_a is always positive.

2. The larger the value of E_a, the slower the rate of a reaction at a given temperature.

3. The larger the value of E_a, the steeper the slope of (ln k) vs (1/T). A high activation energy corresponds to a reaction rate that is very sensitive to temperature.

4. The value of E_a itself DOES NOT CHANGE with temperature.

Effect of temperature on rate of chemical reaction

The ratio $\frac{k_{T+10}}{k_T}$

is called the temperature coefficient and its value is 2 or 3

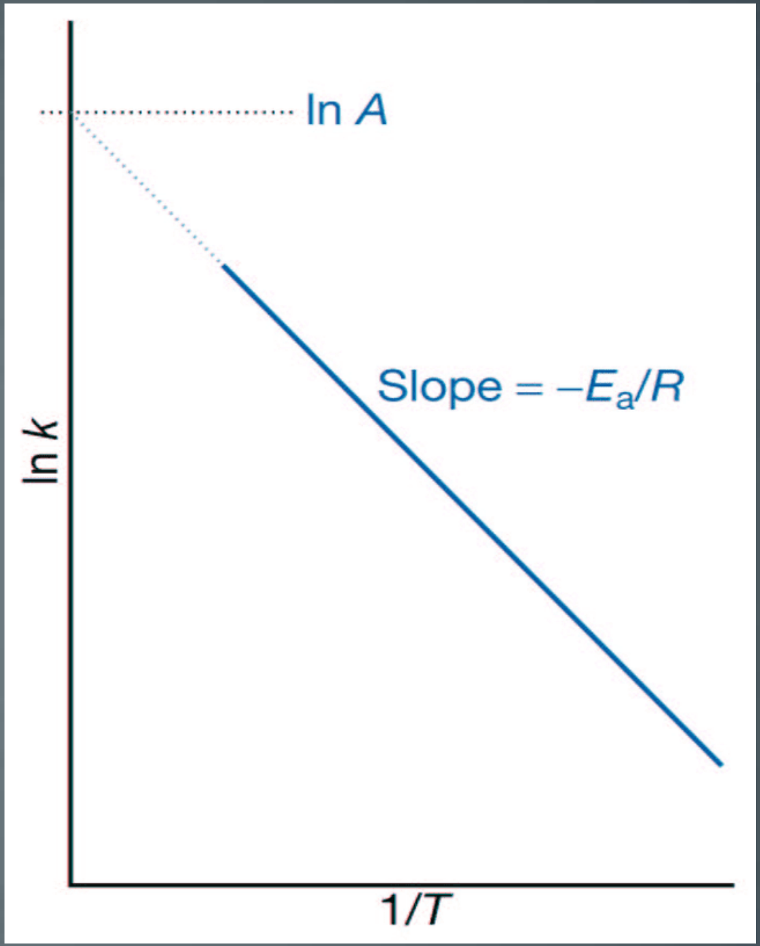
$$k = A.e^{-Ea/RT}$$

A is frequency factor or Arhenius constant,E_a is activation energy

$$\log k = -\frac{E_a}{2.303R}\left[\frac{1}{T}\right] + \log A$$

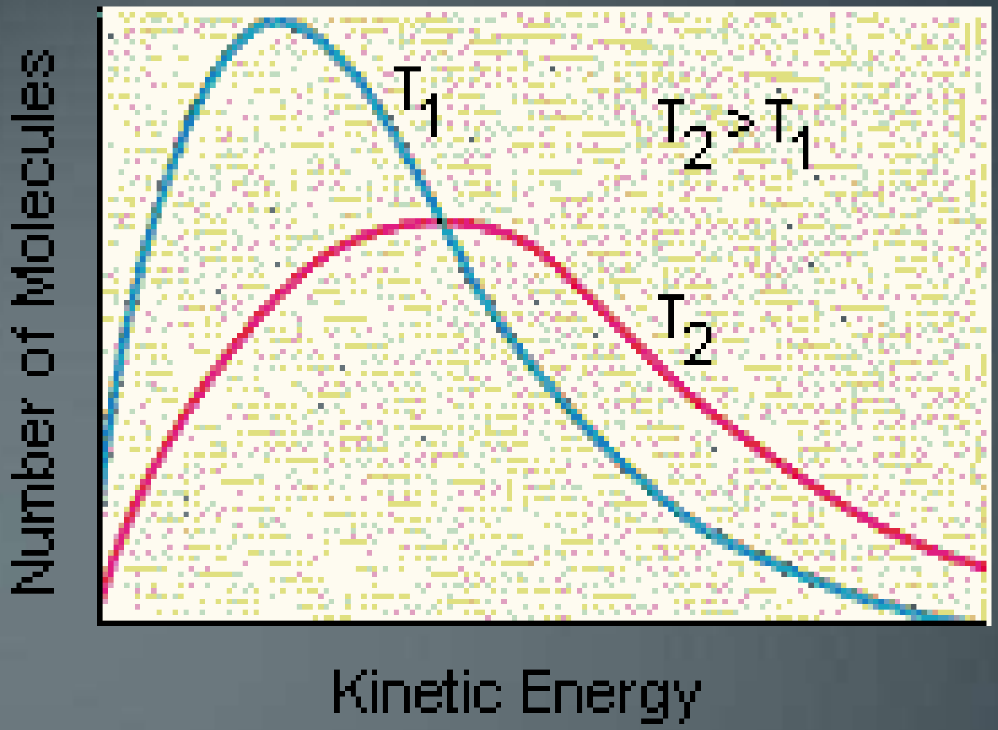
Plot of log k vs 1/T is a straight line & slope =- $E_a/2.303R$

Temperature Dependence



Plot of log k vs 1/T is a straight line & slope =-E_a/2.303R

EFFECT OF TEMPERATURE ON RATE OF CHEMICAL REACTION



$$k = A.e^{-Ea/RT}$$

$$\text{or} \quad \log \frac{k_2}{k_1} = \frac{E_a}{2.303\ R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

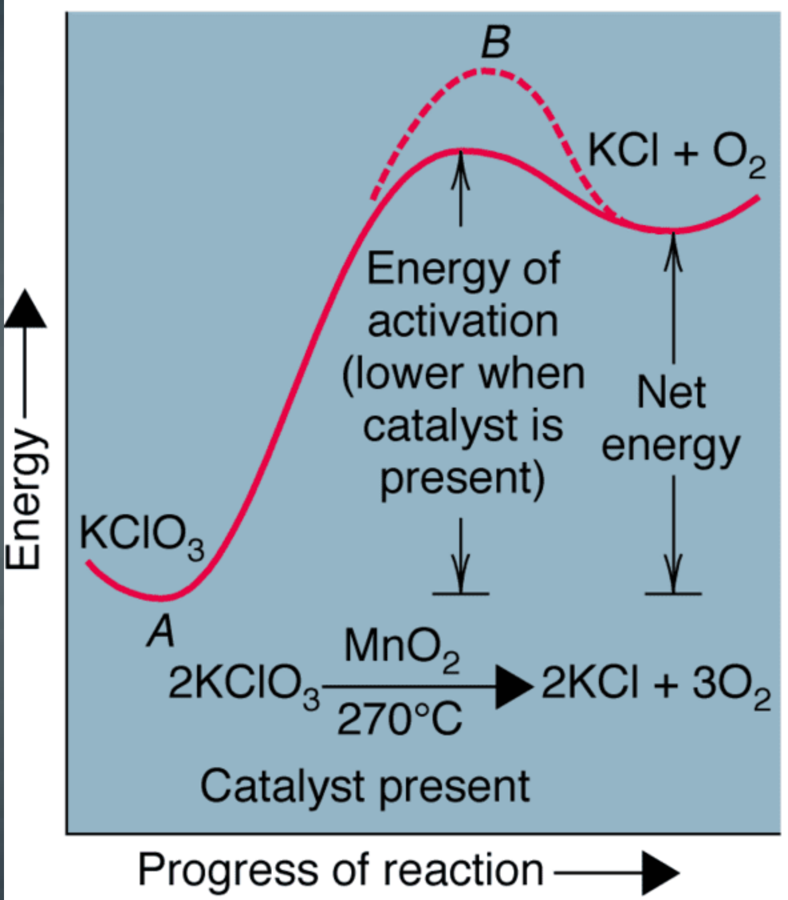
Catalysis

Catalyst: A substance that changes the rate of a reaction without being consumed in the reaction.

- Provides an easier way to react.
- Lower activation energy.
- Still make the same products.
- Enzymes are biological catalysts.

Inhibitor: A substance that <u>de</u>creases the rate of reaction (a negative catalyst).

How catalyst change reaction rate



- Catalysts are the one way to lower the energy of activation
  for a particular reaction.

- The presence of the catalyst alters the path of the reaction.

- The lower activation energy allows the reaction to proceed faster.

Rate-determining Step in a Mechanism

Slowest step:

The rate determining step is the slowest elementary step in a mechanism, and the rate law for this step is the rate law for the overall reaction.

Steady-state approximation:

The steady-state approximation is a general method for deriving rate laws when the relative speed cannot be identified.It is based on the assumption that the concentration of the intermediate is constant.