Welcome to

Aakash + BYJU'S LIVE

Chemical Kinetics and Nuclear Chemistry

Chemistry is always concerned with **change.**

By means of a chemical reaction

Feasibility of a reaction

Thermodynamics

Extent of a chemical reaction

Chemical Equilibrium

Speed of a chemical reaction

Chemical Kinetics

Chemical Kinetics

It deals with the **rate** of a chemical reaction and the **mechanism** by which it proceeds.

Along with feasibility and extent, it is equally important to know the rate and the factors controlling the **rate** of a chemical reaction.

Chemical Kinetics

Thermodynamics vs Chemical Kinetics

Thermodynamics tells only about the **feasibility** of a reaction.

However, **chemical kinetics** tells about the **speed** with which it proceeds.

Rate of a Chemical Reaction

Some reactions are **rapid**

Rate of a Chemical Reaction

Some reactions proceed with moderate Speed

Inversion of cane sugar

$C_{12}H_{22}O_{11} + H_2O \longrightarrow C_6H_{12}O_6 + C_6H_{12}O_6$

Sucrose   Glucose   Fructose

Decomposition of hydrogen peroxide

$2H_2O_2 \longrightarrow 2H_2O + O_2$

Rate of a Chemical Reaction

Some reactions are **very slow**

Rate of a Chemical Reaction

The **rate of change of concentration**, with time, of different chemical species taking part in a chemical reaction.

Known as rate of reaction w.r.t. that **species**

Rate can be expressed as

01 **The rate of decrease** in concentration (disappearance) of **reactants**

02 **The rate of increase** in concentration (appearance) of **products**

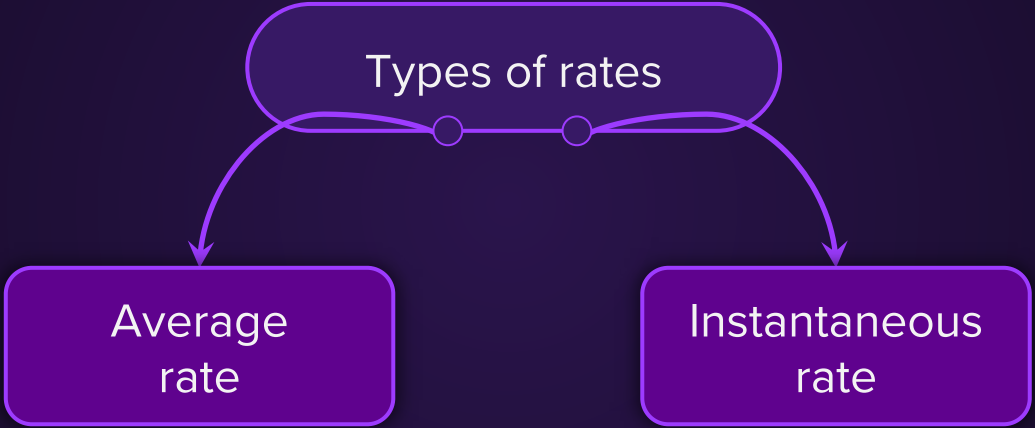
Rate of a Chemical Reaction

For a gaseous reaction at constant temperature,

Concentration $\propto$ Partial pressure of species

Rate is expressed as the **rate of change in partial pressure** of a reactant or a product.

Types of Rate



Types of rates

Average rate

Instantaneous rate

Average Rate of Reaction

For the reaction,

$$R \longrightarrow P$$

$$\text{Average rate} = \frac{\text{Total change in concentration}}{\text{Total time taken}}$$

$$= \left| \frac{C_{\text{final}} - C_{\text{initial}}}{t_{\text{final}} - t_{\text{initial}}} \right|$$

$$= \left| \frac{\Delta C}{\Delta t} \right|$$

Average Rate of Reaction

$R \rightarrow P$

Rate of disappearance of reactant (R)

$$\text{Average rate} = \frac{\text{Decrease in concentration of R}}{\text{Time taken}}$$

$$\text{Average rate} = \left| \frac{[R]_{final} - [R]_{initial}}{t_{final} - t_{initial}} \right|$$

$[R]_{initial}$ = Initial concentration of reactant at $t_{initial}$

$[R]_{final}$ = Final concentration of reactant at t_{final}

$[R]_{final} < [R]_{initial}$

Average Rate of Reaction

$$R \longrightarrow P$$

Rate of appearance of product (P)

$$\text{Average rate} = \frac{\text{Increase in concentration of P}}{\text{Time taken}}$$

$$\text{Average rate} = \left| \frac{[P]_{final} - [P]_{initial}}{t_{final} - t_{initial}} \right|$$

$[P]_{initial}$ = Initial concentration of product at $t_{initial}$

$[P]_{final}$ = Final concentration of product at t_{final}

$[R]_{final} < [R]_{initial}$

Average Rate of Reaction

As we know,

During a reaction

The concentration of the reactant **decreases.**

$[R]_f < [R]_i$

The concentration of the product **increases.**

$[P]_f > [P]_i$

Average Rate of Reaction

The **rate** is defined in a manner so that

It is always a **positive quantity**

For reactant R,

$$\text{Average rate} = \left| \frac{[R]_{\text{final}} - [R]_{\text{initial}}}{t_{\text{final}} - t_{\text{initial}}} \right| = -\frac{\Delta[R]}{\Delta t}$$

For product P,

$$\text{Average rate} = \frac{[P]_{\text{final}} - [P]_{\text{initial}}}{t_{\text{final}} - t_{\text{initial}}} = +\frac{\Delta[P]}{\Delta t}$$

Average Rate of Reaction

$R \longrightarrow P$

1 mol of R → 1 mol of P

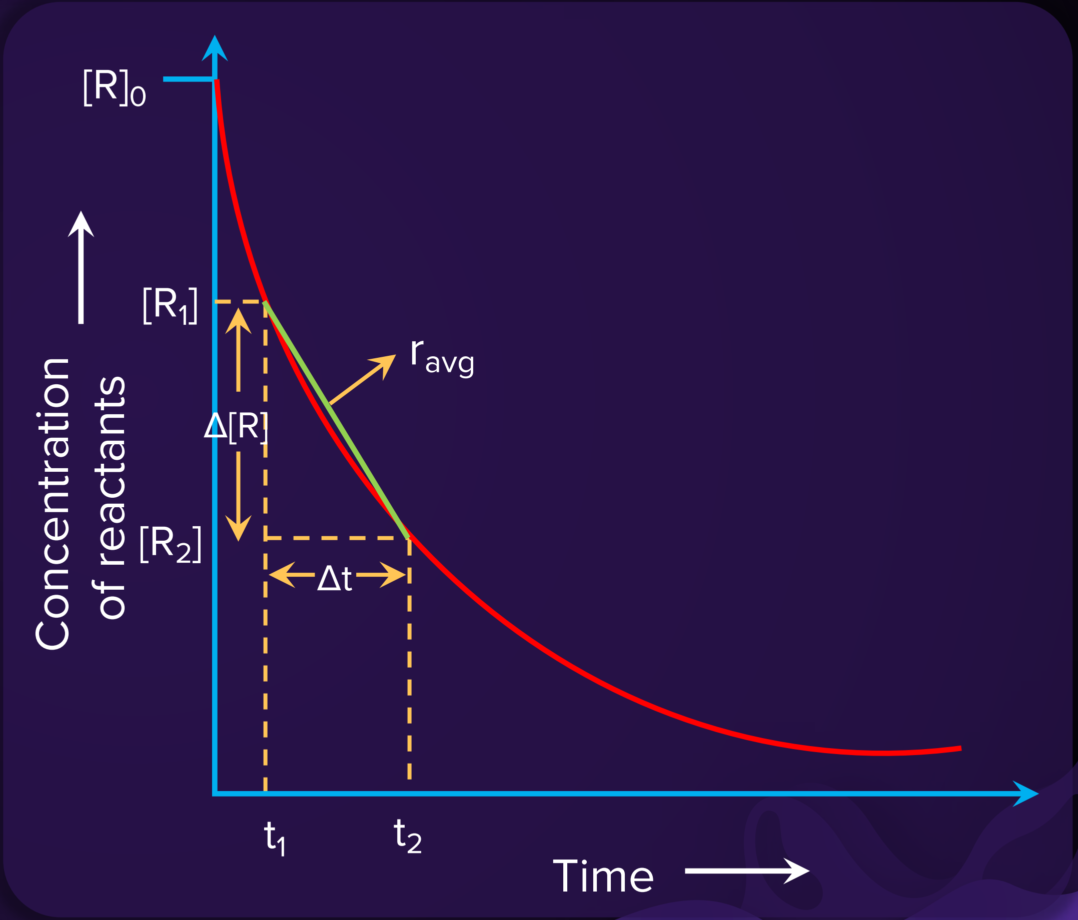
Rate of disappearance of R = Rate of appearance of P

$$\text{Average rate of reaction, } r_{avg} = -\frac{\Delta[R]}{\Delta t} = +\frac{\Delta[P]}{\Delta t}$$

Average Rate of Reaction (Graph)

Concentration of R vs time

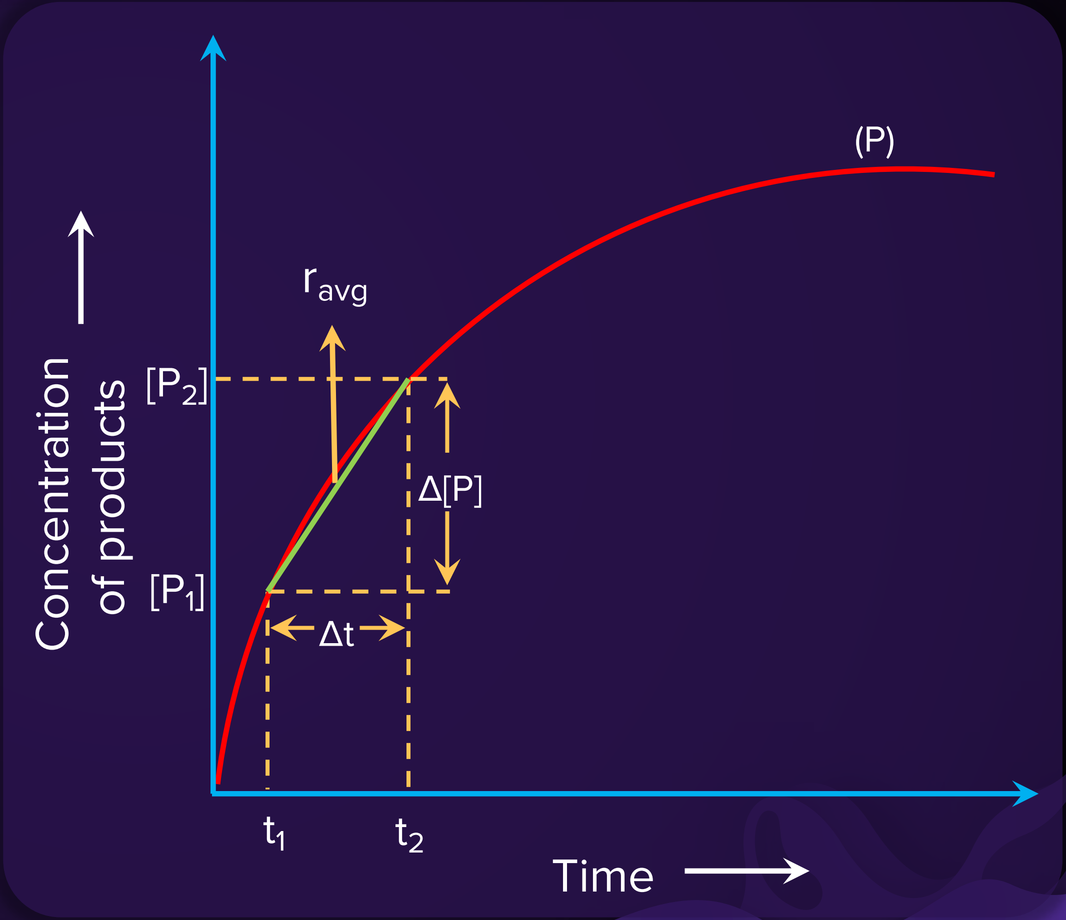
$$\text{Rate} = \frac{-\{[R_2] - [R_1]\}}{(t_2 - t_1)} = -\frac{\Delta[R]}{\Delta t}$$



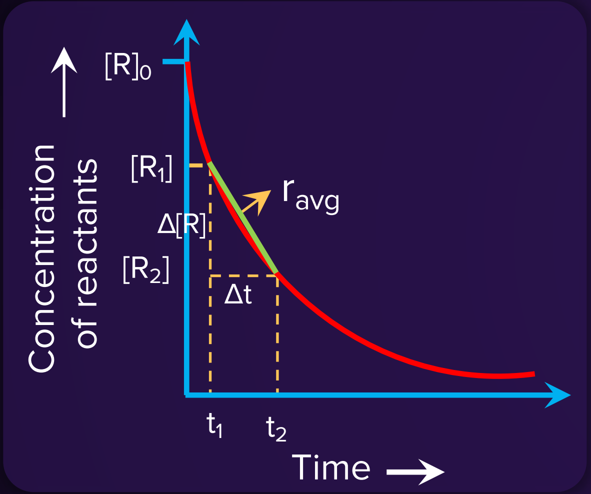
Average Rate of Reaction (Graph)

Concentration of P vs time

$$\text{Rate} = \frac{+\{[P_2] - [P_1]\}}{(t_2 - t_1)} = +\frac{\Delta[P]}{\Delta t}$$



Average Rate of Reaction (Graph)



On a concentration vs time graph,the average rate of reaction is the **slope of a secant joining two points**, which defines concentration at different instants on the curve.

Instantaneous Rate of Reaction

The rate of a reaction at a **particular instant**

For the reaction,

$$R \longrightarrow P$$

$$R_{\text{Instantaneous}} = \left| \lim_{\Delta t \to 0} \left(\frac{\Delta C}{\Delta t} \right) \right| = \left| \frac{dC}{dt} \right|$$

Instantaneous Rate of Reaction

$$R \longrightarrow P$$

$$r_{avg} = -\frac{\Delta[R]}{\Delta t} = +\frac{\Delta[P]}{\Delta t}$$

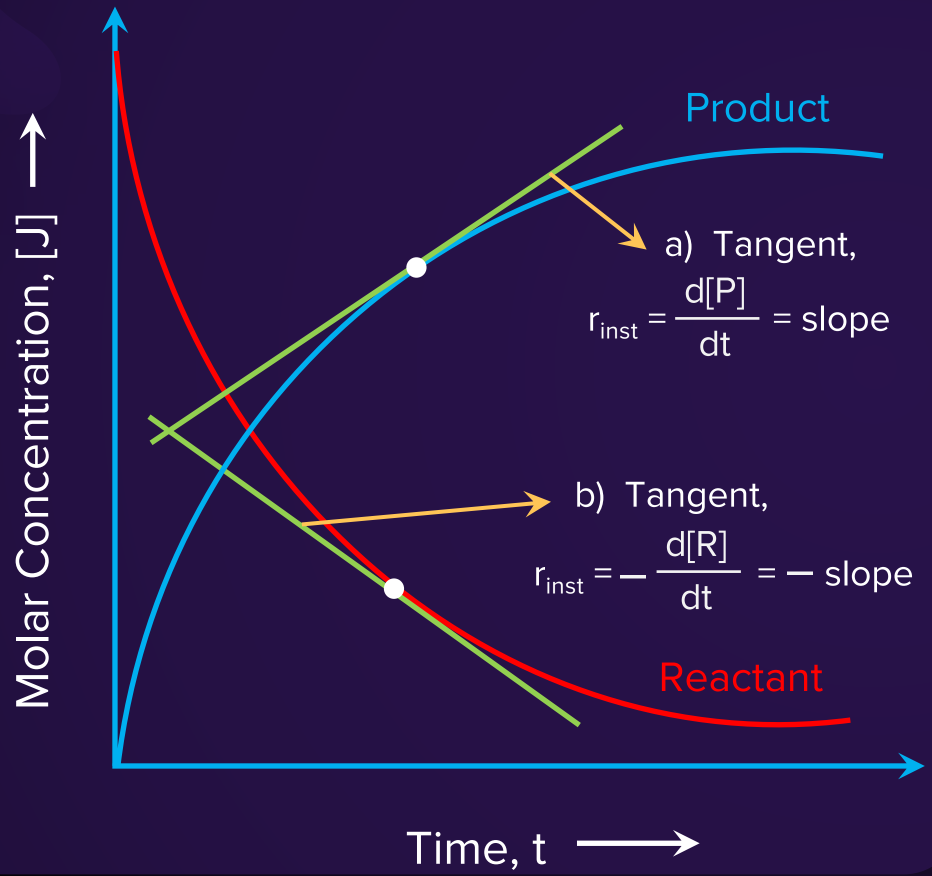
Instantaneous rate of **disappearance of R**

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

Instantaneous rate of **appearance of P**

$$R_{Instantaneous} = +\frac{d[P]}{dt}$$

Instantaneous Rate of Reaction (Graph)



a) Tangent,

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

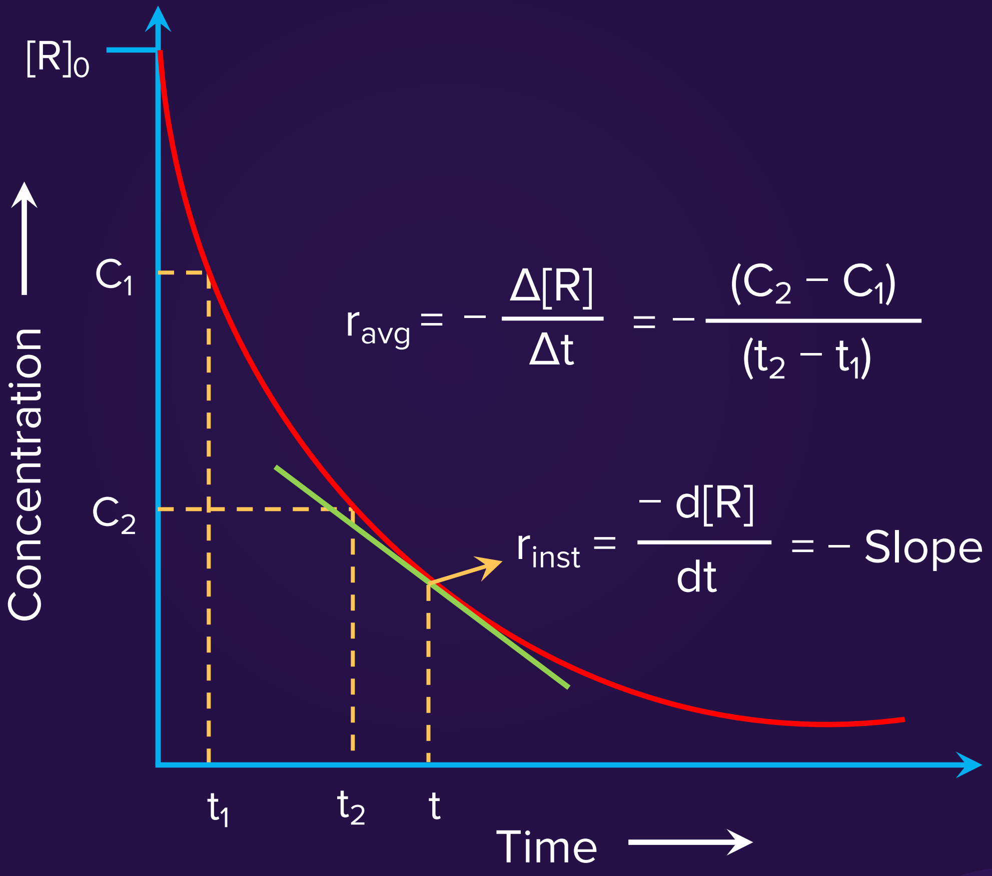
b) Tangent,

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

The **instantaneous rate** of reaction can be determined by drawing a **tangent** at time t on the concentration vs time curve.

For **negative slopes**, the sign is changed when reporting the **rate**. Hence, all reaction rates are **positive**.

Instantaneous vs Average Rate of Reaction (Graph)



$$r_{avg} = -\frac{\Delta[R]}{\Delta t} = -\frac{(C_2 - C_1)}{(t_2 - t_1)}$$

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

Relation between Rates of Different Species Involved in a Reaction

Rate of Reaction

Example

$N_2\,(g) + 3H_2\,(g) \rightarrow 2NH_3\,(g)$

Rate of reaction w.r.t. N_2 $= -\dfrac{d[N_2]}{dt}$

Rate of reaction w.r.t. H_2 $= -\dfrac{d[H_2]}{dt}$

Rate of reaction w.r.t. NH_3 $= +\dfrac{d[NH_3]}{dt}$

These all are correct rate expressions.

However, they are **not equal**

Rate of Reaction

$$N_2\ (g) + 3H_2\ (g) \longrightarrow 2NH_3\ (g)$$

1 mol N_2 reacts with 3 mol H_2 to produce 2 mol NH_3.

$$\text{Rate of consumption of } N_2 = \frac{1}{3}\left(\text{Rate of consumption of } H_2\right) = \frac{1}{2}\left(\text{Rate of formation of } NH_3\right)$$

Rate of a Chemical Reaction

By convention, the rate of a reaction is expressed as the **overall rate of reaction** by dividing the individual rates with their stoichiometric coefficients.

Rate of a Chemical Reaction

$N_2 (g) + 3H_2 (g) \rightarrow 2NH_3 (g)$

Rate of reaction

w.r.t. $N_2 = -\dfrac{d[N_2]}{dt}$

w.r.t. $H_2 = -\dfrac{d[H_2]}{dt}$

w.r.t. $NH_3 = +\dfrac{d[NH_3]}{dt}$

Overall rate of reaction $= -\dfrac{d[N_2]}{dt}$

$= -\dfrac{1}{3}\dfrac{d[H_2]}{dt}$

$= +\dfrac{1}{2}\dfrac{d[NH_3]}{dt}$

Rate of a Chemical Reaction

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

Average rate of reaction, r_{avg}

$$= -\frac{1}{a}\frac{\Delta[A]}{\Delta t} = -\frac{1}{b}\frac{\Delta[B]}{\Delta t} = +\frac{1}{c}\frac{\Delta[C]}{\Delta t} = +\frac{1}{d}\frac{\Delta[D]}{\Delta t}$$

Instantaneous rate of reaction, r_{inst}

$$= -\frac{1}{a}\frac{d[A]}{dt} = -\frac{1}{b}\frac{d[B]}{dt} = +\frac{1}{c}\frac{d[C]}{dt} = +\frac{1}{d}\frac{d[D]}{dt}$$

Important

The **value of the rate of reaction** is **independent** on the stoichiometric coefficients of substances involved in a reaction.

However, the **rate w.r.t. any species is dependent** of its stoichiometric coefficient.

Unit of Rate of a Chemical Reaction

We know,
$1\ L = 1\ dm^3 = 10^{-3}\ m^3 = 10^3\ cm^3$

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

Where,
ΔC: Change in concentration of any species
Δt: Time change corresponding to the concentration change

$$\text{Unit of rate} = \frac{\text{Unit of } \Delta C}{\text{Unit of } \Delta t} = \frac{\text{mol/L}}{\text{s}}$$

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

$$= \text{mol dm}^{-3}\ \text{s}^{-1}$$

Note!

For a gaseous reaction at a constant temperature, rate is expressed as

$$r_{inst} = \frac{dp}{dt}$$

Where,

p: Partial pressure of the component

Unit of rate equation = atm s^{-1}

Factors Affecting Rate of a Chemical Reaction

Kinetic studies help us determine the **speed of a reaction** and describe the **conditions** that can **alter** the reaction rate.

1. Effect of concentration
2. Effect of nature of reactant and product
3. Effect of Pressure
4. Effect of temperature
5. Effect of catalyst

Effect of Concentration

The rate of reaction is often found to be **proportional** to the concentrations of the reactants raised to a power.

Rate Law or Rate Expression

Instantaneous rate

It is an equation that expresses the **rate** of reaction as a **function of the concentration** of all the species present in the overall chemical equation for the reaction at some time.

Simple rate laws can be obtained by starting with pure reactants.

For these reactions,

$$\text{Rate} \propto (\text{concentration})^{\text{order}}$$

$$\text{Rate} = k\,(\text{concentration})^{\text{order}}$$

Rate Law or Rate Expression

$aA + bB \longrightarrow cC + dD$

Rate of reaction $\propto$ $[A]^x [B]^y$

Rate of reaction $=$ $k [A]^x [B]^y$ ...(1)

k: Proportionality constant (rate constant)

x and **y**: May or may not be equal to stoichiometric coefficients (a and b) of reactants

Where a, b, c, and d are stoichiometric coefficients of reactants and products

Rate Law

Rate of reaction = k $[A]^x [B]^y$ ...(1)

Eq. 1 can also be written as

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

Differential rate equation

It is the expression in which the reaction rate is given in terms of the molar **concentration of reactants.**

With **each term** raised to some **power**

Which **may or may not** be the same as the **stoichiometric coefficient** of the reacting species

Rate Law

It can only be established by experiments.

It may differ for the same reaction under different conditions.

Reactant → Product

$$\text{Rate} = k\,[\text{Reactant}]^{\text{order}}$$

Rate Constant

Rate = k[Reactant]^{order}

It is the rate of reaction when the concentration of reactant is **unity.**

$$k = \frac{Rate}{[Reactant]^n}$$

It is also known as the **specific reaction rate**

Where **n** is the order of the reaction

Rate Constant

The rate constant (k) depends **only** on **temperature** and not on concentration.

$$k = \frac{\text{Rate}}{[\text{Reactant}]^n}$$

$$\text{Rate} = \frac{dC}{dt}$$

Unit of concentration → mol L^{-1}

Unit of rate → $(\text{Concentration})^1 \text{ time}^{-1}$

Unit of k → $\text{mol}^{1-n}\ L^{n-1}\ s^{-1}$

Order of a Reaction

$$aA + bB + cC \longrightarrow \text{Products}$$

The **power** to which the **concentration** of a species is raised in a rate law is the **order** of the reaction with respect to that species.

Experimentally,

$$R \propto [A]^p [B]^q [C]^r$$

Where,

p: Order of reaction w.r.t. A
q: Order of reaction w.r.t. B
r: Order of reaction w.r.t. C

Order of a Reaction

$aA + bB + cC \longrightarrow \text{Products}$

Rate $\propto [A]^p [B]^q [C]^r$

Order of a Reaction:
It is the **sum of powers** of the concentration of the reactants in the rate law of a chemical reaction.

$R \propto [A]^p [B]^q [C]^r$

Thus **p, q,** and **r** indicate how **sensitive** the **rate** is to **change in concentration** of A, B, and C, respectively.

Sum of the exponents → $(p + q + r)$

Remember!

$$aA + bB + cC \longrightarrow \text{Products}$$

$$\text{Rate} \propto [A]^p\,[B]^q\,[C]^r$$

‘p’ may or may not be equal to ‘a’.

‘q’ may or may not be equal to ‘b’.

‘r’ may or may not be equal to ‘c’.

Characteristics of Order of a Reaction

1. The order of a reaction can be **zero** or any **whole number.**
2. It can be a **fractional number.**
3. It can even be negative with respect to a particular reactant.

Overall order can never be negative.

Order of a Reaction

Example:

$2N_2O_5\,(g) \longrightarrow 4NO_2\,(g) + O_2\,(g)$

Rate law = $k\,[N_2O_5]^1$

Overall order = 1

Order of a Reaction

Example:

$$5Br^- (aq) + BrO_3^- (aq) + 6H^+ (aq) \longrightarrow 3Br_2 (l) + 3H_2O (l)$$

Rate law = $k [Br^-][BrO_3^-][H^+]^2$

Overall order = $1 + 1 + 2$ = 4

Order of a Reaction

A **balanced equation** does not necessarily give us a **true picture** of how the reaction takes place.

↓

Rarely, a reaction gets completed **in one step**.

For an **elementary reaction,**

The reaction involves only a **single step**.

The sum of stoichiometric coefficients = Order of the reaction

Remember!

For the elementary reaction,

$$H_2 (g) + I_2 (g) \longrightarrow 2HI (g)$$

$$\text{Rate} = k [H_2] [I_2]$$

Overall order = 2

Remember!

For a **complex reaction,**

The reaction involves more than one step.

The order is experimentally calculated.

For example:

$2NO + 2H_2 \rightarrow N_2 + 2H_2O$

Steps involved:

$2NO \rightleftharpoons N_2O_2$ Step 1

$N_2O_2 + H_2 \rightarrow N_2O + H_2O$ Step 2

$N_2O + H_2 \rightarrow N_2 + H_2O$ Step 3

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

Methods to Analyse Rate of a Reaction

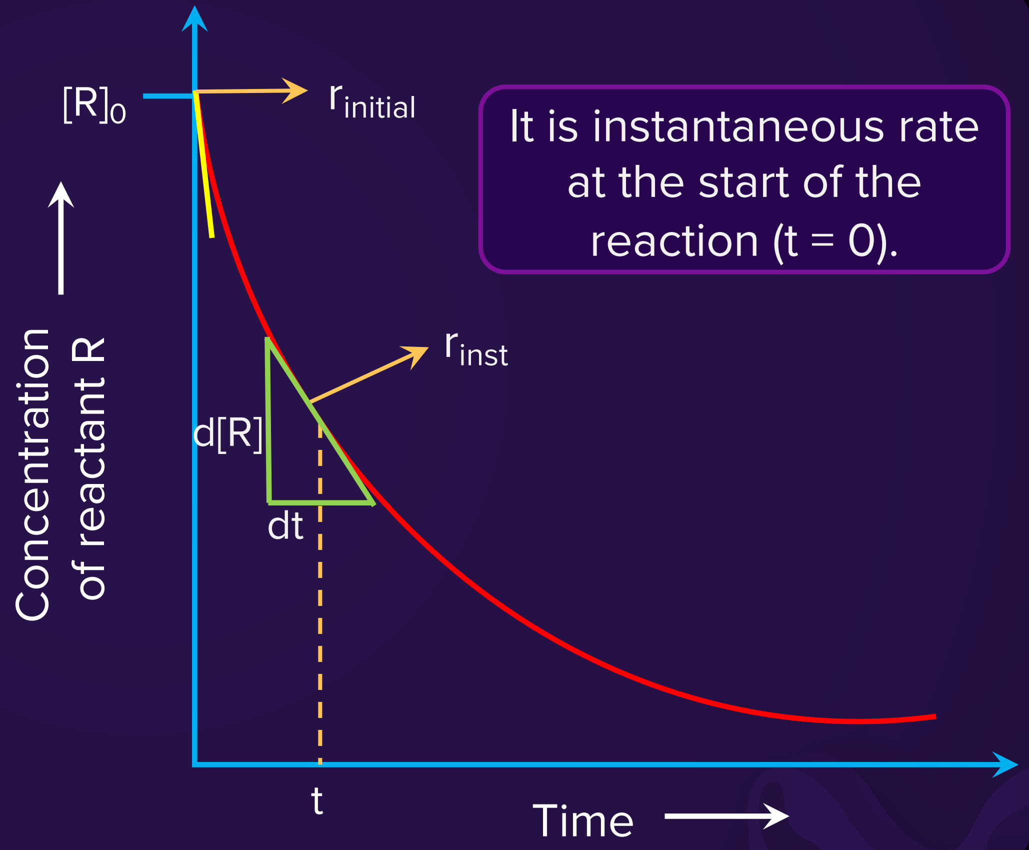
1. Initial rate method
2. Integrated rate law method
3. Graphical method
4. Unit method

Initial Rate Method

aA + bB + cC $\longrightarrow$ Products

The method involves finding the **initial rate** of the reaction

By taking **known** concentrations of different **reactants.**



It is instantaneous rate at the start of the reaction (t = 0).

Initial Rate Method

Involves **comparison** of different **initial rates** of a reaction

By **varying** the concentration of **one** of the reactants

While **other reactants** are kept **constant**

$aA + bB + cC \longrightarrow \text{Products}$

$\text{Rate} = k\,[A]^p\,[B]^q\,[C]^r$

The concentration of A **is changed**, by keeping the concentrations of B and C **same as before**.

Initial Rate Method

Two different initial concentrations of A, $[A_0]_1$, and $[A_0]_2$ are taken.

The initial rates of the reaction are determined as,

$$r_1 = k' [A_0]_1^p$$

$$r_2 = k' [A_0]_2^p$$

$$k' = k [B]^q [C]^r$$

$$\frac{r_1}{r_2} = \left(\frac{[A_0]_1}{[A_0]_2}\right)^p$$

The value of ‘**p**’ can be calculated by measuring the values of r_1, r_2, $[A_0]_1$, and $[A_0]_2$.

Following the same method, **q** and **r** can also be calculated.

Methods to Analyse Rate of a Reaction

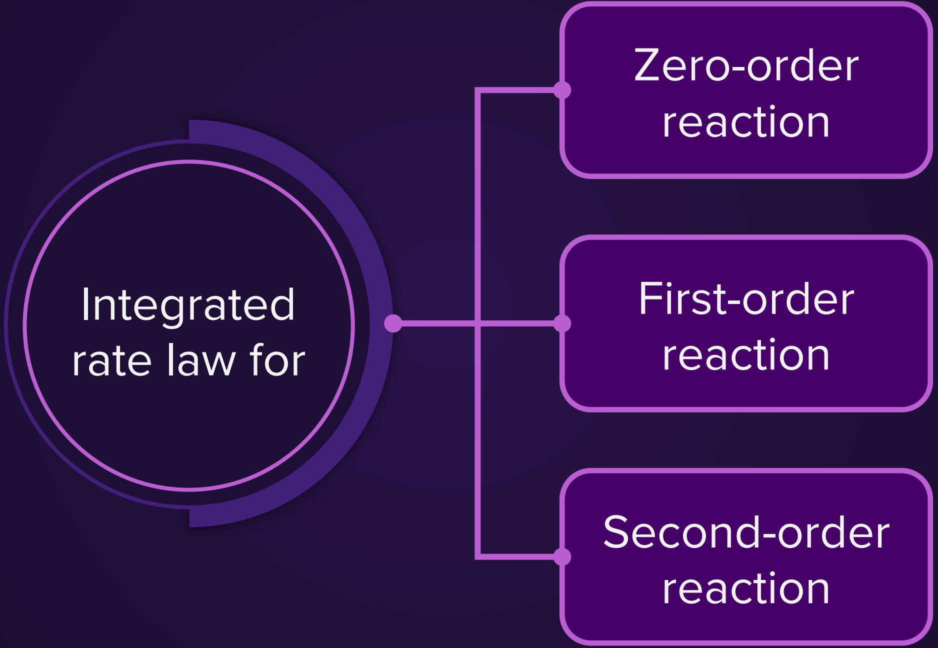
The **rate law** tells about the **rate** of the reaction **dependency** on the concentration of **reactant(s).**

But it does **not** tell how the concentration changes **with time**

Integrated Rate Law Method

This method, **quantitatively,** gives the concentration of reactant(s) as a **function of time.**

The form of the integrated rate equation **depends** on the **order of reaction.**



Integrated rate law for

- Zero-order reaction
- First-order reaction
- Second-order reaction

Zero-Order Reaction

For a general reaction

$$A \longrightarrow \text{Product(s)}$$

According to the rate law,

$$\text{Rate of reaction} = k\,[A]^n$$

For a zero-order reaction

Where,

n : Order = 0

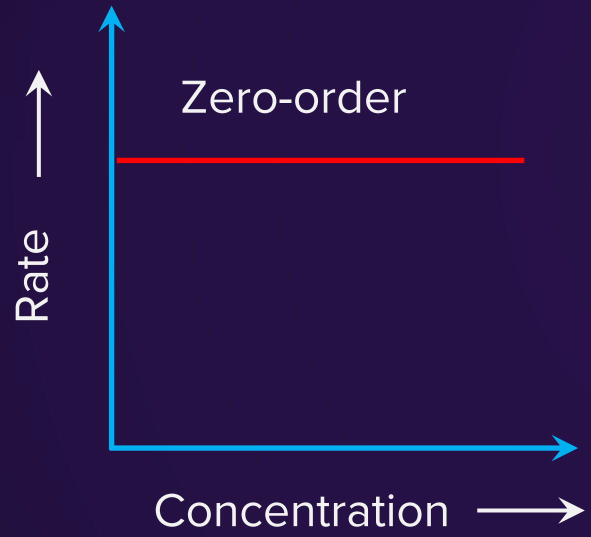
k : Rate constant

[A] : Concentration of reactant A

$$\textbf{Rate} = \textbf{k}$$

Plot of Rate vs Time

Rate = k $[A]^0$



For a zero-order reaction

Rate = $k[A]^n$

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

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

Zero-Order Reaction

Rate = k $[A]^0$

$$-d[A] = k\,dt$$

When time = 0, Concentration of A = $[A]_0$

Initial concentration

Integrating both sides from time (t) = 0 to t

$$-\int_{[A]_o}^{[A]_t} d[A] = k\int_0^t dt$$

When time = t, Concentration of A = $[A]_t$

Zero-Order Reaction

$$-\int_{[A]_0}^{[A]_t} d[A] = k\int_{0}^{t} dt$$

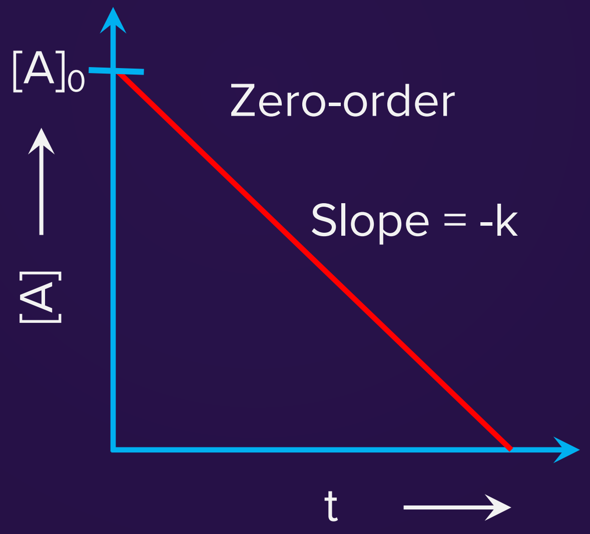
$$\{-[A]\}_{[A]_0}^{[A]_t} = k\{[t]\}_{0}^{t}$$

Integrated rate law of zero-order

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

Plot of Concentration of Reactant vs Time

$$[A]_t = [A]_0 - kt \quad \dots (1)$$



Rate Constant for Zero-Order Reaction

Unit of k = $\text{mol}^{1-n}\ \text{L}^{n-1}\ \text{s}^{-1}$

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

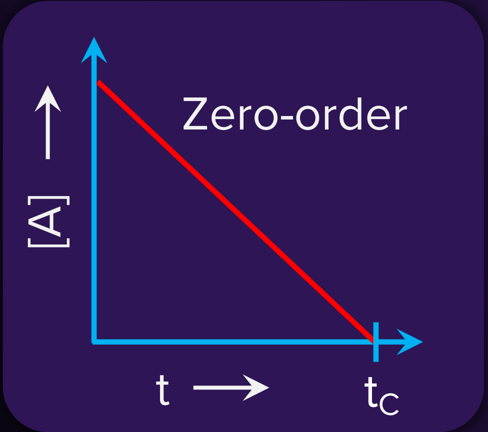
Unit of k → $\text{Concentration}^{1}\ \text{time}^{-1}$

So, Unit of k → $\text{mol L}^{-1}\ \text{s}^{-1}$

Time of Reaction Completion (t_C)

At this time, the reactants are consumed completely.

$[A]_{tc} = 0$



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

So, at t_c,

$$k = \frac{[A]_0 - 0}{t_c}$$

$$\boxed{t_c = \frac{[A]_0}{k}}$$

Half-Life Period ($t_{1/2}$)

When the **concentration** of reactants becomes **half** of its **initial concentration**

It means that the reaction is **half-completed.**

At

$t = t_{1/2}$

$$[A]_t = \frac{[A]_o}{2}$$

Half-Life Period ($t_{1/2}$)

$$k = \frac{[A]_0 - [A]_t}{t} \quad \dots (1)$$

Putting concentration value at $t_{1/2}$ in eq. (1),

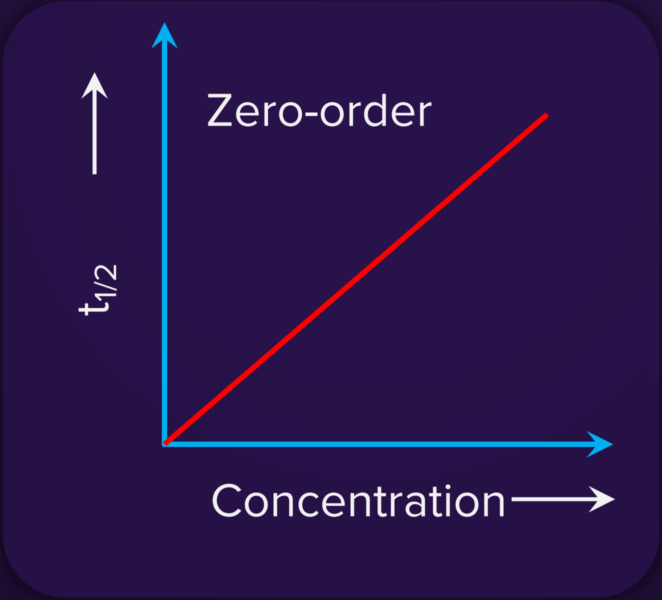
$$t_{1/2} = \frac{[A]_o - \{[A]_o/2\}}{k}$$

$$t_{1/2} = \frac{[A]_o}{2k}$$

$$t_{1/2} \propto [A]_0$$

Plot of $t_{1/2}$ vs Concentration

$t_{1/2} \propto [A]_o$



Examples of Zero-Order Reaction

Generally, the **decomposition of gases on metal surfaces** at high concentration follows zero-order kinetics.

i $2NH_3(g) \xrightarrow{Pt} N_2(g) + 3H_2(g)$

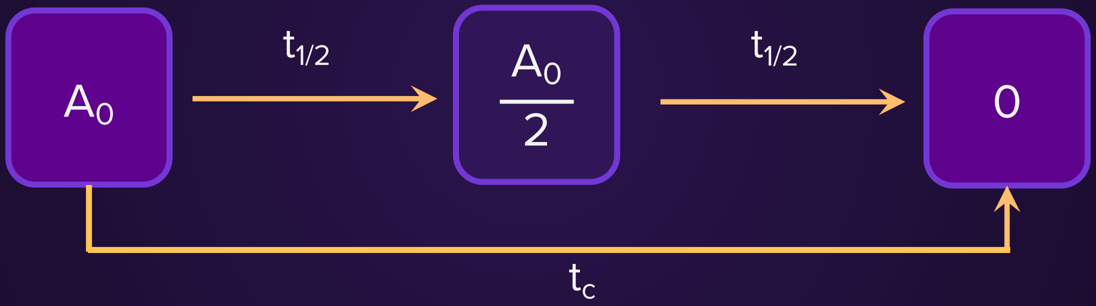
ii $2HI(g) \xrightarrow{Au} H_2(g) + I_2(g)$

iii $2PH_3(g) \xrightarrow{Ni} 2P(g) + 3H_2(g)$

iv $H_2(g) + Cl_2(g) \xrightarrow{h\nu} 2HCl(g)$

Zero-Order Reaction

In a zero-order reaction **equal concentration** of reactants get consumed in **equal time.**



$$A_0 \xrightarrow{t_{1/2}} \frac{A_0}{2} \xrightarrow{t_{1/2}} 0$$

$$A_0 \xrightarrow{t_c} 0$$

Example

$$[R] \quad 100 \xrightarrow{t = 10\ s} 90 \xrightarrow{t = 5\ s} 85 \xrightarrow{t = 2.5\ s} 82.5$$

Zero-Order Reaction

Generally, in a zero-order reaction,

$$nA \rightarrow \text{Product}$$

$$\text{Rate} = k\,[A]^0$$

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

Replace k by nk in all the previous formulas.

$$\text{Rate} = \mathbf{nk}$$

$$[A]_0 - [A]_t = \mathbf{nkt}$$

$$t_c = \frac{[A]_0}{nk}$$

First-Order Reaction

For a general reaction,

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

According to the rate law,

$$\text{Rate (R)} = k\,[A]^n$$

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

For a first-order reaction,

Where,

n : Order = 1

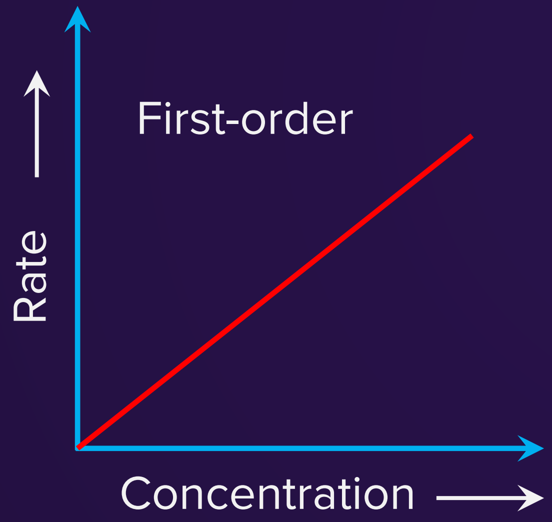
k : Rate constant

[A] : Concentration of reactant A

$$\text{Rate} = k\,[A]$$

Plot of Rate vs Time

$$R = k[A]$$



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

$$R = k[A]$$

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

First-Order Reaction

$$A \longrightarrow \text{Products}$$

Time = 0	a	0
Time = ‘t’	$a - x$	x

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

$$-\frac{d(a-x)}{dt} = k\,(a-x)$$

First-Order Reaction

$$\frac{dx}{dt} = k\,(a - x)$$

As ‘a’ is a constant value,

$$\frac{dx}{a - x} = k\,dt$$

$$\int_0^x \frac{dx}{a - x} = k \int_0^t dx$$

Integrating both sides,

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

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

First-Order Reaction

The integrated rate law of first-order reaction

$$\ln \frac{a}{a-x} = kt \quad \dots (1)$$

$$\frac{1}{t} \ln \frac{[A]_0}{[A]} = k$$

$$\ln \frac{[A]_0}{[A]} = \mathbf{kt} \quad \dots (2)$$

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

First-Order Reaction

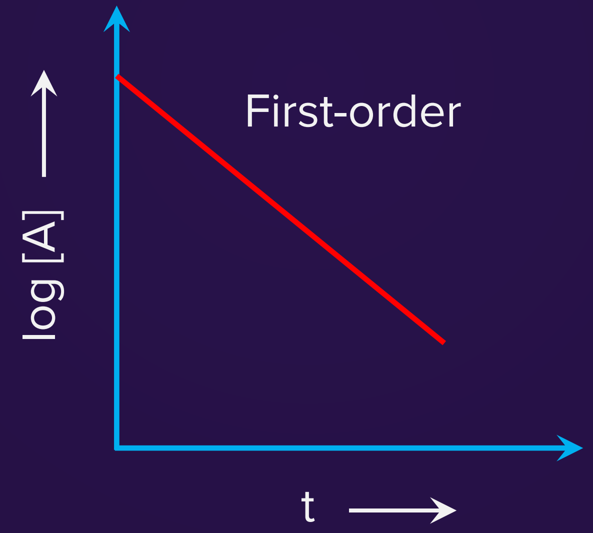
$$\frac{2.303}{t}\log\frac{[A]_0}{[A]} = k$$

$$\log[A]_0 - \log[A] = \frac{kt}{2.303}$$

$$\log [A] = \log[A]_0 - \frac{kt}{2.303}$$

Plot of log [A] vs Time

$$\log[A] = \log[A]_0 - \frac{kt}{2.303}$$



First-Order Reaction

$$\ln \frac{[A]_0}{[A]} = kt \quad \dots (2)$$

Multiplying eq. (2) by -1,

$$-\ln \frac{[A]_0}{[A]} = -kt$$

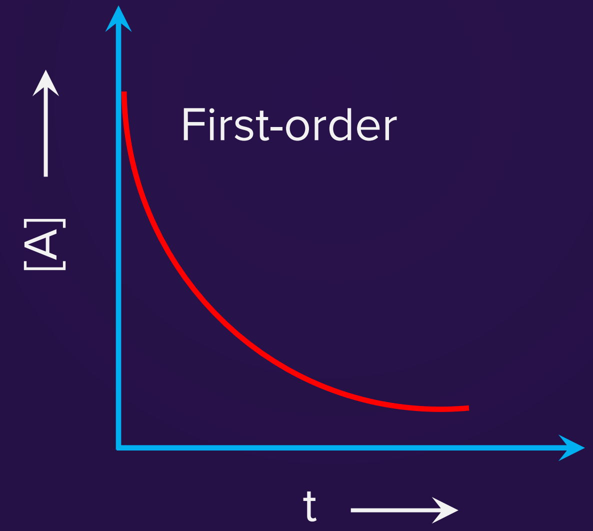
$$\ln \frac{[A]}{[A]_0} = -kt$$

Eliminating natural log from both the sides,

$$[A] = [A]_0 e^{-kt} \quad \dots (3)$$

Plot of [A] vs Time

$$[A] = [A]_0 \, e^{-kt}$$



Half-Life Period for First-Order Reaction

$$\ln \frac{a}{a-x} = kt \quad \ldots(1)$$

Reaction will be half-completed.

At

$t = t_{1/2}$

$$x = \frac{a}{2}$$

Putting the value of x in eq. (1),

$$\ln \frac{a}{a-\left(\frac{a}{2}\right)} = kt_{1/2}$$

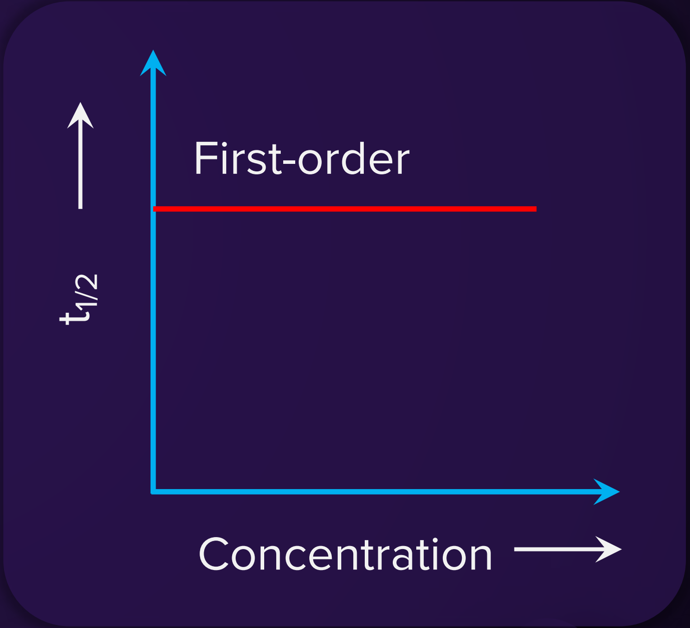
$$t_{1/2} = \frac{1}{k}\ln 2$$

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

Plot of $t_{1/2}$ vs Concentration

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

Does not depend on the concentration of reactants



Average Life for First-Order Reaction

There is another important parameter → Average life (t_{av})

$$t_{av} = \frac{1}{k}$$

k: Rate constant of a reaction

Time of Completion of Reaction

From the first-order rate expression,

$$[A] = [A]_o\, e^{-kt} \quad ...(3)$$

At completion,

The reactant concentration will be zero. So, $[A] = 0$

Putting the value of [A] in eq. (3),

$$0 = [A]_o\, e^{-kt}$$

$$e^{-kt} = 0$$

It will happen when,

$$t_c = \infty$$

Unit of Rate Constant (k)

Rate = k [Conc.]

Unit of rate → mole L^{-1} sec^{-1}

Unit of conc. → mole L^{-1}

Unit of k → sec^{-1}

Note!

Generally, for a first-order reaction,

$$nA \rightarrow \text{Product}$$

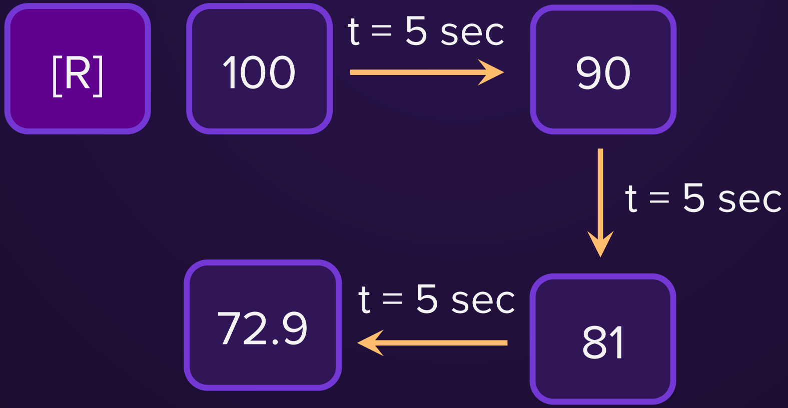
$$\text{Rate} = k\,[A]$$

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

Note!

In the first-order reaction, an **equal percentage** of reactants get consumed in **equal time.**

Example



[R]

100

t = 5 sec

90

t = 5 sec

81

t = 5 sec

72.9

Examples

1 Decomposition of **H_2O_2** takes place.

$$2H_2O_2\,(aq) \xrightarrow{MnO_2} 2H_2O\,(l) + O_2\,(g)$$

2 **All radioactive decays** are always first-order kinetics.

$$^{226}_{88}Ra \longrightarrow {}^{222}_{86}Rn + {}^{4}_{2}He$$

Second-Order Reaction

For a general reaction,

$$A + A \longrightarrow \text{Product(s)}$$

According to the rate law,

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

For a second-order reaction

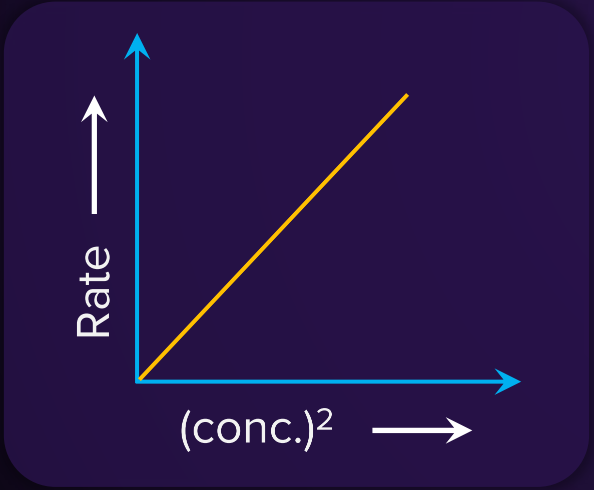
Where,

n : Order = 2
k : Rate constant
[A] : Concentration of reactant A

$$\textbf{Rate} = k\,[A]^2$$

Second-Order Reaction

Rate = k $[A]^2$



A	+ A	$\rightarrow$ Products
a	a	0
$(a - x)$	$(a - x)$	x

Rate = k $[A]^2$

Second-Order Reaction

$$\frac{dx}{dt} = k\,(a-x)^2$$

$$\int_0^x \frac{dx}{(a-x)^2} = \int kdt$$

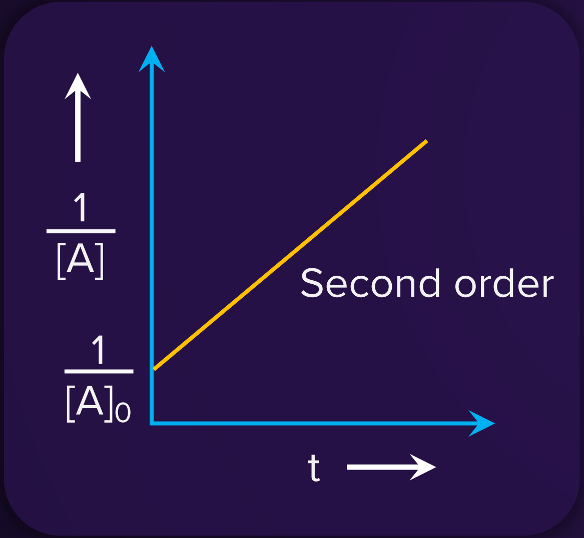
$$\left(\frac{1}{(a-x)}\right)_0^x = kt$$

$$\frac{1}{(a-x)} - \frac{1}{a} = kt$$

or

$$\frac{1}{[A]} - \frac{1}{[A]_0} = \mathbf{kt}$$

Second-Order Reaction



$$\frac{1}{[A]} - \frac{1}{[A]_0} = kt$$

At

$t = t_{1/2}$

$$[A]_t = \frac{[A]_0}{2}$$

Half-Life Period ($t_{1/2}$)

$$k = \frac{1}{t}\left(\frac{1}{[A]_t} - \frac{1}{[A]_0}\right) \quad \text{... (1)}$$

Putting the concentration value at $t_{1/2}$ in eq. (1),

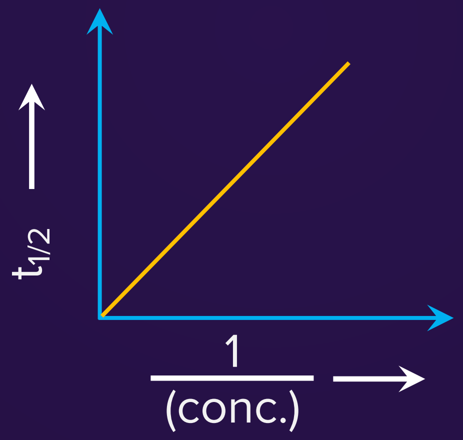
$$t_{1/2} = \frac{1}{k}\left(\frac{2}{[A]_0} - \frac{1}{[A]_0}\right)$$

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

$$t_{1/2} \propto \frac{1}{[A]_0}$$

Second-Order Reaction

$$t_{1/2} \propto \frac{1}{[A]_0}$$



Unit of Rate Constant (k)

Rate = k [Concentration]^{n}

Unit of k: mol^{1-n} L^{n-1} s^{-1}

Unit of concentration → mol L^{-1}

Unit of rate → mol L^{-1} s^{-1}

Unit of k → mol^{1-n} L^{n-1} s^{-1}

For zero order (n = 0) → mol L^{-1} s^{-1}

For first order (n = 1) → s^{-1}

For second order (n = 2) → mol^{-1} L^{1} s^{-1}

Pseudo Order Reactions

The **order** of a reaction is sometimes **altered** by conditions.

A reaction whose **order** is **different from the actual order** due to **excess** concentration of **one** of the reactants is known as pseudo order reaction.

Depending upon the **conditions**, a **second**-order reaction can behave **as a first**-order reaction.

Pseudo First-Order Reaction

For a second-order reaction,

$$A + B \longrightarrow \text{Product(s)}$$

$$\text{Rate} = k\,[A][B]$$

If the concentration of **one reactant**, A, is taken in **excess,**

The **change** in concentration of A is **negligible** during the reaction.

Pseudo First-Order Reaction

So, it can be considered as **constant.**

Now, the reaction **rate** depends on the concentration of the **other reactant** (B) **only.**

The reaction becomes a **first-order** reaction.

Pseudo First-Order Reaction

Rate = k [A] [B]

A + B → Product(s)

Rate = k′ [B]

Where k′ = k[A]

The reactions that are actually of **second (or higher)** order but **behave as first**-order reactions

Pseudo first-order reactions

Examples of Pseudo First Order Reaction

Hydrolysis of Ethyl Acetate

0.01 mol of ethyl acetate + 10 mol H_2O

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

t = 0	0.01	10	0	0
t = t	0.01-x	10-x	x	x

Hydrolysis of Ethyl Acetate

$$CH_3COOC_2H_5 + H_2O \longrightarrow CH_3COOH + C_2H_5OH$$

Rate = $k\,[CH_3COOC_2H_5]\,[H_2O]$

Rate = $k'[CH_3COOC_2H_5]$

As the change of $[H_2O]$ during the reaction is negligible (≈ 0.01 mol out of 10 mol consumed),

$k\,[H_2O]$ = Constant = k'

Pseudo first-order reaction

Hydrolysis of Ethyl Acetate

$C_{12}H_{22}O_{11}$ + H_2O → $C_6H_{12}O_6$ + $C_6H_{12}O_6$

Sucrose | Water (excess) | Glucose | Fructose

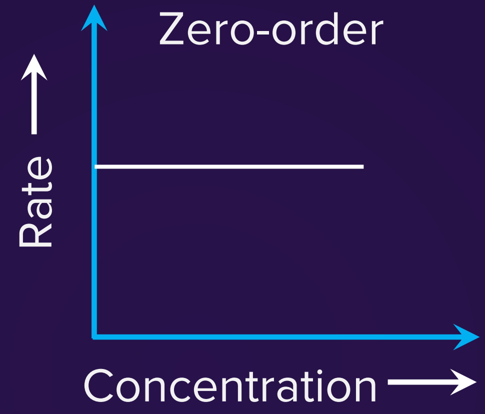
Rate = k [sucrose] [water]

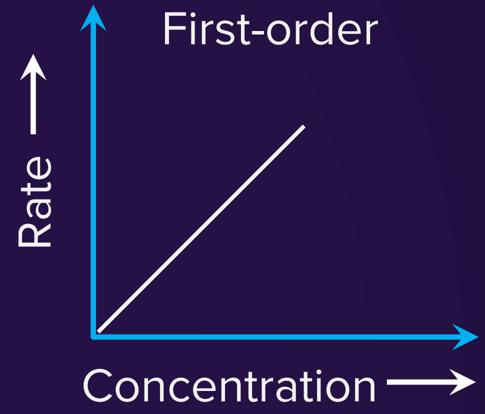
Rate = k′ [sucrose]

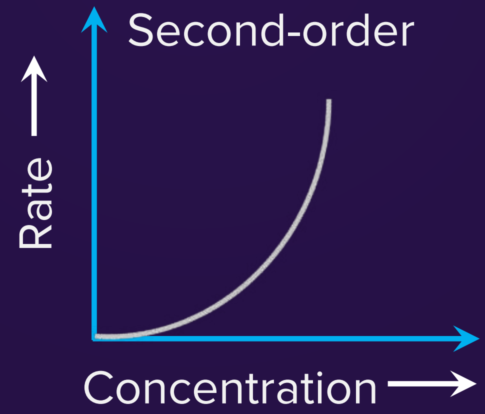
Rate vs Concentration of Reactant(s)

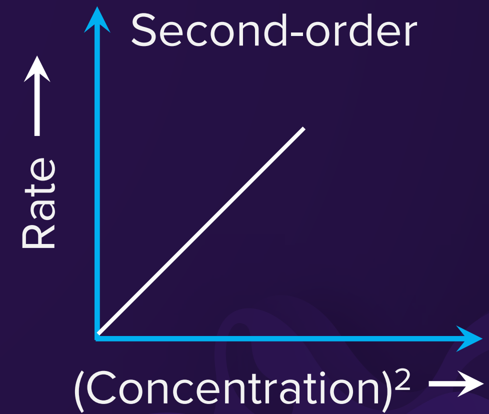
For nth order reaction

$$\boxed{\text{Rate} = k\,[A]^n}$$


Zero-order

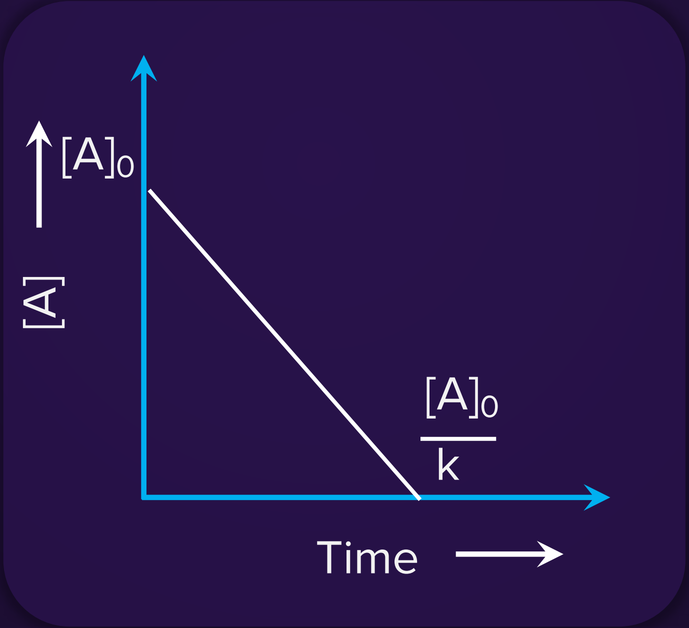

First-order


Second-order


Second-order

Concentration of Reactant(s) vs Time (For Zero-Order)

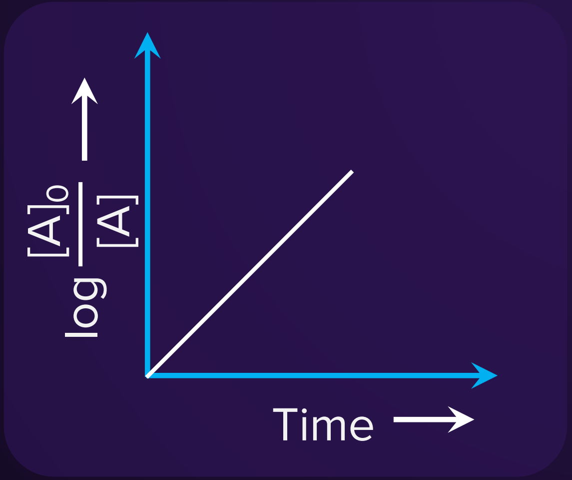
$$[A] = [A]_0 - kt$$

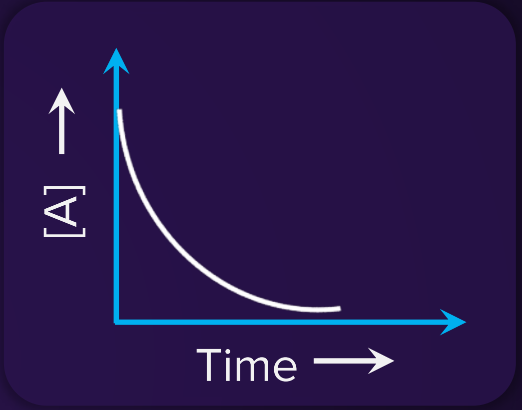


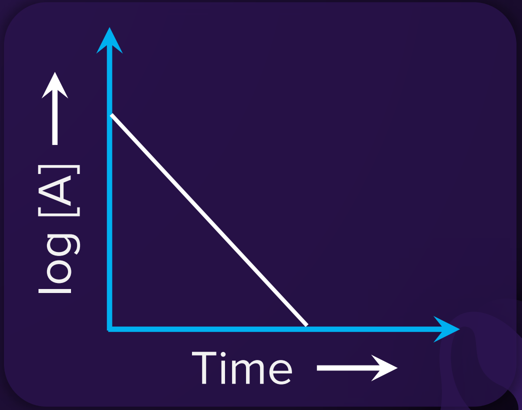
Concentration of Reactant(s) vs Time (For First-Order)

$$[A] = [A]_0\, e^{-kt}$$

$$\log[A] = \log[A_0] - \frac{kt}{2.303}$$

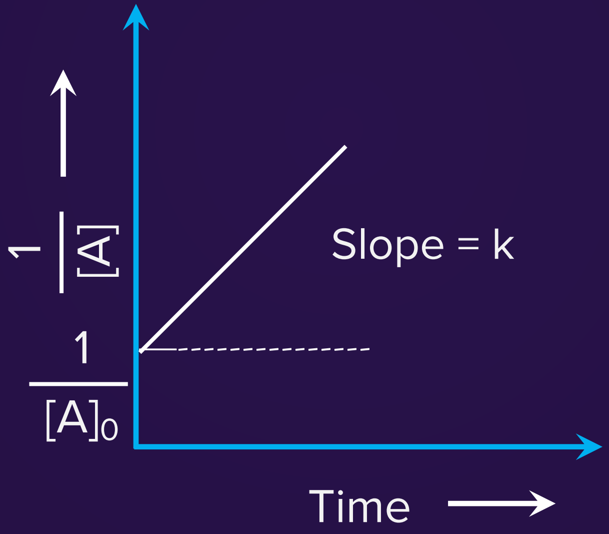






Concentration of Reactant(s) vs Time (For Second-Order)

$$\frac{1}{[A]} = kt + \frac{1}{[A]_0}$$

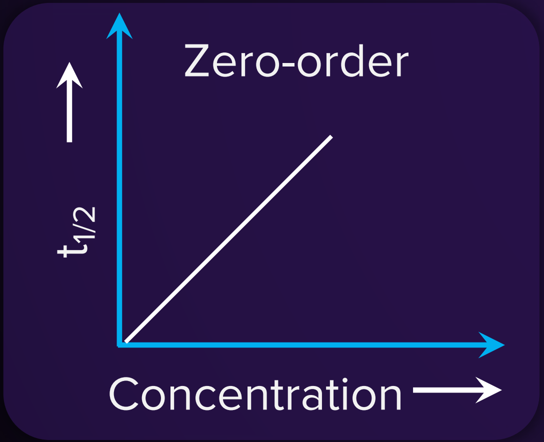


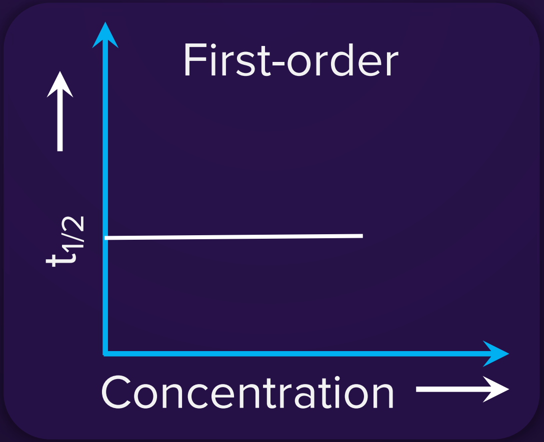
$t_{1/2}$ vs Concentration of Reactant(s)

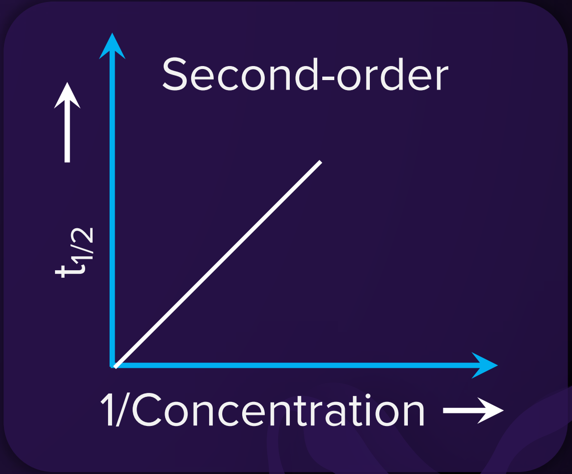
$$t_{1/2} = \frac{[A]_0}{2k}$$

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

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







Unit Method

For an n^th^ order reaction, we know that,

$$k = \frac{\text{Rate}}{[\text{Concentration}]^n}$$

Unit of k = $\text{mol}^{1-n}\,\text{L}^{n-1}\,\text{s}^{-1}$

In this method, the **order** of a reaction can be determined by observing the **unit** of the **rate constant**.

Unit of k: $\text{mol}^{1-n}\,\text{L}^{n-1}\,\text{s}^{-1}$

For zero order (n = 0) → $\text{mol L}^{-1}\,\text{s}^{-1}$

For first order (n = 1) → s^{-1}

For second order (n = 2) → $\text{mol}^{-1}\,\text{L}^{1}\,\text{s}^{-1}$

Half-Life Method

For a reaction, half-life can be determined at **two different initial concentrations** and related to the **order of the reaction.**

For a general **n^{th} order** reaction,

$$A \longrightarrow \text{Product(s)}$$

We know,

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

Half-Life Method

For the reaction,

$A \longrightarrow \text{Product (s)}$

If, Initial concentration of A $=$ $[A]_0$

So, $t_{1/2} \propto \dfrac{1}{[A]_0^{n-1}}$ ...(1)

At a different initial concentration $[A]_0$,

Initial concentration of A $=$ $[A]_0'$

New half-life,

$t'_{1/2} \propto \dfrac{1}{[A]_0'^{\,n-1}}$ ...(2)

Half-Life Method

$$t_{1/2} \propto \frac{1}{[A]_0^{n-1}} \quad \text{...(1)}$$

$$t'_{1/2} \propto \frac{1}{[A]_0'^{\,n-1}} \quad \text{...(2)}$$

On dividing eq. (1) by eq. (2), we get,

$$\frac{t_{1/2}}{t'_{1/2}} = \left(\frac{[A]'_0}{[A]_0}\right)^{n-1} \quad \text{...(3)}$$

'**n**' can be calculated by measuring $t_{1/2}$, $t'_{1/2}$, $[A]_0$, and $[A]'_0$ values.

Methods to monitor the progress of a reaction

- Pressure measurement
- Volume measurement
- Titration method
- Optical rotation method

In the following methods, **only** the **first-order** reaction kinetics is considered.

Pressure Measurement

As we know,

$$PV = nRT$$

V: Volume
n: Number of moles
P: Pressure
R: Gas constant
T: Temperature

So, $P = \frac{n}{V} RT$

$$P \propto \frac{n}{V}$$

$P \propto$ Concentration

Pressure Measurement

So, for the reactions involving **gaseous** reactants and products

Pressure is considered to **monitor** the reaction instead of concentration

$$A\,(g) \longrightarrow B\,(g) + C\,(g)$$

Progress of a reaction involving **gaseous** reactants/products can be monitored by

Measuring the **total pressure** at a **fixed** volume and temperature

Pressure Measurement

In terms of concentration

$$A \longrightarrow B + C$$

At time t, $a - x$ x x

$$A(g) \longrightarrow B(g) + C(g)$$

	A (g)	B (g)	C (g)
t = 0	P_0	0	0
t = t	$P_0 - P_r$	P_r	P_r

P_0: Initial pressure

P_r: Pressure due to amount of reactant consumed up to time ‘t’

Pressure Measurement

The pressure measurement can be done in two ways

(i) Partial pressure of the reactant

(ii) Total pressure of the reaction system

Pressure Measurement

	A		B	C
In terms of concentration	A	⟶	B +	C
At time t,	$P_0 - P_r$		P_r	P_r

Total pressure at time 't' → P_t

According to Dalton's law,

$$P_t = (P_0 - P_r) + P_r + P_r$$

$$P_t = P_0 + P_r$$

$$P_r = P_t - P_0$$

Pressure Measurement

As, Concentration $\propto$ Pressure

$$a \propto P_0$$

$$a - x \propto P_0 - P_r$$

$$\frac{a}{a - x} = \frac{P_0}{P_0 - P_r} \quad \ldots(1)$$

Pressure Measurement

$$\frac{a}{a-x} = \frac{P_0}{P_0 - P_r} \quad \ldots(1)$$

$P_t = (P_0 - P_r) + P_r + P_r$
$P_t = P_0 + P_r$

For the first-order reaction,

$$kt = \ln \frac{a}{a-x} = \ln \frac{[A]_0}{[A]}$$

Substituting values from eq. (1) in the first law expression,

$$kt = \ln \frac{P_0}{P_0 - P_r} = \ln \frac{[P_A]_0}{[P_A]}$$

Substituting the value of P_r,

$$kt = \ln \frac{P_0}{2P_0 - P_t}$$

Volume Measurement

In terms of concentration	$A \longrightarrow$	$B +$	C
At time = t;	$a - x$	x	x
At time = t_∞;	0	a	a

Monitoring the **progress** of a reaction

By measuring the **volume** of the **product** formed

$$A(s) \longrightarrow B(l) + C(g)$$

	C (g)
t = 0	0
t = t	V_t
t = t_∞	V_∞

V_t: The volume of C collected at time ‘t’

V_∞: The volume of C collected at the end of the reaction

Volume Measurement

In terms of concentration

$$A \longrightarrow B + C$$

At time t,	$a - x$	x	x
At time t_∞,	0	a	a

First-order integrated rate law,

$$kt = \ln \frac{a}{a - x} \quad \text{...(1)}$$

a (amount of solid taken initially) $\propto$ Volume of gas collected at infinite time V_∞

Amount of solid decomposed (x) $\propto$ Volume of gas collected at any time V_t

Volume Measurement

$$kt = \ln \frac{a}{a - x} \quad \ldots(1)$$

$$a \propto V_\infty$$
$$x \propto V_t$$

$$a - x \propto V_\infty - V_t$$

Putting these values in eq. (1),

$$kt = \ln \frac{V_\infty}{V_\infty - V_t}$$

Titration Method

By measuring the **volume of titrating agent**, we can monitor the amount of **reactant remaining** or the amount of **product formed** at any time.

Decomposition reaction

$$2H_2O_2\ (l) \xrightarrow{\Delta} 2H_2O\ (l) + O_2\ (g)$$

The progress of a reactant is monitored by titrating a fixed volume of **H_2O_2 solution** in a **$KMnO_4$ solution** in an **acidic medium**.

The **volume** of $KMnO_4$ used corresponds to the **undecomposed** hydrogen peroxide.

Titration Method

The volume of $KMnO_4$ used initially

Assuming it as a first-order reaction,

$V_0 \propto$ Initial concentration of H_2O_2 (a)

$V_t \propto$ Concentration of H_2O_2 at that instant (a − x)

The volume of $KMnO_4$ used after time ‘t’

Titration Method

The integrated rate law for a first-order reaction,

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

Applying eq. (1) in the rate law expression,

$$kt = \ln \frac{V_0}{V_t}$$

Optical Rotation Method

It is used for **optically active** samples. It is applicable if there is **at least one** optically active species involved in chemical reaction.

The optically active species may be present in the **reactant** or the **product**.

Inversion of Cane Sugar (Sucrose)

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+} C_6H_{12}O_6 + C_6H_{12}O_6$$

Sucrose	Glucose	Fructose
(dextro–rotatory)	(dextro–rotatory)	(laevo–rotatory)
$+66.5^\circ$	$+52.5^\circ$	-92°

$$\underbrace{+52.5^\circ \qquad -92^\circ}_{\text{(laevo–rotatory)}}$$

Inversion of Cane Sugar (Sucrose)

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+} C_6H_{12}O_6 + C_6H_{12}O_6$$

$t = 0$	a		0	0
$t = t$	$a - x$		x	x
$t = t_c$	0		a	a

Inversion of Cane Sugar (Sucrose)

It is found that Rotation at infinite time $(r_0 - r_\infty)$ $\propto$ Initial concentration of sucrose (a)

Rotation at any instant of time $(r_0 - r_t)$ $\propto$ Amount of sucrose hydrolysed (x)

Where,

a: Initial concentration

x: Amount consumed

r_0: Optical rotation at t = 0

r_t: Optical rotation at t = t

r_∞: Optical rotation at t = ∞

Inversion of Cane Sugar (Sucrose)

$$a - x \propto (r_0 - r_\infty) - (r_0 - r_t)$$

$$a - x \propto r_t - r_\infty$$

The integrated rate law for first-order reaction

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

$$kt = \ln \frac{r_0 - r_\infty}{r_t - r_\infty}$$

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

Elementary reaction:

$$aA + bB \rightarrow \text{Product}$$

$$\text{Molecularity} = (a + b)$$

1, 2, or 3

Molecularity is simply the sum of the **stoichiometric coefficients** of the different reactants.

Molecularity of a Reaction

Elementary reactions involving more than three molecules

Are not known

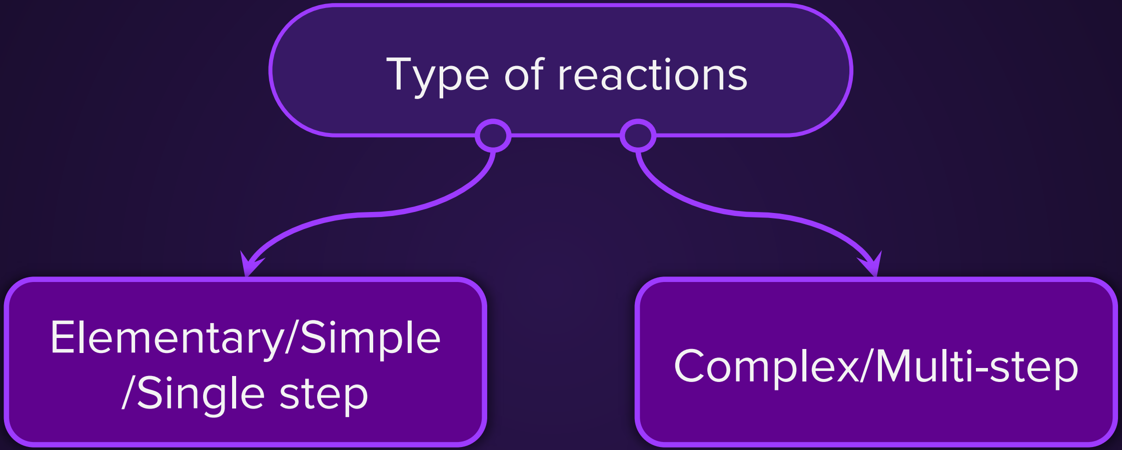
So, Molecularity $\leq$ 3

Comparison Between Order and Molecularity

	Molecularity of reaction	Order of reaction
1	It is defined as the **number of reactants** taking part in a chemical reaction. $NH_4NO_2 \rightarrow N_2 + 2H_2O$ Molecularity = 1	It is defined as the **sum of the power** of concentration terms that appear in rate law. $NH_4NO_2 \rightarrow N_2 + 2H_2O$ Rate = $k[NH_4NO_2]$ Order = 1
2	It is always a **whole number**. It can neither be zero nor be fractional.	It may be **zero, fractional, or integer**.

Comparison Between Order and Molecularity

	Molecularity of reaction	Order of reaction
3	It is defined **only for elementary** reactions.	It is defined for **elementary as well as complex** reactions.
4	It is a **theoretical** value.	It is an **experimental** value.



Type of reactions

- Elementary/Simple /Single step
- Complex/Multi-step

Elementary/Simple/Single Step Reaction

These reactions take place in a **single** step

Without the formation of any **intermediate**

Formed **during the course** of a reaction, but **not present** in the **overall** balanced equation

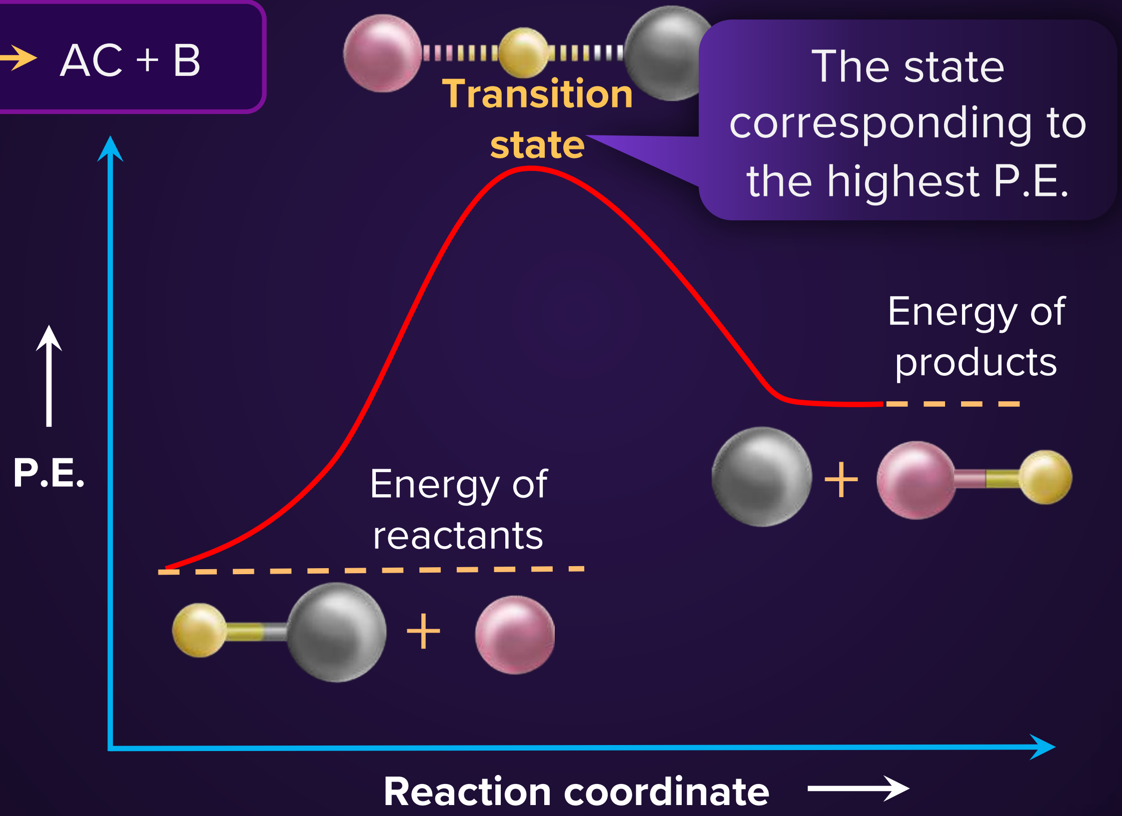
For the elementary reaction,

$$H_2(g) + I_2(g) \longrightarrow 2HI(g)$$

$$\text{Rate} = k[H_2][I_2]$$

Elementary/Simple/Single Step Reaction

AB + C ⟶ AC + B



Elementary/Simple/Single Step Reaction

Example

For these type of reactions

Molecularity = Order of a reaction

Stoichiometric coefficient of any reactant = Order with respect to that reactant

Elementary reaction:

$aA + bB \rightarrow \text{Product}$

Rate = $k[A]^a[B]^b$

Molecularity/ Order = a + b

Complex Reaction

For the complex reaction,

$2NO + 2H_2 \rightarrow N_2 + 2H_2O$

Reaction that proceeds in **more than two** steps or follows some **mechanism**

Sequence of steps that converts reactants into products

$2NO \rightleftharpoons N_2O_2$ Step 1

$N_2O_2 + H_2 \rightarrow N_2O + H_2O$ Step 2

$N_2O + H_2 \rightarrow N_2 + H_2O$ Step 3

Complex Reaction

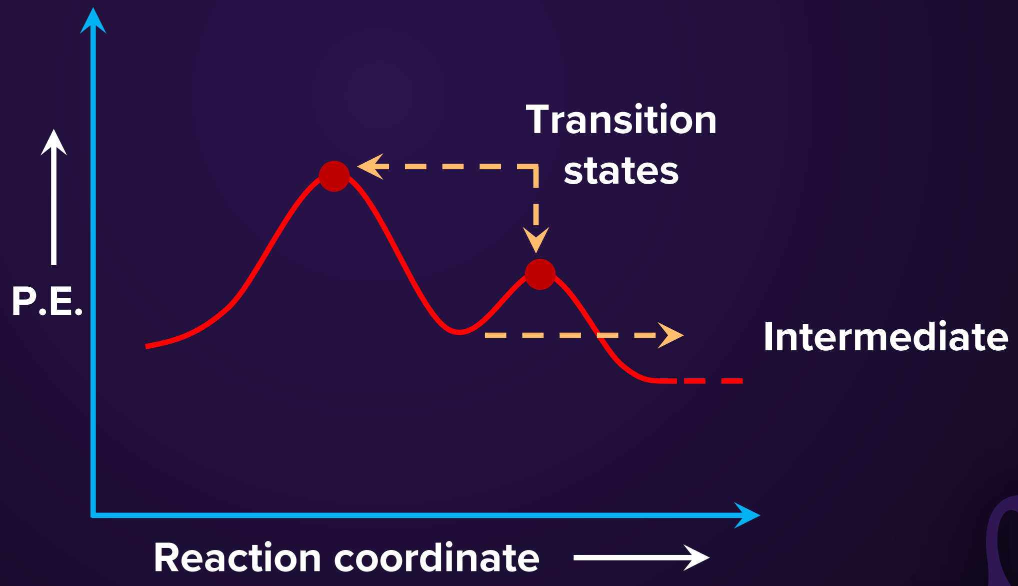
As it consists of **multiple** steps

Every step behaves as an **elementary** reaction

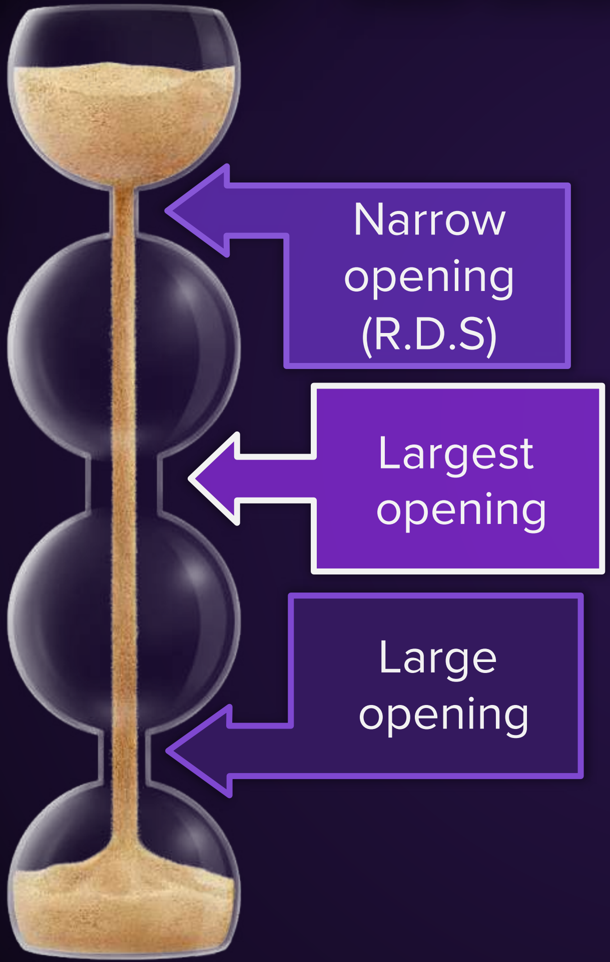
So, **each step** has its own **molecularity**

Complex Reaction

A → Intermediate → P



Rate Determining Step (R.D.S.)



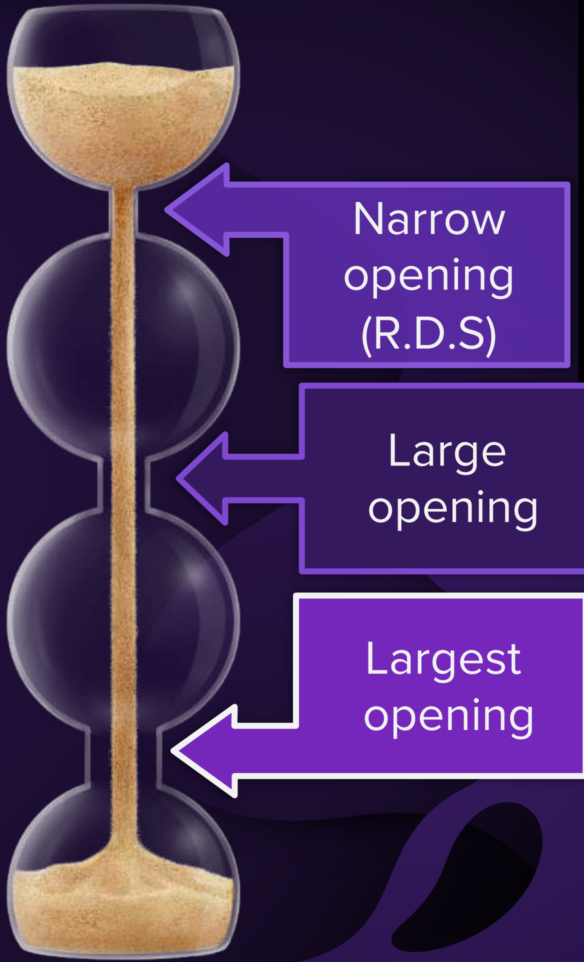
Narrow opening (R.D.S)

Largest opening

Large opening

The **rate** of flow of sand is decided only by the **narrow opening.**

Similarly, the **rate** of reaction is decided only by the **slowest step.**



Narrow opening (R.D.S)

Large opening

Largest opening

Rate Determining Step (R.D.S.)

Large opening

Narrow opening (R.D.S)

Large opening

The **rate** of flow of sand is decided only by the **narrow opening.**

Rate Determining Step (R.D.S.)

The order of any reaction (complex) has to be always determined **experimentally**

The step of a complex reaction that is the **slowest** and on which, the overall reaction **rate is dependent**.

Effect of the Temperature on Rate of Reaction

Generally, for a chemical reaction with rise in temperature by **10°**, the **rate constant** is nearly **doubled**.

The **effect** of temperature on reaction rate

Can be **mathematically** expressed using

Temperature coefficient

Temperature Coefficient

The ratio of the rate of reaction at two different temperatures differing by → 10°C

$$\text{Temperature coefficient (T.C.)} = \frac{k_{t+10}}{k_t}$$

$$\approx \text{2 to 3}$$

Arrhenius Theory

For a reaction, the relationship between **temperature** and **rate constant** follows the equation

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

The **temperature dependence** of the rate of a chemical reaction can be **accurately** explained by **Arrhenius theory.**

Where,

k : Rate constant

A : Arrhenius factor or frequency factor or pre-exponential factor

E_a: Activation energy (in J/mol)

R : Gas constant

T : Temperature of reaction **(K)**

Trying to Interpret Arrhenius Theory

Example

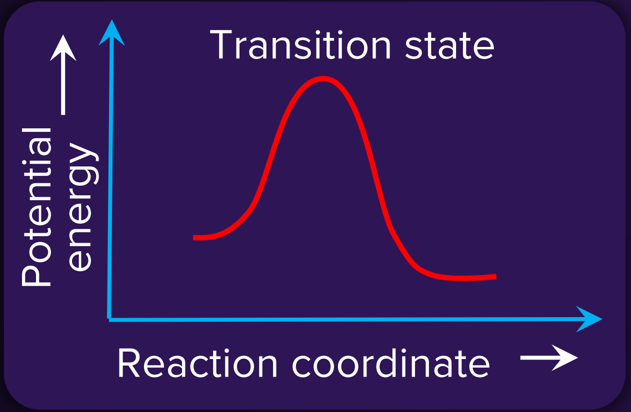
Elementary reaction

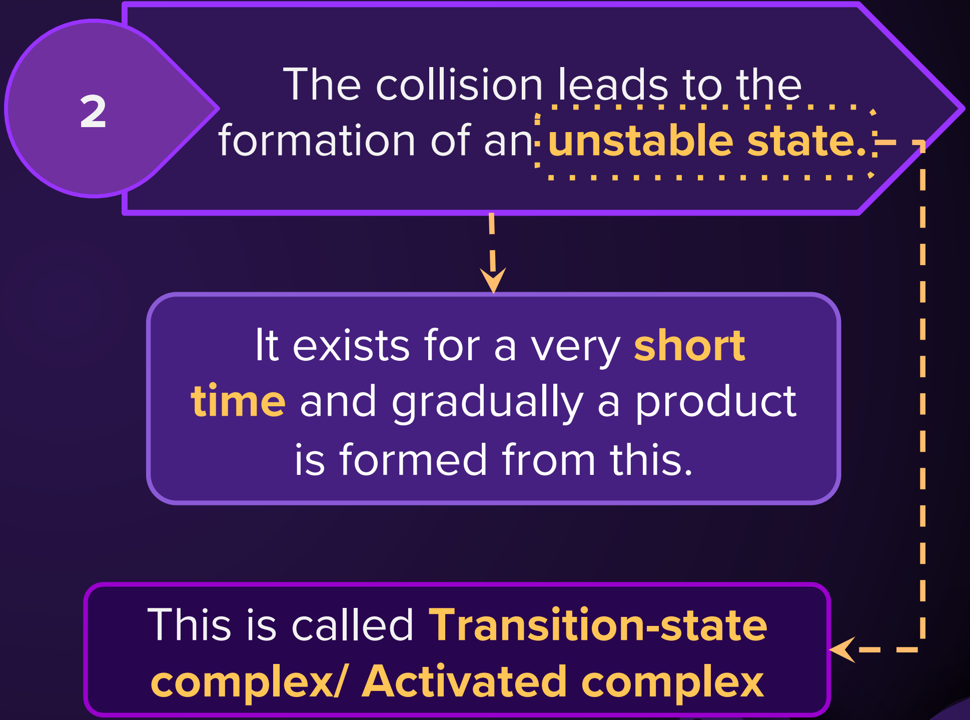
$A_2 + B_2 \rightarrow 2AB$

According to Transition state theory,

1 The reaction can take place only when a molecule of A_2 and a molecule of B_2 **collide.**

Trying to Interpret Arrhenius Theory



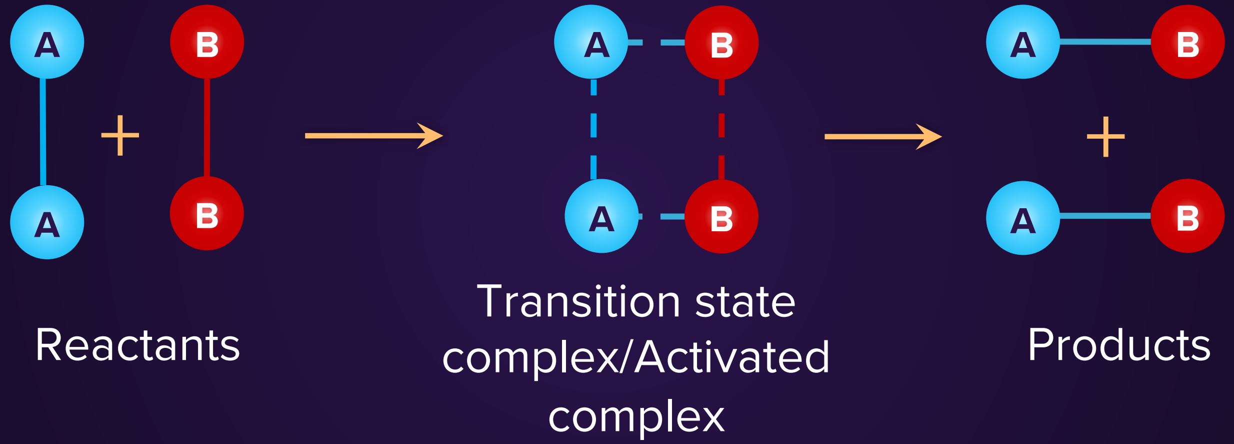


2 The collision leads to the formation of an **unstable state.**

It exists for a very **short time** and gradually a product is formed from this.

This is called **Transition-state complex/ Activated complex**

Reaction and Transition State Complex



Reactants

Transition state complex/Activated complex

Products

Trying to Interpret Arrhenius Theory

3

Energy required to form the activated complex

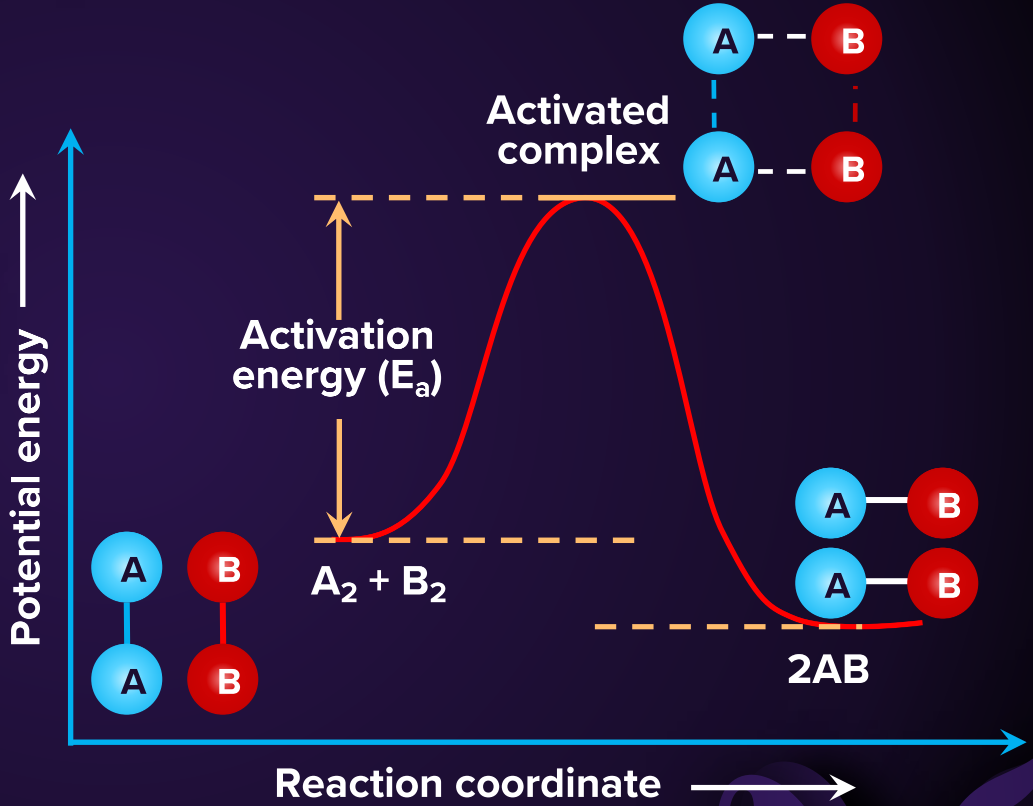
Activation energy

Plot of Potential Energy vs Reaction Coordinate

$A_2 + B_2 \longrightarrow 2AB$

Endothermic or exothermic

The **final enthalpy** of the reaction depends upon the **nature** of reactants and products.



Enthalpy Change During a Reaction

We know enthalpy change for a reaction

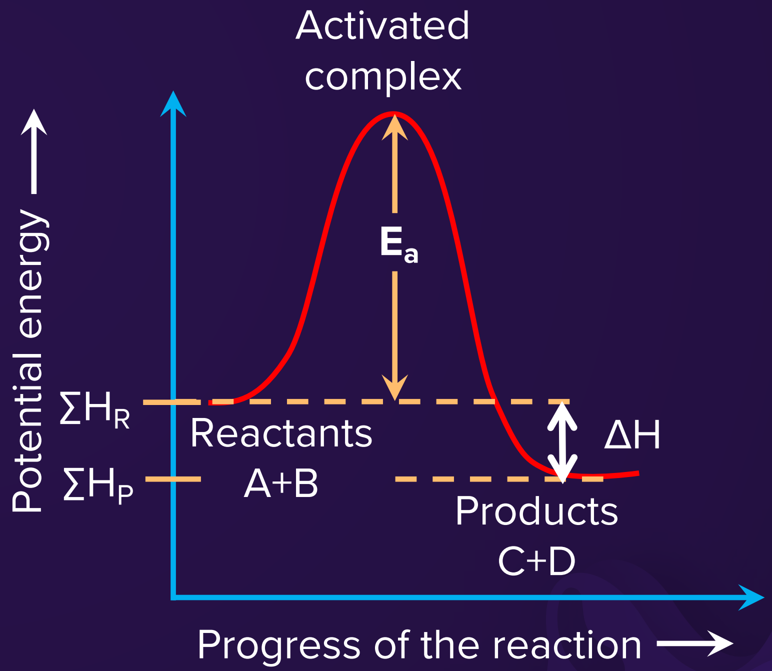
$A + B \longrightarrow C + D$

For exothermic reaction $\Delta H < 0$

$\Delta H = \Sigma H_P - \Sigma H_R$

ΣH_P = Summation of enthalpies of product(s)

ΣH_R = Summation of enthalpies of reactant(s)

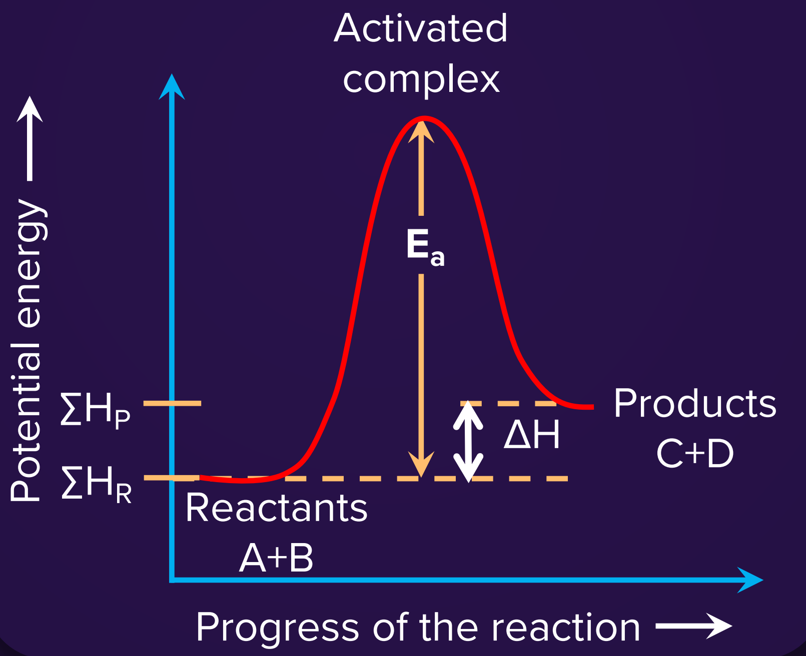


Enthalpy Change During a Reaction

$A + B \rightarrow C + D$

For endothermic reaction

$\Delta H = \Sigma H_P - \Sigma H_R > 0$



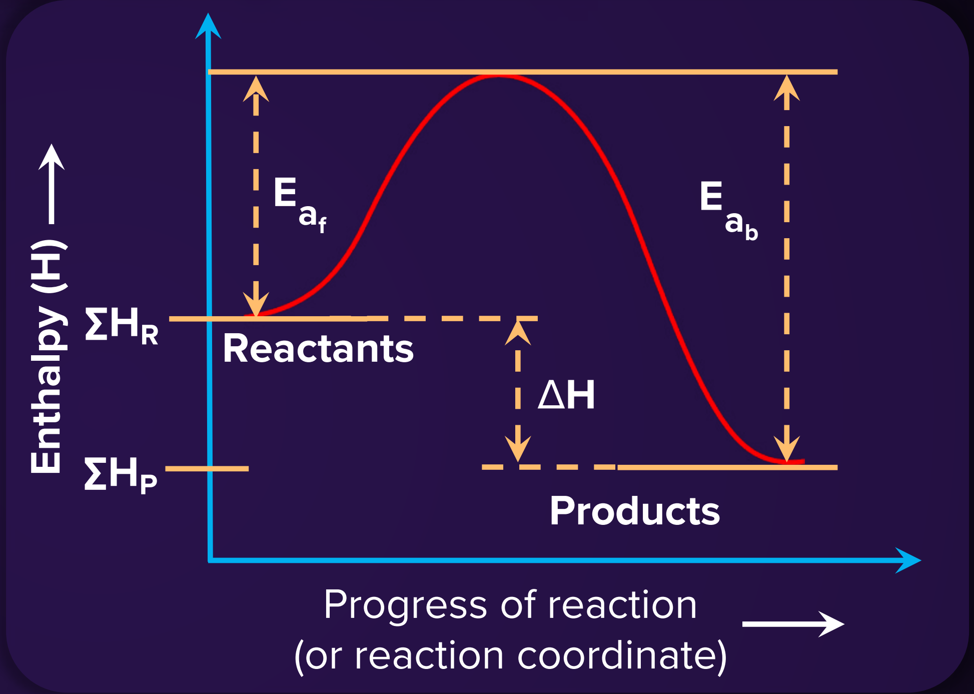
Enthalpy Change During a Reaction

For a **reversible** exothermic reaction

$Reactants \rightleftharpoons Products$

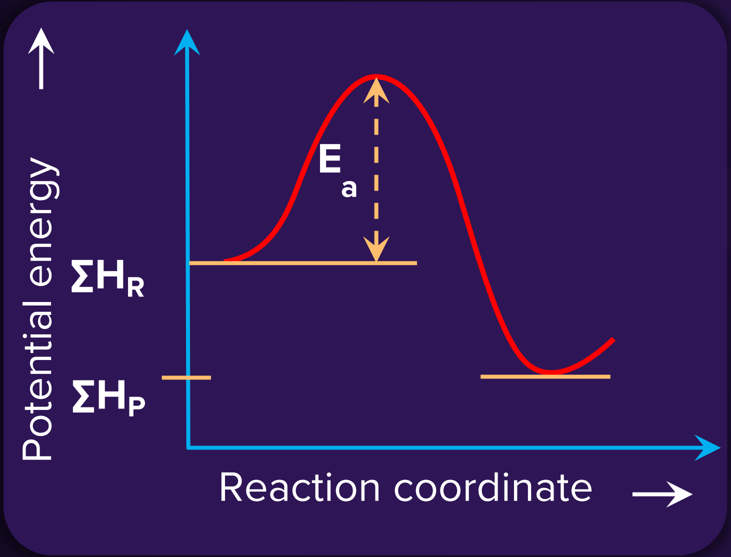
Enthalpy change can also be expressed in terms of **activation energy**,

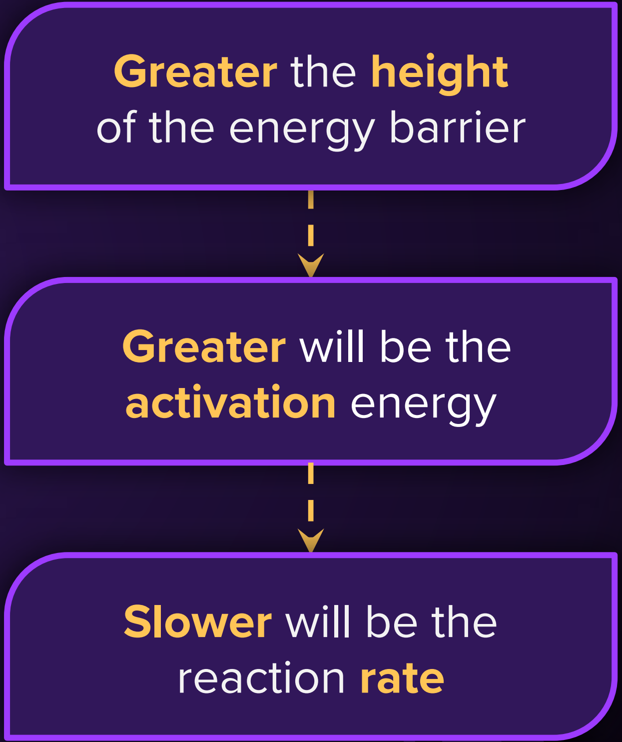
$\Delta H = E_{a_f} - E_{a_b}$



E_{a_f} = Activation energy of the forward reaction
E_{a_b} = Activation energy of the backward reaction

Remember!





Greater the **height** of the energy barrier

Greater will be the **activation** energy

Slower will be the reaction **rate**

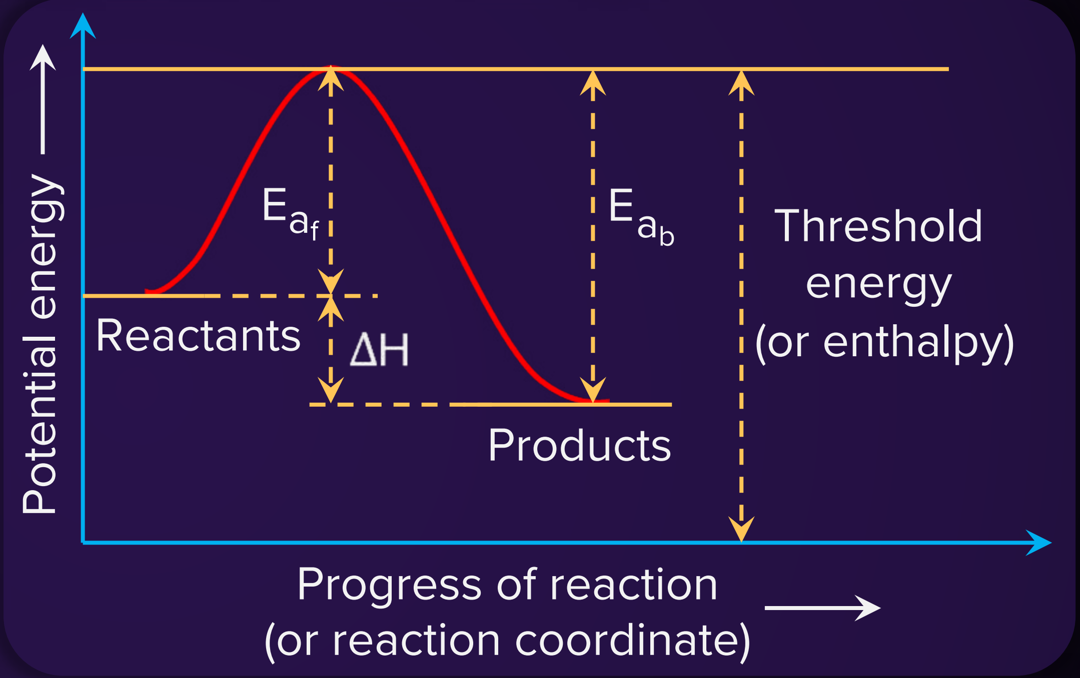
Activation Energy vs Threshold Energy

Threshold energy

The **minimum** energy that the colliding reactant molecules must possess for the chemical reaction to occur.

Activation energy

The **extra** energy required by a reactant to participate in a reaction.



E_T = E_a + Energy of reactant molecule

Maxwell–Boltzmann Statistics and Arrhenius Theory

All molecules in the reacting species **do not** have the **same kinetic energy.**

↓

It is difficult to **predict the behaviour** of any **one molecule** with precision.

↓

Statistics is used to predict the behaviour of a **large number of molecules.**

The distribution of kinetic energy may be described by plotting the fraction of molecules (**N_E / N_T**) with a given kinetic energy (E) **versus kinetic energy.**

Where,
N_E is the number of molecules with energy, E
N_T is the total number of molecules

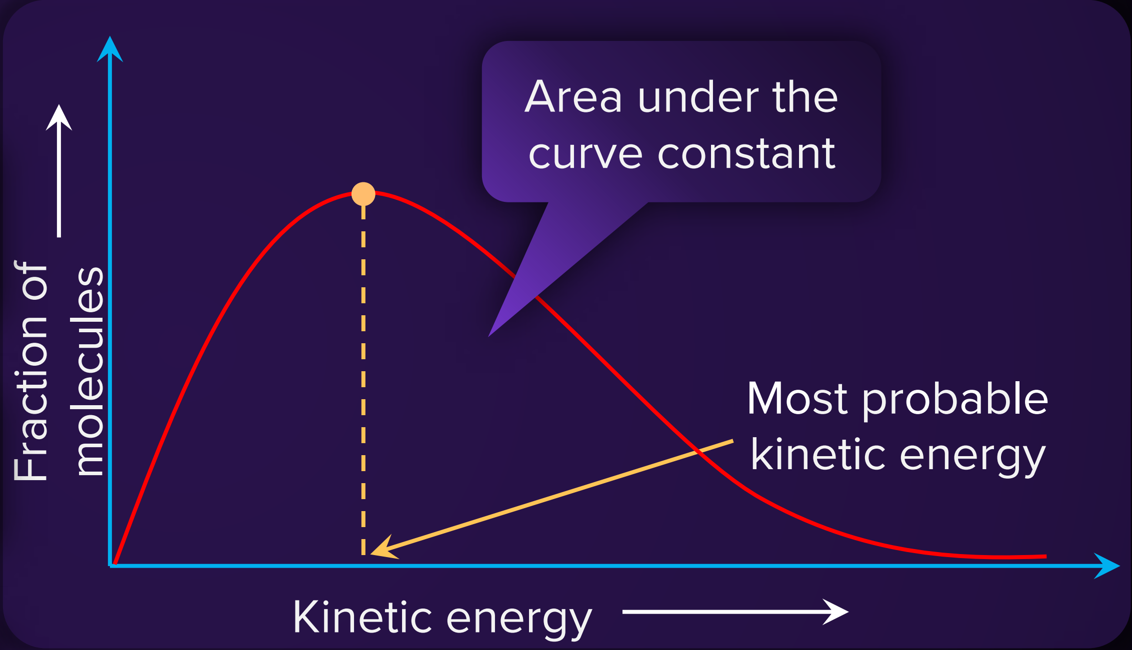
Maxwell–Boltzmann Statistics and Arrhenius Theory

When temperature is raised

The **maxima** of the curve moves to the higher energy value

Curve **broadens out**

Greater proportion of molecules possess much **higher energies**

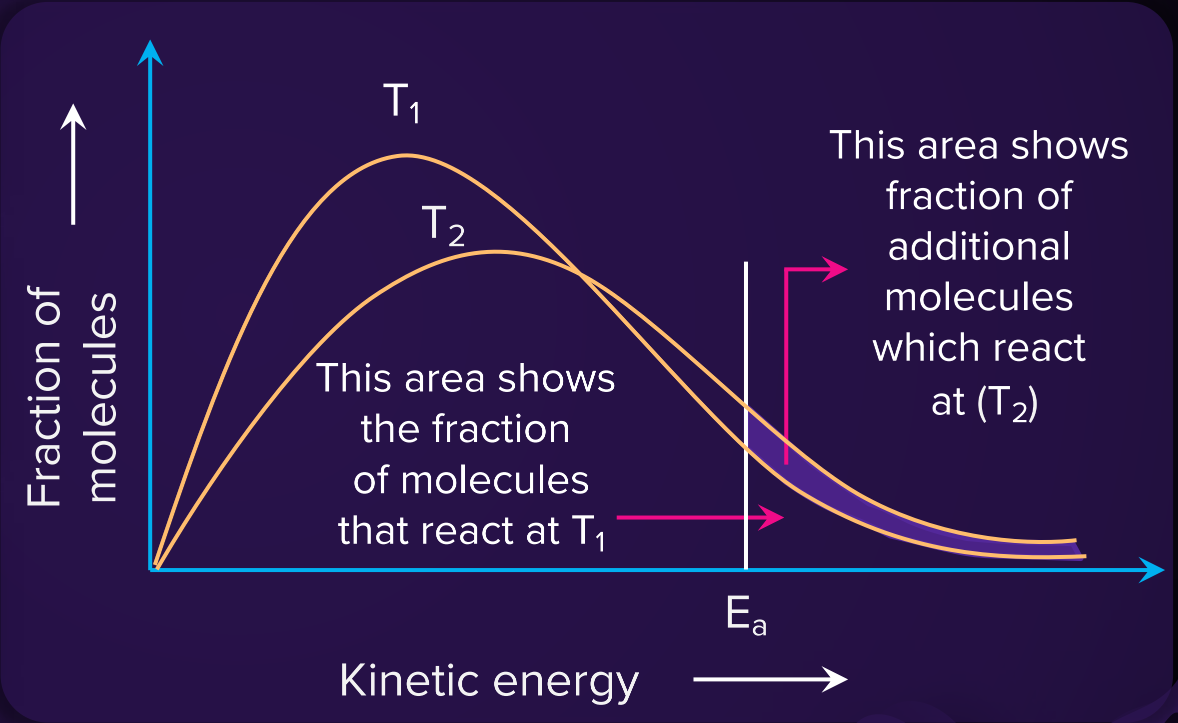


Maxwell–Boltzmann Statistics and Arrhenius Theory

Increasing temperature

Increases the fraction of molecules

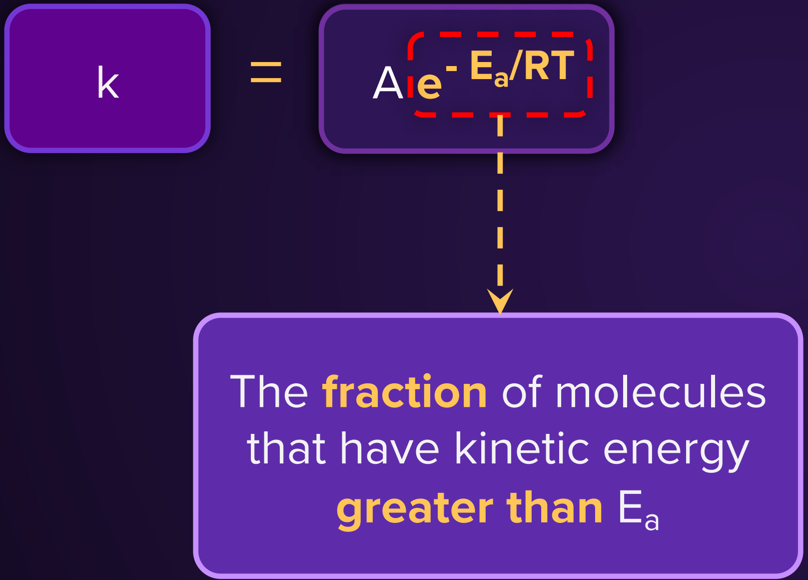
Which **collide** with energies **greater than** activation energy (E_a)



This area shows the fraction of molecules that react at T_1

This area shows fraction of additional molecules which react at (T_2)

Maxwell–Boltzmann Statistics and Arrhenius Theory



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

The **fraction** of molecules that have kinetic energy **greater than** E_a

By **increasing** the temperature or **decreasing** the activation energy, the **rate of reaction increases.**

Calculation of Activation Energy (E_a)

Calculation of activation energy (E_a)

- Graphically
- By measuring rate constant (k) at two different temperatures

Graphically

Arrhenius equation

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

Taking natural logarithm on both sides

$$\ln k = \ln [A\,e^{-E_a/RT}]$$

$$\ln k = \ln A - \frac{E_a}{RT} \quad ....(1)$$

Plotting ln k versus (1/T), can give a straight line

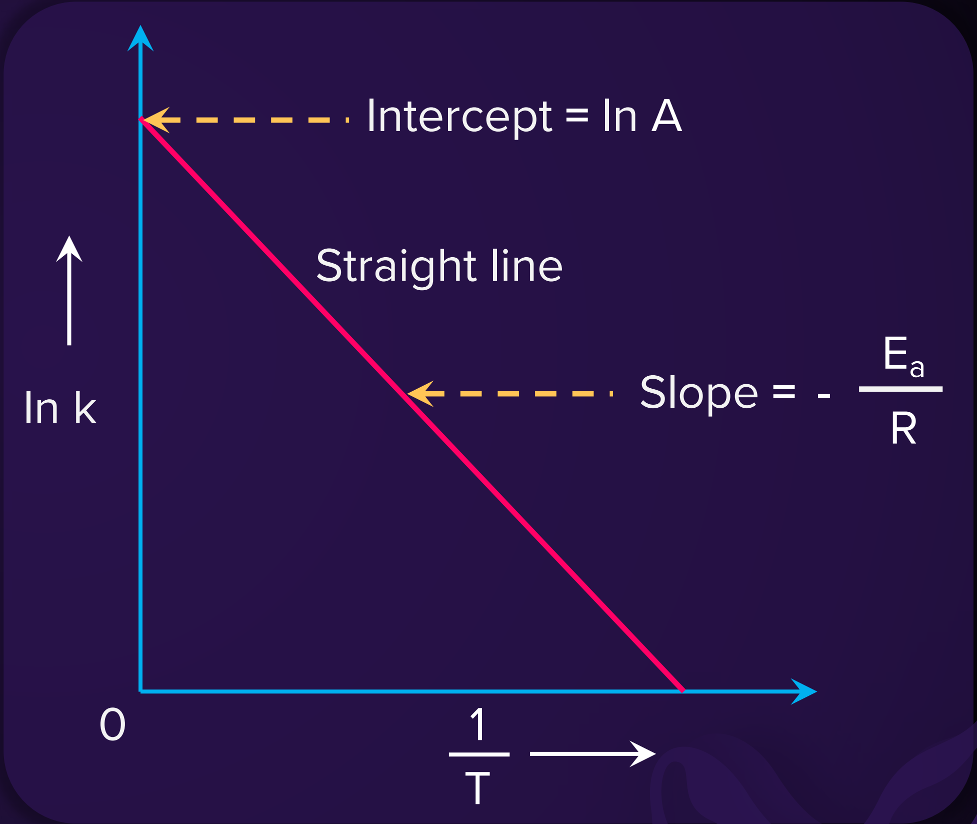
$$\ln k = \ln A - \frac{E_a}{R} \times \frac{1}{T}$$

Plot of ln k vs 1/T

$$\ln k = \ln A - \frac{E_a}{R} \times \frac{1}{T} \quad ...(1)$$

Slope $= -\frac{E_a}{R}$

From the graph → E_a can be calculated



Rate Constant at Different Temperatures

At temperature T_1, Arrhenius equation:

$$\ln k_1 = \ln A - \frac{E_a}{RT_1} \quad \text{...(1)}$$

k_1: Rate constant at temperature T_1

At temperature T_2, Arrhenius equation:

$$\ln k_2 = \ln A - \frac{E_a}{RT_2} \quad \text{...(2)}$$

k_2: Rate constant at temperature T_2

Rate Constant at Different Temperatures

$$\ln k_1 = \ln A - \frac{E_a}{RT_1} \quad \dots (1)$$

$$\ln k_2 = \ln A - \frac{E_a}{RT_2} \quad \dots (2)$$

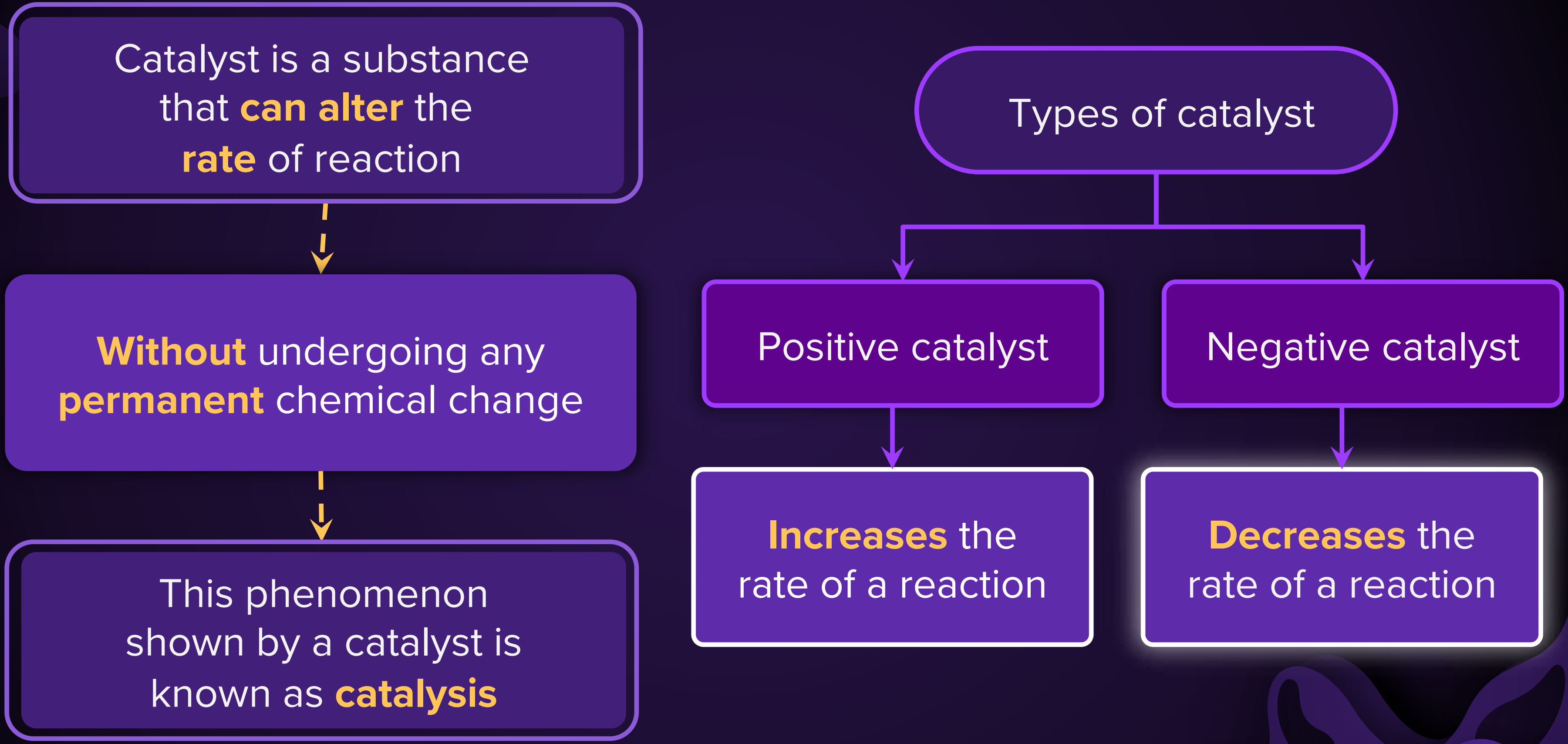
Subtracting eq (1) from eq (2)

$$\ln k_2 - \ln k_1 = \frac{E_a}{RT_1} - \frac{E_a}{RT_2}$$

$$\ln \frac{k_2}{k_1} = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \quad \dots (3)$$

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \quad \dots (4)$$

Catalyst



Catalyst is a substance that **can alter** the **rate** of reaction

Without undergoing any **permanent** chemical change

This phenomenon shown by a catalyst is known as **catalysis**

Types of catalyst

Positive catalyst

Increases the rate of a reaction

Negative catalyst

Decreases the rate of a reaction

Catalysis

Generally, by the term “**catalysed reaction**”

The presence of a **positive** catalyst is assumed

Example

Thermal decomposition of H_2O_2 is **accelerated**

By the presence of MnO_2

$$2H_2O_2 + MnO_2 \longrightarrow 2H_2O + O_2\uparrow + MnO_2$$

General Characteristics of Catalyst

1 A catalyst **does not initiate** any reaction; it simply **speeds up** the reaction.

2 Only a **small amount** of catalyst can catalyse a large amount of reactants.

3 A catalyst does **not alter** the position of **equilibrium**

It only **reduces the time** taken to reach the equilibrium

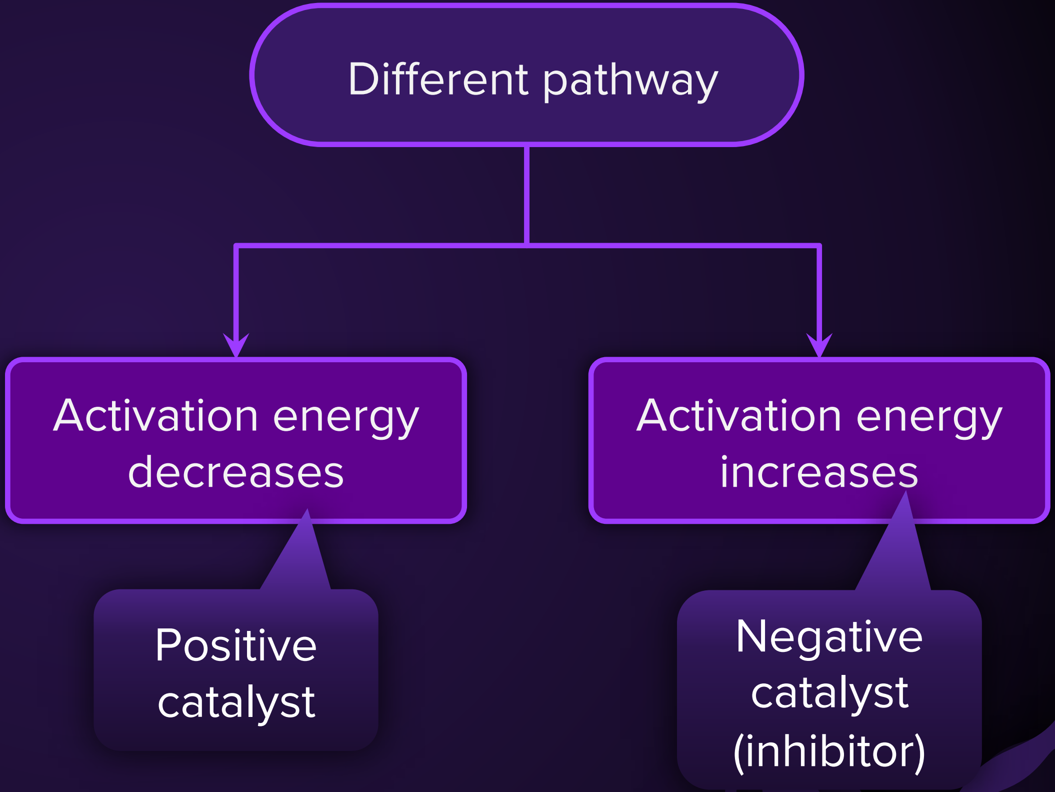
4 It does **not alter** the Gibbs energy (**ΔG**) of a reaction

Catalyses **spontaneous** reactions but **not non-spontaneous** reactions

Function of Catalysts

A catalyst provides an **alternate** pathway or reaction mechanism

By **reducing** the activation energy between reactants and products and hence, **lowering** the potential energy **barrier.**



Different pathway

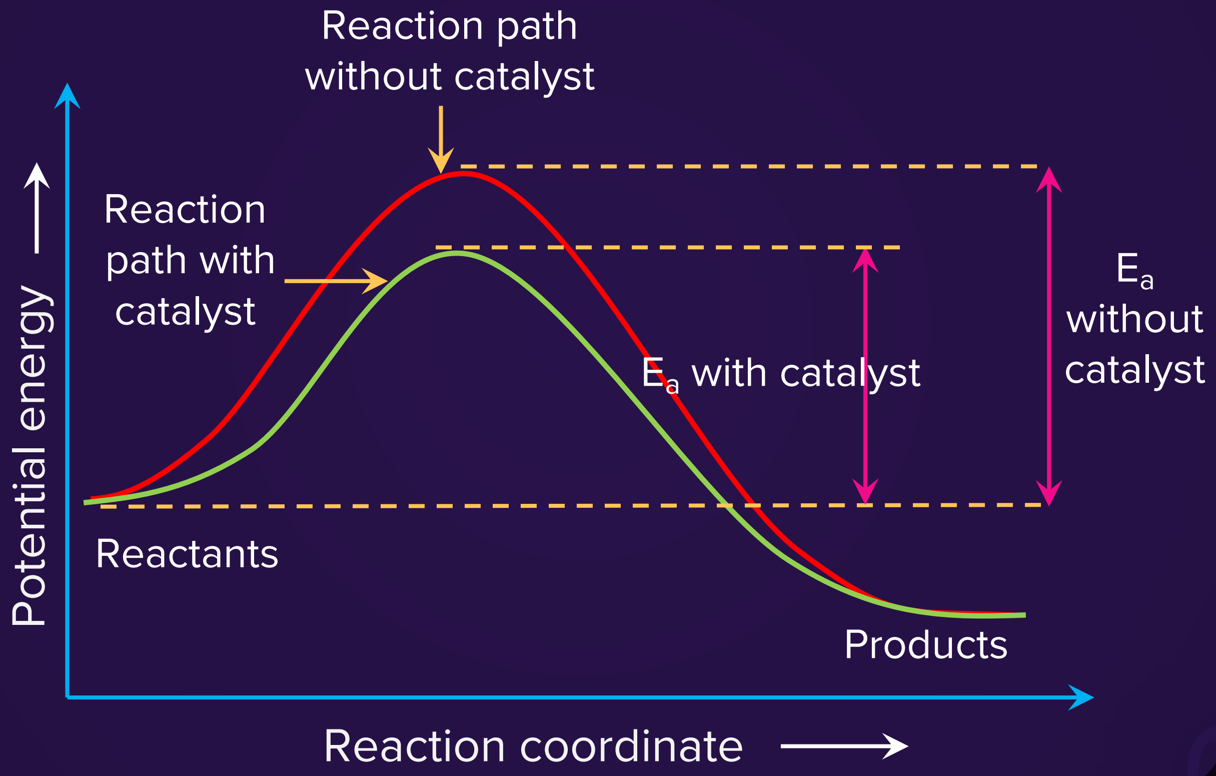
Activation energy decreases

Positive catalyst

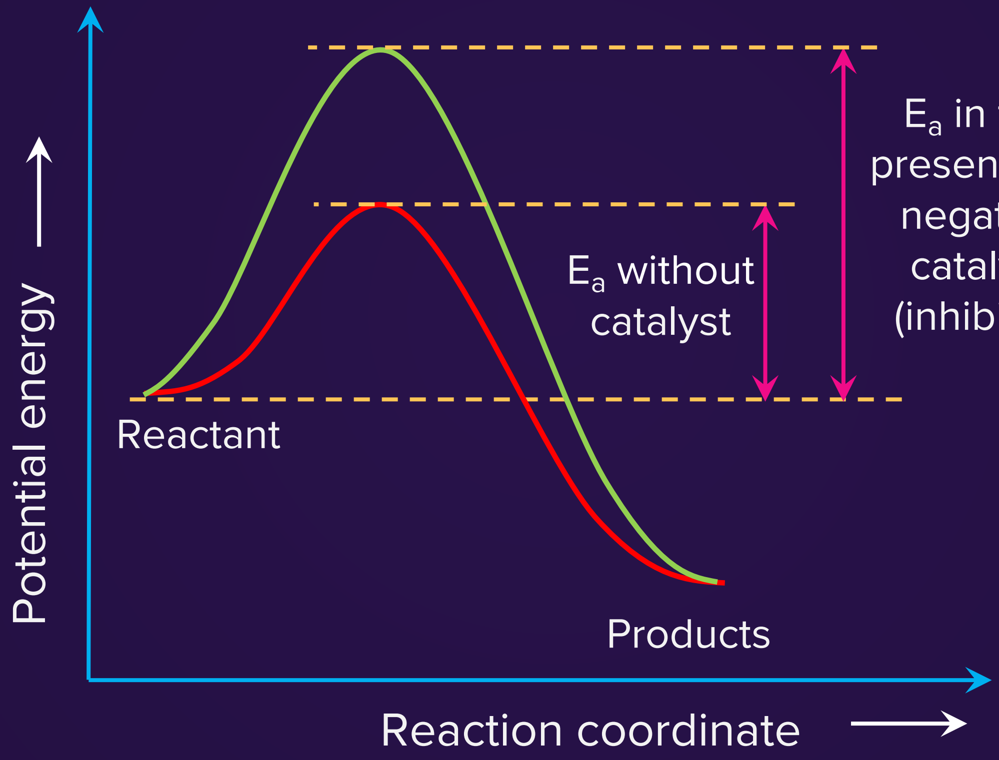
Activation energy increases

Negative catalyst (inhibitor)

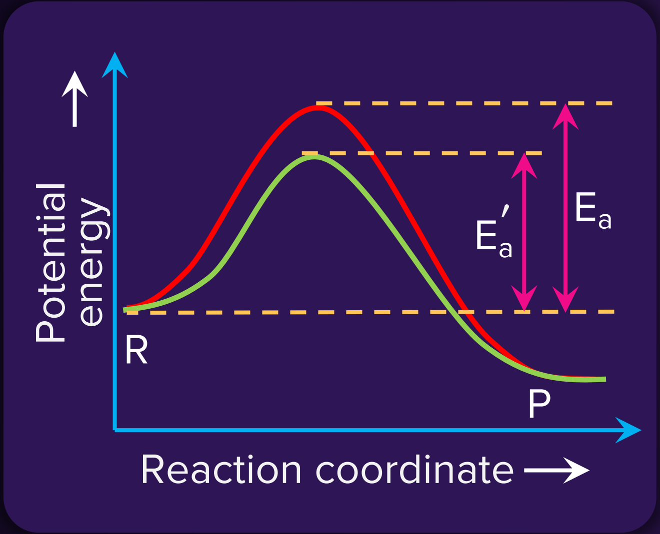
Positive Catalyst



Negative Catalyst



Arrhenius Equation (With and Without Catalyst)



Without catalyst

$$k = Ae^{-E_a/RT} \quad \dots (1)$$

With catalyst

$$k_{cat} = Ae^{-E_a'/RT} \quad \dots (2)$$

k: Rate constant without catalyst

k_{cat}: Rate constant with catalyst

E_a: Activation energy without catalyst

E_a': Activation energy with catalyst

Arrhenius Equation (With and Without Catalyst)

$$k = Ae^{-E_a/RT} \quad \text{... (1)}$$

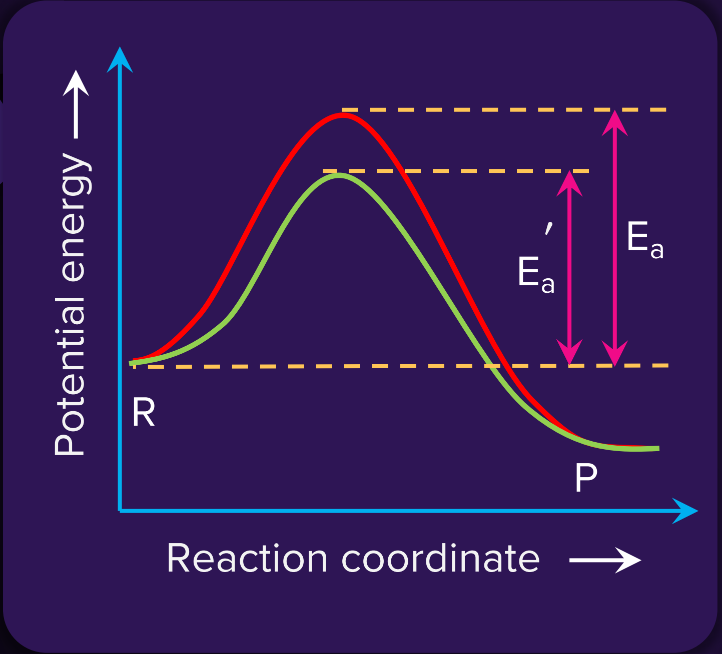
$$k_{cat} = Ae^{-E_a'/RT} \quad \text{... (2)}$$

Comparing eq. (1) and eq. (2)

$$\frac{k_{cat}}{k} = \frac{e^{-E_a'/RT}}{e^{-E_a/RT}}$$

$$\frac{k_{cat}}{k} = e^{(E_a - E_a')/RT}$$

Arrhenius Equation (With and Without Catalyst)



We know,

$E_a > E_a'$

$$\frac{k_{cat}}{k} = e^{(E_a - E_a')/RT} > 1$$

$k_{cat} > k$

Rate of catalysed reaction > Rate of uncatalysed reaction

Arrhenius Equation Variation With E_a and Temperature

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

Rate of a catalysed and an uncatalysed reaction can be **equal** if

The **temperature** of the uncatalysed reaction is **more** than the catalysed reaction

Arrhenius Equation Variation With E_a and Temperature

$$k = Ae^{-E_a/RT_1} \quad \text{... (1)}$$

$$k_{cat} = Ae^{-E_a'/RT_2} \quad \text{... (2)}$$

Assuming the **rate of reaction** of catalysed and the uncatalysed reactions are **equal**

$$e^{-E_a/RT_1} = e^{-E_a'/RT_2} \quad \text{... (3)}$$

T_1 : Temperature at which uncatalysed reaction occurs

T_2 : Temperature at which catalysed reaction occur

Arrhenius Equation Variation With E_a and Temperature

$$e^{-E_a/RT_1} = e^{-E_a'/RT_2} \quad \text{... (3)}$$

From eq. (3),

$$\frac{E_a}{T_1} = \frac{E_a'}{T_2}$$

$$E_a > E_a'$$

We get,

$$T_1 > T_2$$

Though **Arrhenius** equation is applicable under a wide range of circumstances

A more **advanced** theory was developed

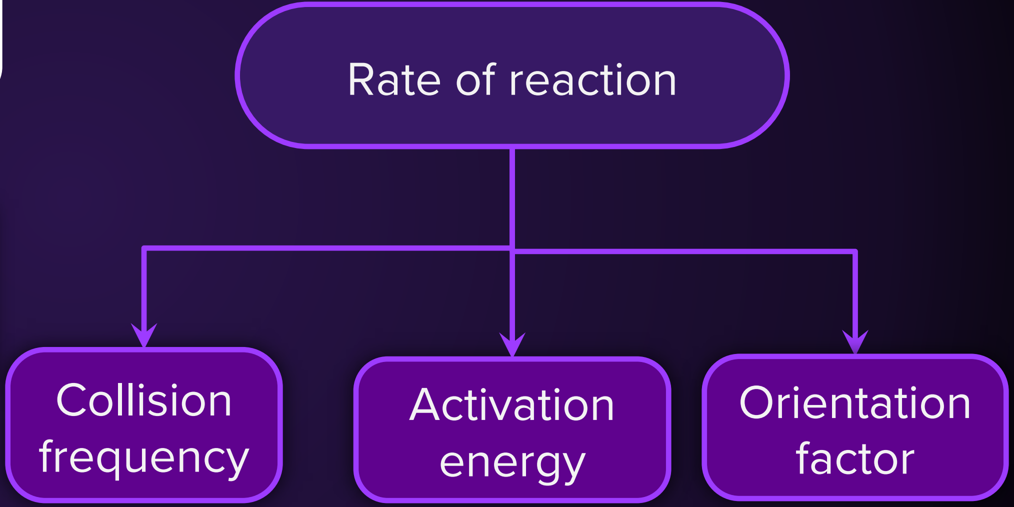
With greater **insights** into the **energetic** and **mechanistic** aspects of reactions

Collision Theory

The reactant molecules are assumed to be **hard spheres**

A reaction **occurs** when molecules, having **sufficient** energy, **collide** with each other

It is based on the **kinetic theory** of gases



Rate of reaction

Collision frequency

Activation energy

Orientation factor

Collision Frequency

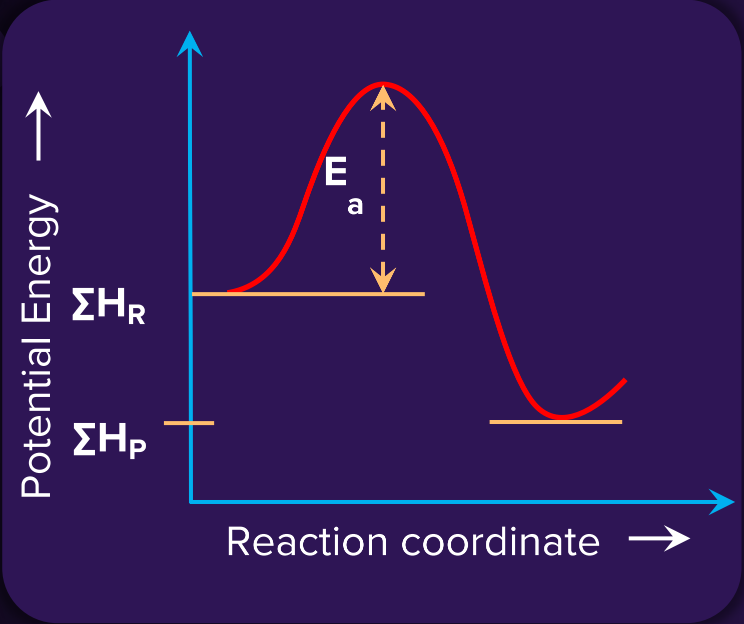
The number of **collisions** per **second** per unit **volume** of the reaction mixture is

Known as **collision frequency (Z)**

Collision frequency can be **increased** by increasing the **concentration** and **temperature**

Both factors contribute towards **more** number of **collisions** per unit time per unit volume

Activation Energy



Not all collisions result in **product** formation

A few reactant molecules acquire **activation** energy

Activation energy is **inversely** related to the **rate** of a reaction

Collision Theory

For a **bimolecular elementary** reaction

$$A + B \longrightarrow \text{Products}$$

$$\text{Rate} = Z_{AB}\, e^{-E_a/RT} \quad \dots (1)$$

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

Collision Theory

$$\text{Rate} = Z_{AB}\, e^{-E_a/RT} \quad \dots (1)$$

Rate expression predicts the value of **rate constant** fairly accurately for **simple** atoms/molecules

For **complex** molecules, significant **deviations** are observed

Not all collisions lead to product formation i.e., only few collisions are **effective**.

Collision Theory

The **collisions** in which molecules collide with sufficient threshold **energy** and proper **orientation**

So as to facilitate the **breaking** of bonds between the reacting species and the **formation** of new bonds to form products

Effective Collision

How can we predict if the collisions are effective or not?

Conditions

- ☑ Sufficient kinetic energy
- ☐ Proper orientation

Sufficient Kinetic Energy

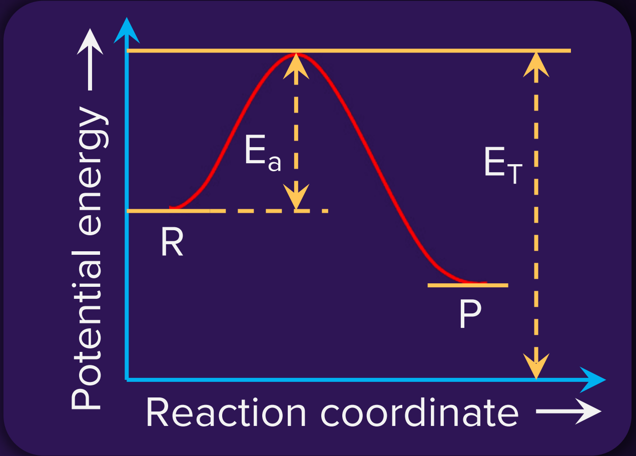
The **minimum** amount of energy

↓

The colliding **molecules** must **possess** to participate in a chemical reaction

↓

Threshold energy



So, if Energy of colliding molecule ≥ Threshold energy

Only the molecule that satisfies this condition **can** cross the energy **barrier.**

Proper Orientation

Conditions

- ☑ Sufficient kinetic energy
- ☑ Proper orientation

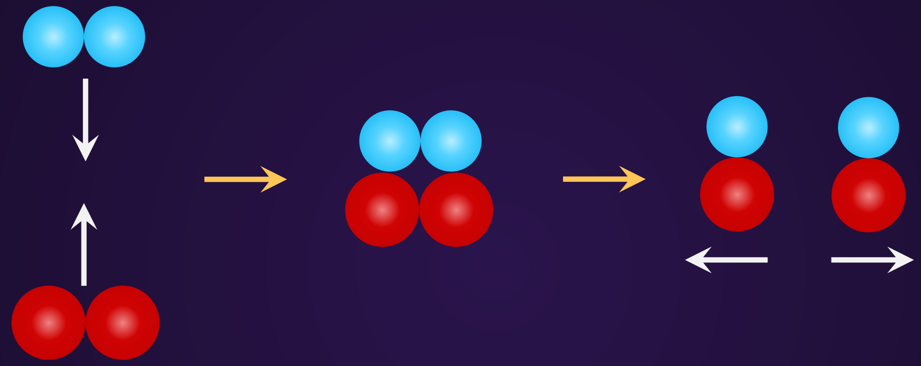
Energy alone does **not** determine the **effectiveness** of a collision

↓

The reacting molecules must **collide** in a proper **orientation** to make the collision **effective.**

Proper Orientation

Proper collision



Reactants

Transition state

Product

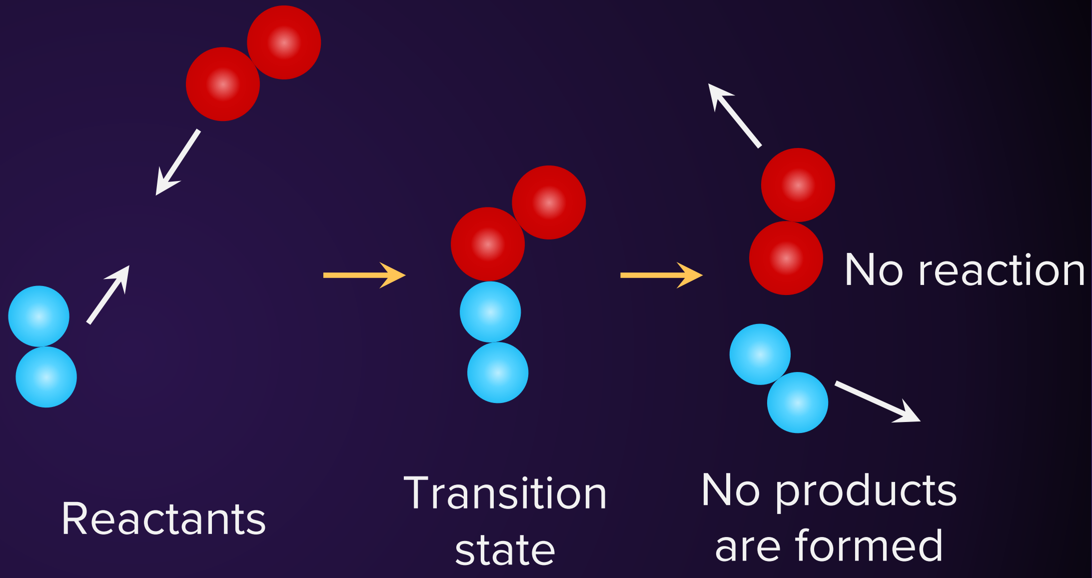
$A_2 + B_2 \rightarrow 2AB$

Proper Orientation

Improper collision

The **proper orientation** of the reactant molecules leads to **bond formation**

Whereas **improper orientation** makes them simply bounce back and **no products** are formed.



Effective Collision

To account for proper orientation

A factor "**P**" is introduced

Probability or steric factor

Final expression of rate becomes

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

Orientation factor

Radioactivity

Spontaneous disintegration of nuclei due to the emission of radiations like **α, β, γ** is called radioactivity.

Nuclei phenomenon

Radioactivity is **independent** of external conditions like temperature, pressure etc. and **physical state** of substance.

Properties of α, β and γ Radiations

Property	α-rays	β-rays	γ-rays
Nature	$_2He^4$ (nucleus of He atom)	$_{-1}e^0$	EM radiation
Velocity	Relatively low (depends on the source)	Greater than α - particles	Very high (3×10^8 m/sec)
Ionising power	Very high	Less than α - particles	Very low
Penetrating power	Low	Intermediate (much greater than α - particles)	Very high

Group Displacement Law

1

When one **α** emission takes place from a nuclei, the newly formed nuclei occupies **two** positions **left** in the periodic table.

2

When one **β** emission takes place from a nuclei, the newly formed nuclei occupies **one** position **right** in the periodic table.

Note

Exceptions are possible in the group displacement law

$${}_{92}U^{238} \longrightarrow {}_{90}Th^{234} + {}_{2}He^{4}$$

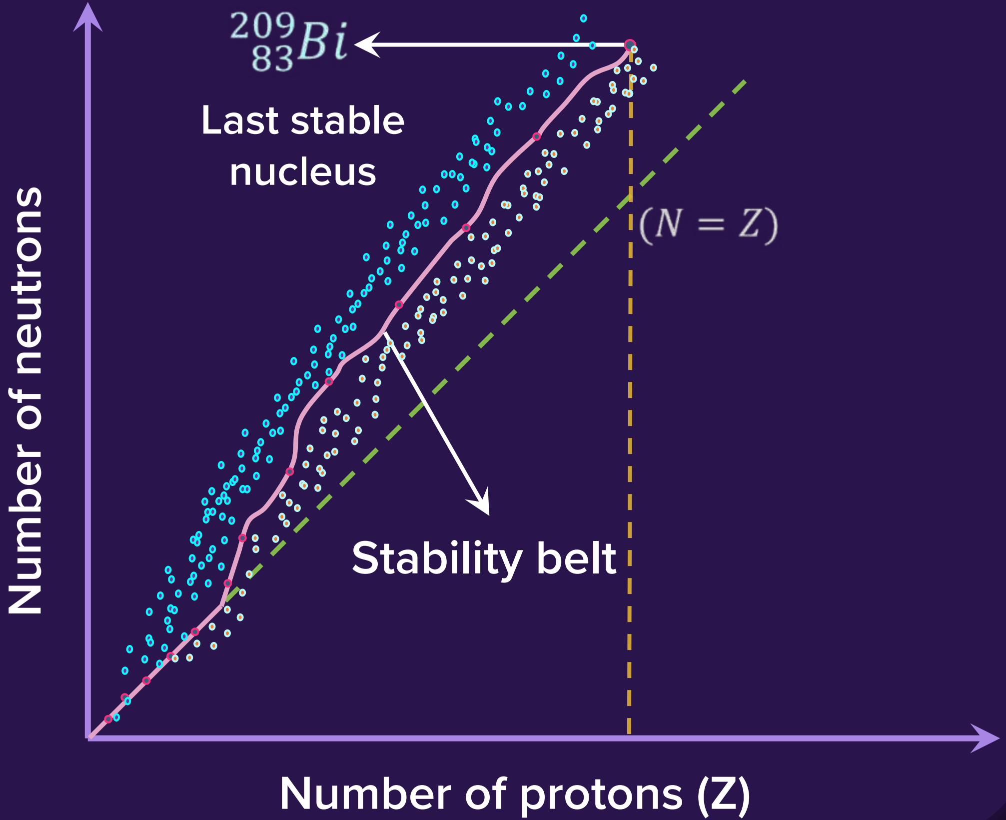
f-Block element (Group-3)

f-Block element (Group-3)

Nuclear Stability

High stability of most nuclei of stable elements is due to the **very strong nuclear forces** that operate within the nucleus (or at nuclear distance, of the order of 10^{-15} m or fm)

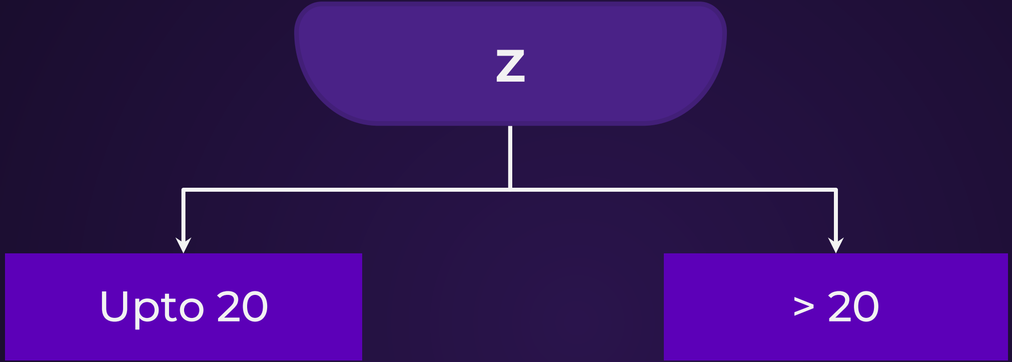
Nuclear Stability



Nuclear Stability

Isotopes which lie in **band of stability** (stability belt) are found to be stable (non-radioactive).

Nuclear Stability



Z

Upto 20

> 20

Stable nuclei with n/p ratio nearly 1 : 1

n/p ratio increases with Z in stable nuclei region

More number of neutrons are required to reduce repulsion between protons.

Nuclear Stability

For heavier isotopes, **n/p ratio** for stable isotopes may be as high as nearly **1.5**.

Unstable isotopes will try to be in the band of stability after **adjustment** of their **n/p ratio**.

Nuclear Stability

Case 1

If **n/p ratio** is high

If n/p ratio is **high**

Stability will be gained by **losing β-particle**.

$$_0n^1 \longrightarrow {}_1H^1 + {}_{-1}e^0$$

(β-particle)

Example

${}_{6}C^{12}$ (stable) $\frac{n}{p} = \frac{6}{6}$

${}_{6}C^{14}$ (radioactive) $\frac{n}{p} = \frac{8}{6}$ (High)

Example

$${}_{6}C^{14} \longrightarrow {}_{7}N^{14} + {}_{-1}e^{0}$$

${}_{6}C^{14}$ $\quad \frac{n}{p} = \frac{8}{6}$

${}_{7}N^{14}$ $\quad \frac{n}{p} = \frac{7}{7}$

Nuclear Stability

Case 2

If **n/p ratio** is low

If n/p ratio is **low,** it is adjusted by

- 01 α-Particle Emission
- 02 Emission of Positron
- 03 K-shell Electron Capture

Nuclear Stability

1 By α-particle emission

Generally observed in heavier isotopes

$$_{Z}X^{A} \longrightarrow {}_{Z-2}X'^{A-4} + {}_{2}He^{4}$$

$$_{92}U^{238} \longrightarrow {}_{90}Th^{234} + {}_{2}He^{4}$$

Nuclear Stability

2 By emission of **positron**

Generally observed in lighter isotopes

$_{Z}Y^{A} \longrightarrow {}_{Z-1}Y'^{A} + {}_{1}e^{0}$

$_{11}Na^{22} \longrightarrow {}_{10}Ne^{22} + {}_{1}e^{0}$

$_{1}p^{1} \longrightarrow {}_{0}n^{1} + {}_{1}e^{0}$ (From nucleus)

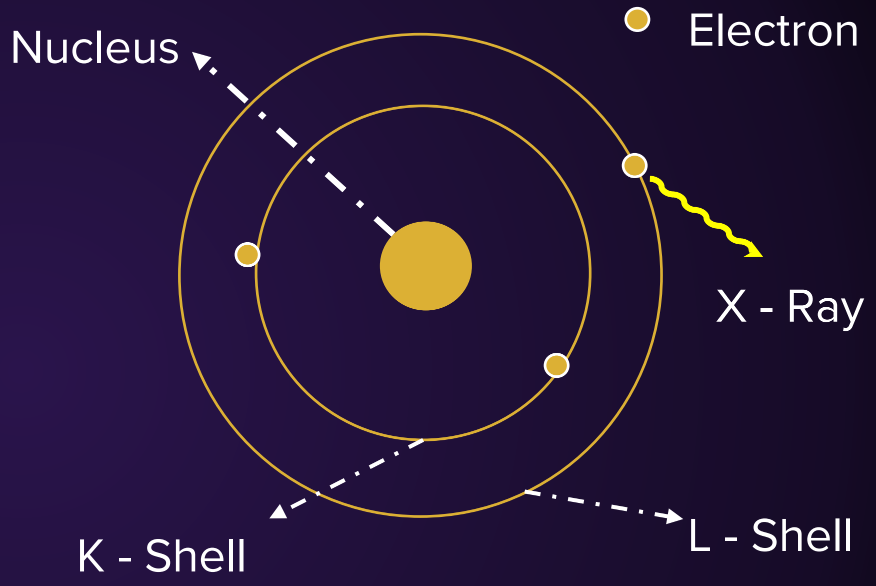
Nuclear Stability

3

By K-shell electron capture

In some radioisotopes stability (usually for elements with high Z) is gained by K-shell electron capture by the nucleus.

$${}_{80}Hg^{197} + {}_{-1}e^{0} \longrightarrow {}_{79}Au^{197}$$



$${}_{Z}X'^{A} + {}_{-1}e^{0} \longrightarrow {}_{Z-1}X''^{A}$$

K-shell

Mass Defect and Binding Energy

It is experimentally found that atoms of every element is **slightly lighter in mass** than the sum of masses of its constituent particles.

When protons and neutrons combine to form nucleus, there is a mass loss called **mass defect**.
An equivalent amount of energy is released which is called **binding energy.**

Oxygen atom → 8p, 8n, $8e^-$

Observed mass of O^{16} atom ≈ 15.99 amu

Mass sum of 8p, 8n, $8e^-$ ≈ 16.13 amu

Mass Defect and Binding Energy

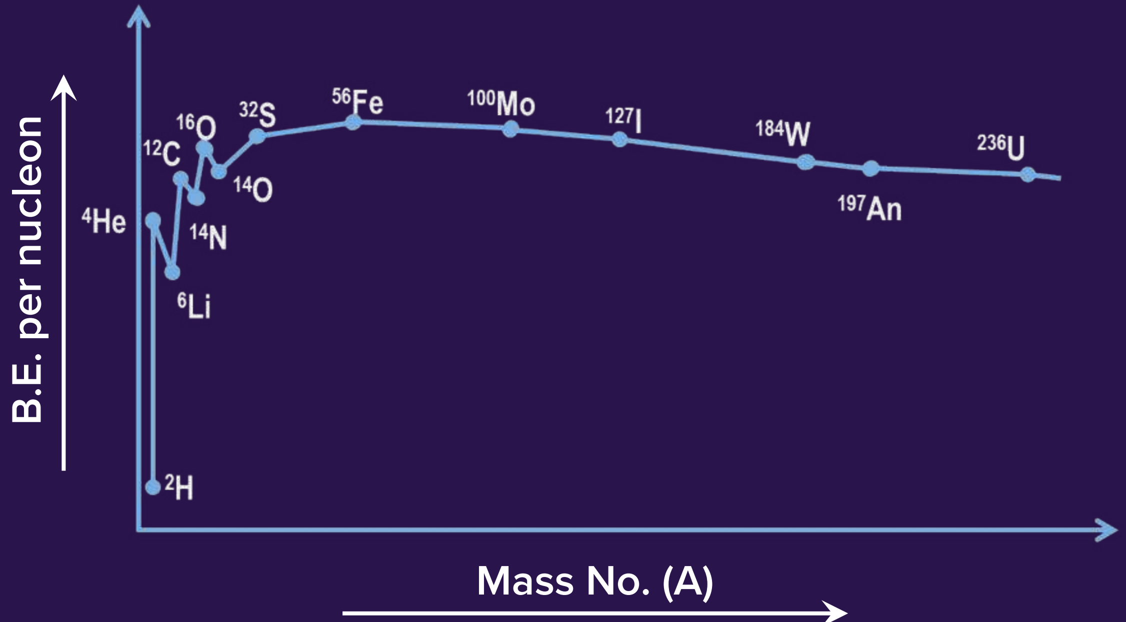
$$E = \Delta m \times c^2$$

Where,
E is binding energy
Δm is mass defect
c is velocity of light ($c = 3 \times 10^8\ ms^{-1}$)

1 amu = 931.5 MeV

Higher the **binding energy** per nucleon, **greater** will be the **stability** of nucleus.

Mass Defect and Binding Energy



Binding Energy (B.E.)

B.E. per nucleon is found to be **maximum** for mass number **near 60**.

Lighter nuclei may undergo **fusion** while **heavier nuclei** may undergo **fission** to get into stability zone under appropriate conditions.

Types of Nuclear Reactions

Nuclear reaction

01 Nuclear fission

02 Nuclear fusion

Nuclear Fission

The heavier nuclei being unstable have tendency to **split** into medium nuclei.

This process is called **fission.**

Example

$$ {}_{92}U^{235} + {}_{0}n^{1} \longrightarrow {}_{92}U^{*236} \longrightarrow \text{Various nuclei and neutron} $$

Nuclear Fusion

The **lighter nuclei** being unstable have tendency to **fuse** into a medium nucleus.

This process is called **fusion**.

Example

$${}_1H^2 + {}_1H^3 \longrightarrow {}_2He^4 + {}_0n^1$$

Hydrogen bomb is based on fusion.

Very high temperature is required

Rate of Radioactive Decay

All radioactive disintegrations follow **1st order** kinetics.

$$A \longrightarrow B + C$$

$$-\frac{dN}{dt} = \lambda N$$

Where, initial nuclei of A is N_0

and at time t, remaining nuclei of A is N

$\frac{-dN}{dt}$ is rate of decay/ Activity (A)

λ is decay constant

Units Of Activity

Curie (Ci) = 3.7×10^{10} dps

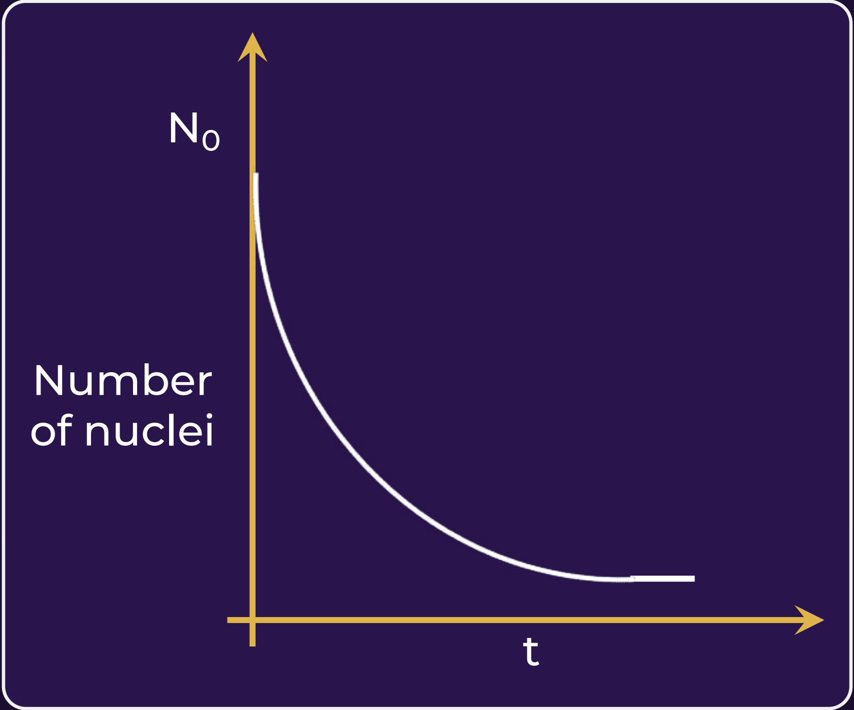
Millicurie (mCi) = 3.7×10^{7} dps

Microcurie (μCi) = 3.7×10^{4} dps

Rutherford (1 Rd) = 1×10^{6} dps

Where dps = disintegration per second

Rate of Radioactive Decay



Rate of Radioactive Decay

λ is independent of temperature

$$\frac{-dN}{N} = \lambda dt$$

$$\int \frac{-dN}{N} = \int \lambda dt$$

$$N = N_0 e^{-\lambda t}$$

$$N = N_0 e^{-\lambda t}$$

$$\lambda = \frac{1}{t} \ln\left(\frac{N_0}{N}\right)$$

Half Life of Radioactive Decay

$t = t_{1/2};\ N = N_0/2$

$$\lambda = \frac{1}{t_{1/2}} \ln\left(\frac{N_0}{N_0/2}\right) = \frac{\ln 2}{t_{1/2}}$$

$$t_{1/2} = \frac{\ln 2}{\lambda} = \frac{0.693}{\lambda}$$

Average Life of Radioactive Decay

$$t_{avg} = \frac{\int_0^\infty dN.t}{N_0} = \frac{1}{\lambda}$$

$$t_{avg} = \frac{1}{\lambda} = 1.44\ t_{1/2}$$

Carbon Dating

C^{14} is used to determine age of organic materials like **animal fossil** or **wooden logs**.

In living matter existing in nature

Radioactive

Stable

$_6C^{14}$: $_6C^{12}$

1 : 10^{12}

In upper atmosphere

$$_7N^{14} + {}_0n^1 \longrightarrow {}_6C^{14} + {}_1p^1$$

Carbon Dating

Ratio of radioactive carbon in dead animals or trees **decreases** with respect to time.

$$t = \frac{1}{\lambda} \ln\left(\frac{A_0}{A}\right)$$

A_0 = Activity of fresh wood piece
A = Activity of old wood piece