

Welcome to



Aakash



BYJU'S LIVE

Chemical Kinetics

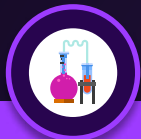
$$\ln \frac{[A]_t}{[A]_0} = -kt$$



$$k = Ae^{-\frac{E_a}{RT}}$$

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





Chemistry is always concerned with **change**.

By means of a chemical reaction

Feasibility of a reaction

Extent of a chemical reaction

Speed of a chemical reaction

Chemical Equilibrium

Thermodynamics

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**

Example:
Burning of
LPG fuel





Rate of a Chemical Reaction



Some reactions are **very slow**

Example:
Rusting of
iron



Rate of a Chemical Reaction



Rate can be expressed as

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**

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,

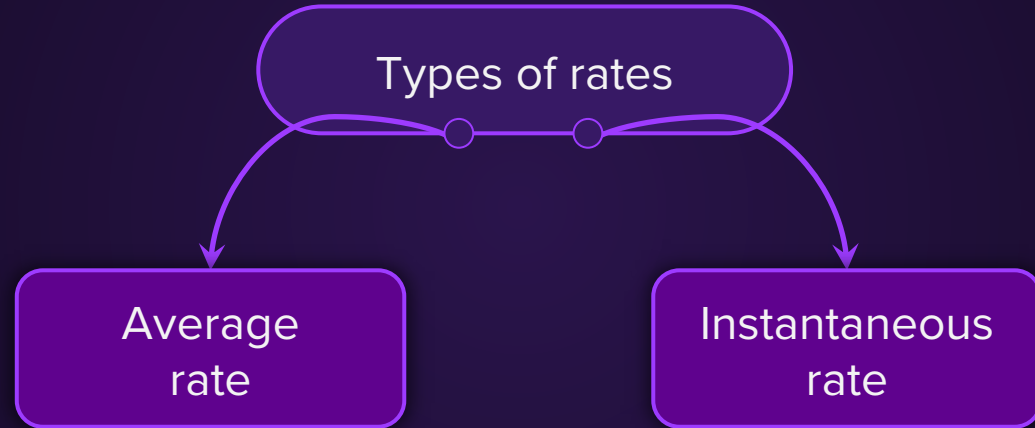
Concentration

\propto

Partial pressure
of species

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

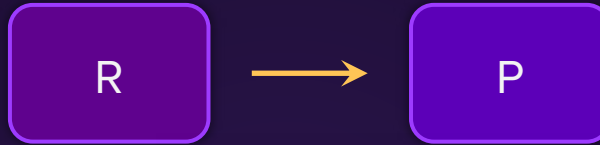
Types of Rate



Average Rate of Reaction



For the reaction,

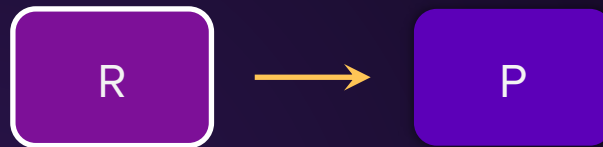


$$\boxed{\text{Average rate}} = \frac{\text{Total change in concentration}}{\text{Total time taken}}$$

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

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

Average Rate of Reaction



Rate of disappearance of reactant (R)

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

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

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

Average
rate

=

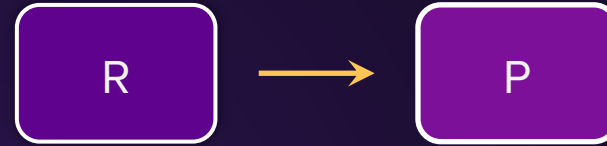
Decrease in concentration of R
Time taken

Average
rate

=

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

Average Rate of Reaction



Rate of appearance of product (P)

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

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

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

Average
rate

=

Increase in concentration of P
Time taken

Average
rate

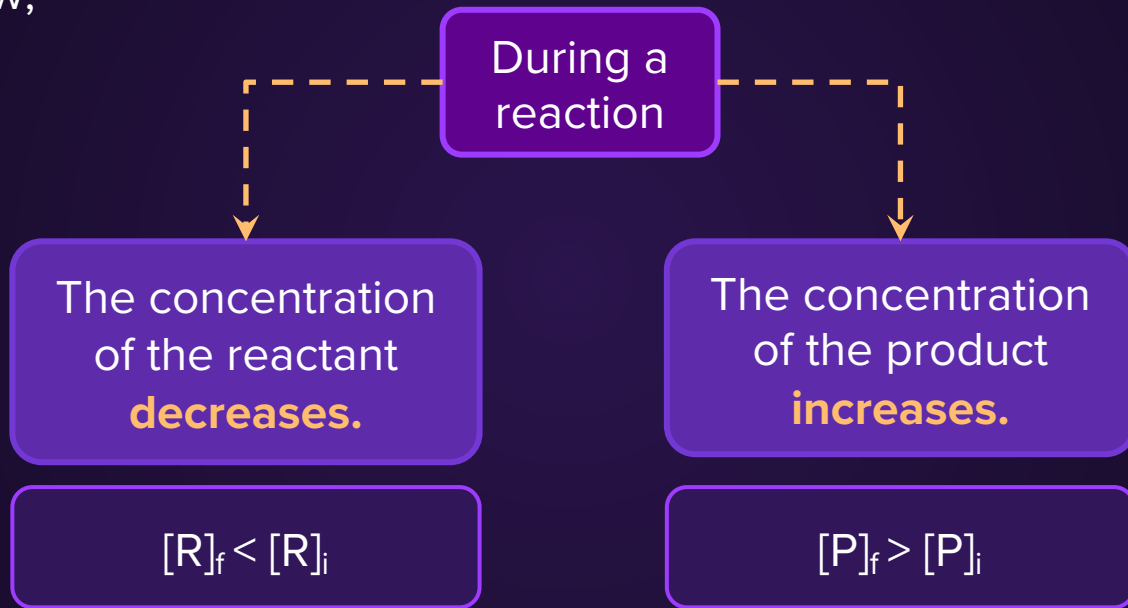
=

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

Average Rate of Reaction



As we know,



Average Rate of Reaction



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



It is always a **positive quantity**

For reactant R,

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,

Average
rate

=

$$\frac{[P]_{\text{final}} - [P]_{\text{initial}}}{t_{\text{final}} - t_{\text{initial}}}$$

=

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

Average Rate of Reaction



1 mol of R



1 mol of P

Rate of
disappearance of R

=

Rate of
appearance of P

Average rate of
reaction, r_{avg}

=

$$-\frac{\Delta[\text{R}]}{\Delta t}$$

=

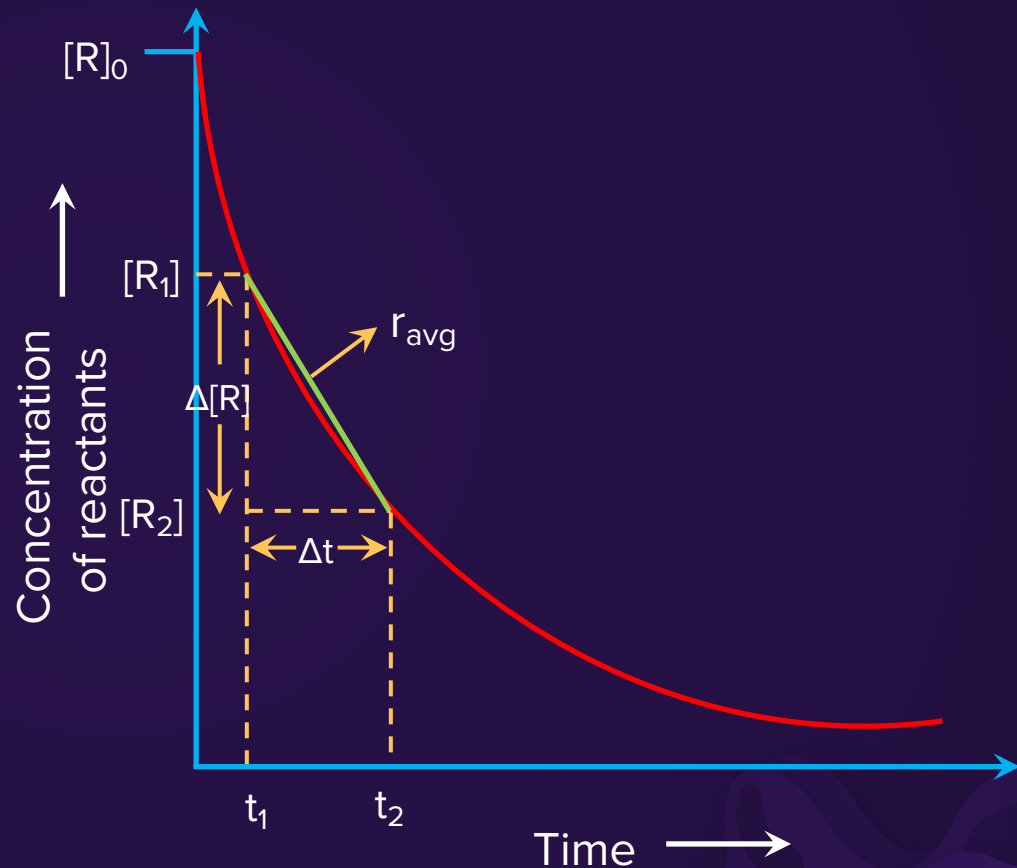
$$+\frac{\Delta[\text{P}]}{\Delta t}$$

Average Rate of Reaction (Graph)



Concentration of R vs time

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

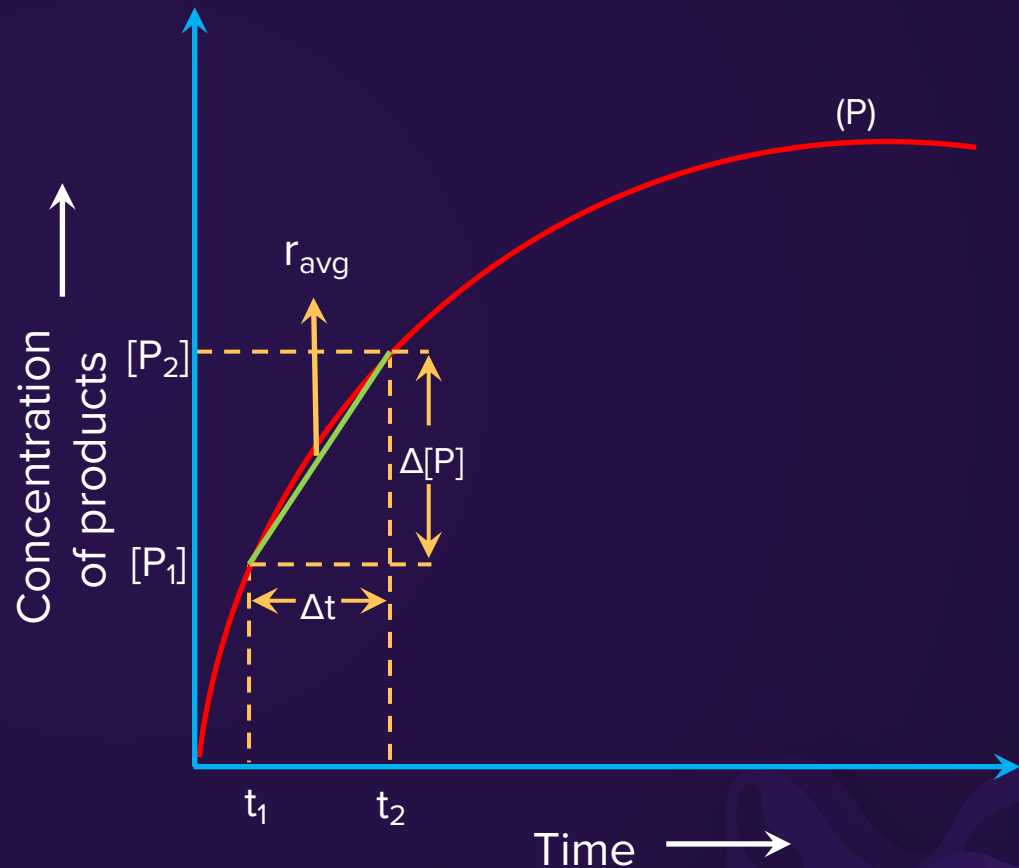


Average Rate of Reaction (Graph)



Concentration of P vs time

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



Instantaneous Rate of Reaction



Rate of reaction
at a **particular
instant**



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

Instantaneous rate of
disappearance of R

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

Instantaneous rate of
appearance of P

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

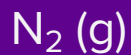


Relation Between Rates of Different Species Involved in a Reaction

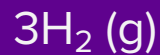
Rate of Reaction



Example



+



These all are correct rate expressions.

However, they are **not equal**

Rate of reaction
w.r.t. N_2

=

$$-\frac{d[\text{N}_2]}{dt}$$

Rate of reaction
w.r.t. H_2

=

$$-\frac{d[\text{H}_2]}{dt}$$

Rate of reaction
w.r.t. NH_3

=

$$+\frac{d[\text{NH}_3]}{dt}$$

Rate of Reaction



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

Rate of
consumption of N_2

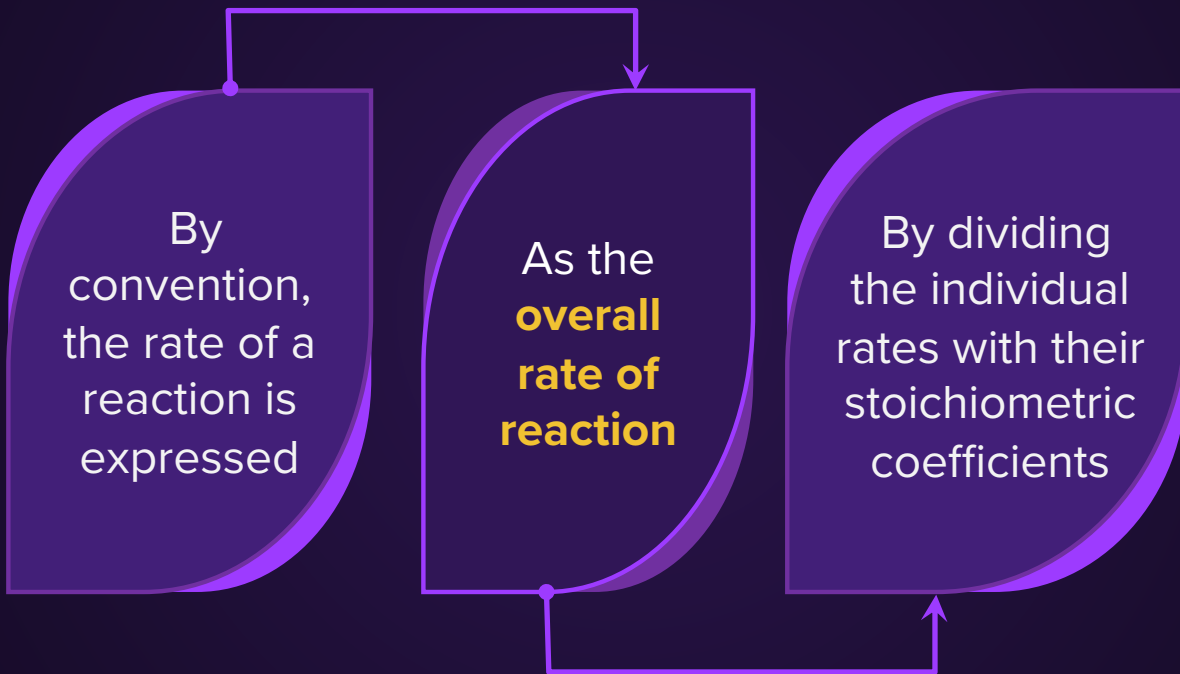
=

$$\frac{1}{3} \left[\text{Rate of consumption of } \text{H}_2 \right]$$

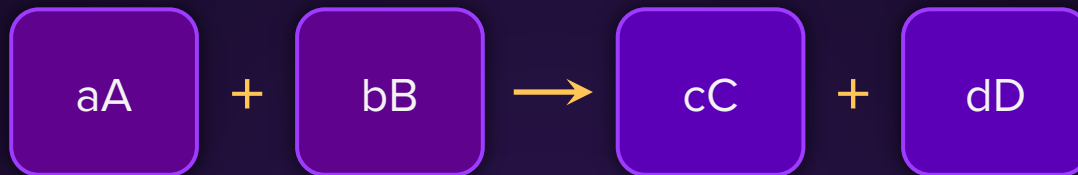
=

$$\frac{1}{2} \left[\text{Rate of formation of } \text{NH}_3 \right]$$

Rate of a Chemical Reaction



Rate of a Chemical Reaction



Average rate
of reaction,
 r_{avg}

$$= -\frac{1}{a} \frac{\Delta[A]}{\Delta t} = -\frac{1}{b} \frac{\Delta[B]}{\Delta t}$$

Instantaneous
rate of
reaction, r_{inst}

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

$$= +\frac{1}{c} \frac{\Delta[C]}{\Delta t} = +\frac{1}{d} \frac{\Delta[D]}{\Delta t}$$

$$= +\frac{1}{c} \frac{d[C]}{dt} = +\frac{1}{d} \frac{d[D]}{dt}$$

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,

$$1 \text{ L} = 1 \text{ dm}^3 = 10^{-3} \text{ m}^3 = 10^3 \text{ cm}^3$$

Rate

=

$$\frac{\Delta C}{\Delta t}$$

Where,

ΔC : Change in concentration
of any species

Δt : Time change corresponding
to the concentration change

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

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

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

3

Effect of Pressure

Effect of temperature

4

5

Effect of catalyst

2

Effect of nature of reactant and product

Effect of Concentration



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

From law of mass action, we know

Rate of
reaction

\propto

Concentration
of reactants

Generally, rate of reaction decreases with passage of time,



Due to decrease in
concentration of reactants

Rate Law or Rate Expression



Instantaneous
rate

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

For these reactions,

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.

Rate

\propto

(concentration)^{order}

Rate

=

k (concentration)^{order}

Rate Law or Rate Expression



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



$$\text{Rate of reaction} = k [A]^x [B]^y \quad \dots(1)$$

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.

Reactant



Product

It may differ for the same reaction under different conditions.

Rate

=

k [Reactant]^{order}



Note!



For **homogeneous gas phase reactions**, it is often more convenient to express the **rate law** in terms of **partial pressure**, which is related to molar concentration as:

$$p_J$$
$$=$$
$$RT[J]$$

Rate Constant



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

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

k

$=$

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

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

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

Unit of rate

$$(\text{Concentration})^1 \text{ time}^{-1}$$

Unit of k

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

Order of a Reaction



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



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

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!



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



'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



The order of a reaction can be **zero** or any **whole number**.



It can be a **fractional number**.



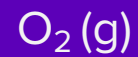
It can even be negative with respect to a particular reactant.

Overall order can never be negative.

Order of a Reaction



Example:



Rate law

=

$$k [\text{N}_2\text{O}_5]^1$$

Overall
order

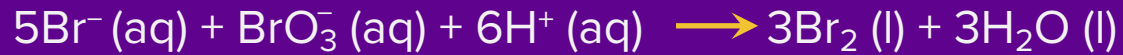
=

1

Order of a Reaction



Example:



Rate law

=

$$k [\text{Br}^{-}] [\text{BrO}_3^{-}] [\text{H}^{+}]^2$$

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**.

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

For an **elementary reaction**,

The sum of
stoichiometric
coefficients

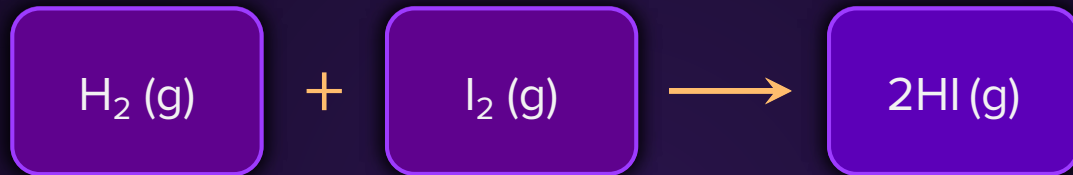
=

Order of the
reaction

Remember!



For the elementary reaction,



$$\text{Rate} = k [\text{H}_2] [\text{I}_2]$$

$$\text{Overall order} = 2$$

Remember!



For a **complex reaction**,

The reaction involves more than one step.

The order is experimentally calculated.

For example:



Steps involved:



Step 1



Step 2



Step 3

Rate

=

$$k [\text{NO}]^2 [\text{H}_2]$$

Methods to Analyse Rate of a Reaction



1

Initial rate method

Integrated rate
law method

2

3

Graphical method

Unit method

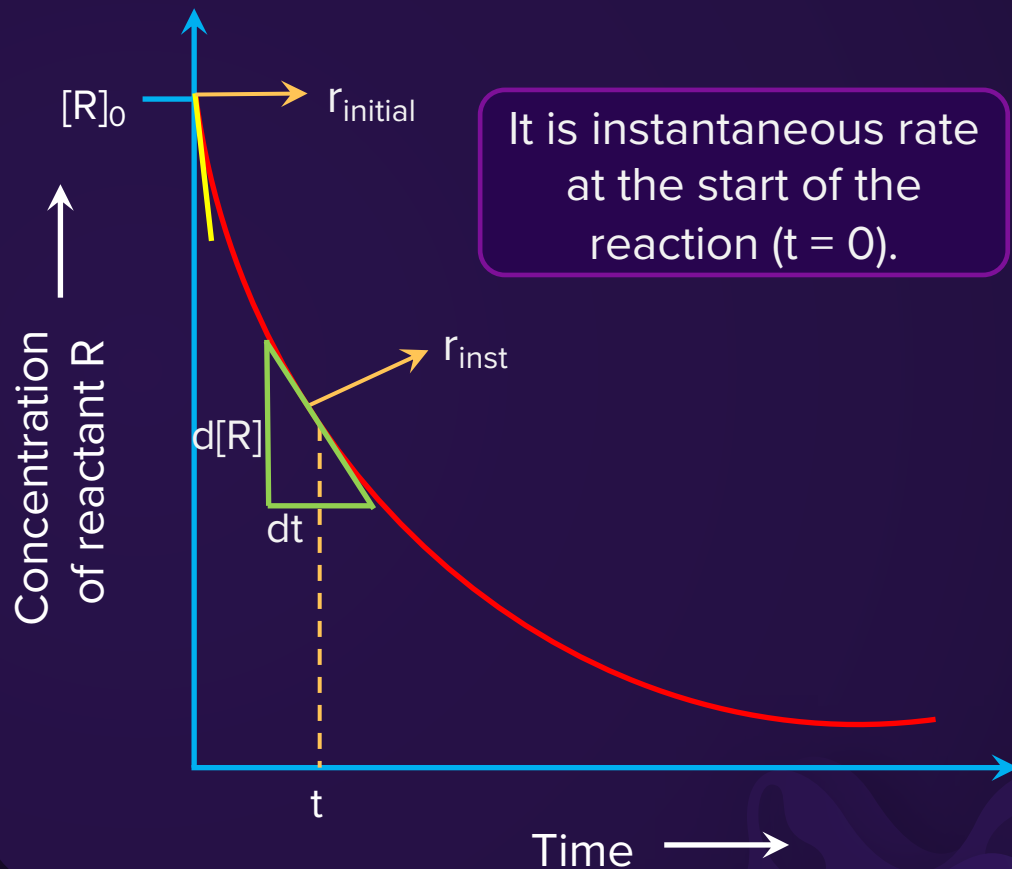
4

Initial Rate Method



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

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



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**



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 **dependency** of the **rate** of the reaction 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

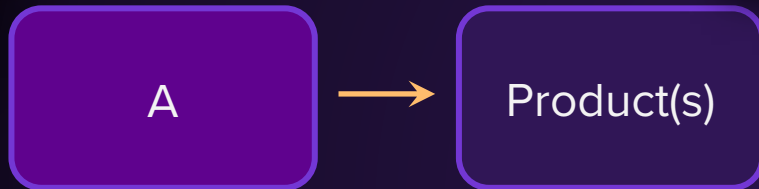
First-order
reaction

Zero-Order Reaction



For a general reaction

For a zero-order
reaction



Where,

n : Order = 0
 k : Rate constant
 $[A]$: Concentration of reactant A

According to the rate law,

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

$$\boxed{\text{Rate}} = \boxed{k}$$

Plot of Rate vs Time



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

For a zero-order reaction

Rate

=

$$k[A]^n$$

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

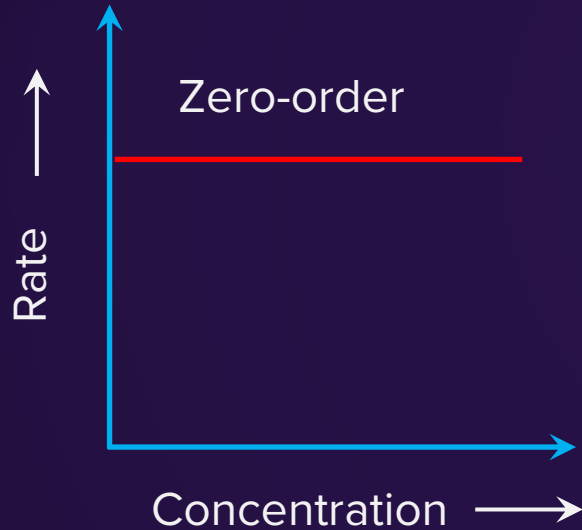
=

$$k[A]^0$$

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

=

k



Zero-Order Reaction



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

$$-d[A]$$

=

$$k dt$$

When
time = 0

Concentration
of A

=

$$[A]_0$$

Initial
concentration

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

$$-\int_{[A]_0}^{[A]_t} d[A]$$

=

$$k \int_0^t dt$$

When
time = t

Concentration
of A

=

$$[A]_t$$

Zero-Order Reaction



$$-\int_{[A]_0}^{[A]_t} d[A] = k \int_0^t dt$$

**Integrated rate
law of zero-order**

$$\{-[A]\}_{[A]_0}^{[A]_t}$$

=

$$k\{[t]\}_0^t$$

$$[A]_0$$

—

$$[A]_t$$

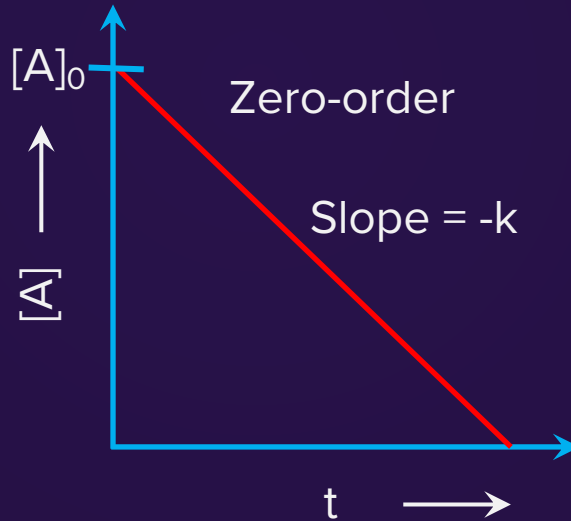
=

$$kt$$

Plot of Concentration of Reactant vs Time



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



Rate Constant for Zero-Order Reaction



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

k

$=$

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

Unit of k



Concentration¹ time⁻¹

So,

Unit of k



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

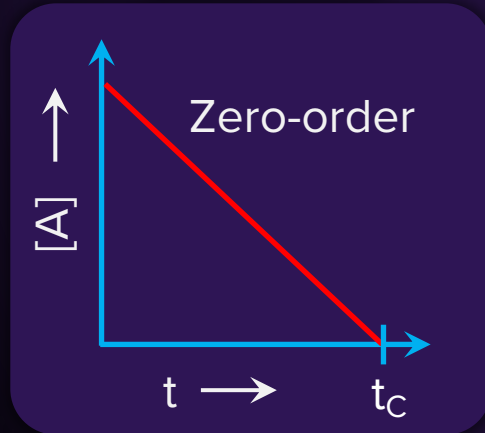
Time of Reaction Completion (t_c)



At this time, the reactants are consumed completely.



$$[A]_{t_c} = 0$$



k

$=$

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

So, at t_c ,

k

$=$

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

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.**

A_t

$$t = t_{1/2}$$

$[A]_t$

=

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

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



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

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

$$t_{1/2}$$

$$=$$

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

$$t_{1/2}$$

$$=$$

$$\frac{[A]_o}{2k}$$

$$t_{1/2}$$

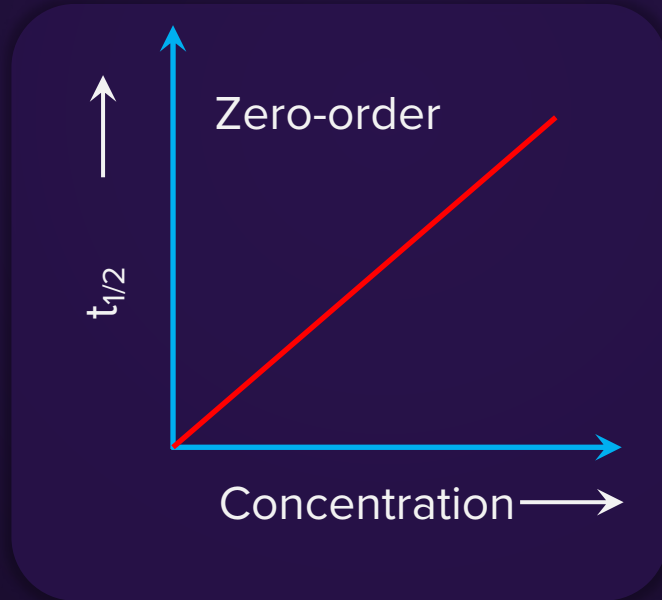
$$\propto$$

$$[A]_o$$

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



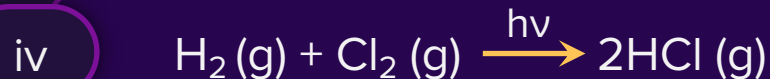
$$t_{1/2} \propto [A]_0$$



Examples of Zero-Order Reaction



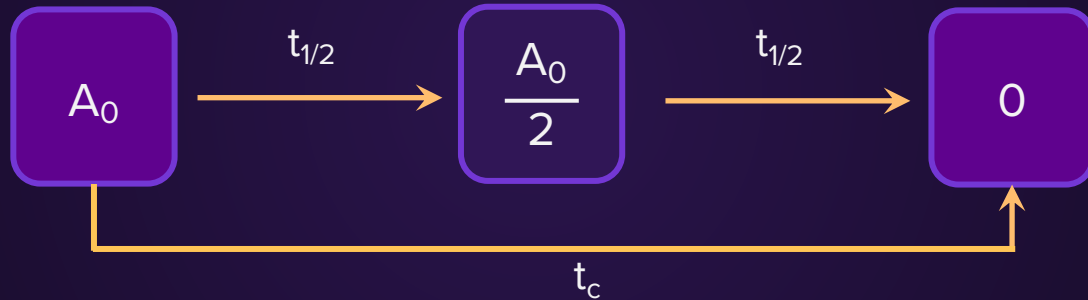
Generally,
the **decomposition of
gases on metal surfaces**
at high concentration
follows zero-order
kinetics.



Zero-Order Reaction



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



Example

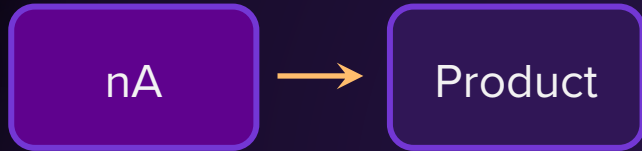


Zero-Order Reaction



Generally, in a zero-order reaction,

Replace k by nk in all the previous formulas.



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

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

$$\text{Rate} = nk$$

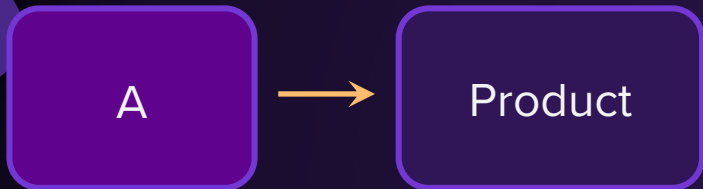
$$[A]_0 - [A]_t = nkt$$

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

First-Order Reaction



For a general reaction,



According to the rate law,

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

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

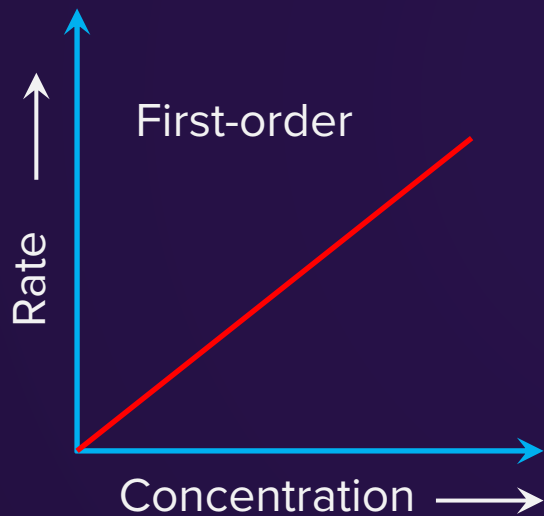
For a first-order reaction,

Where,

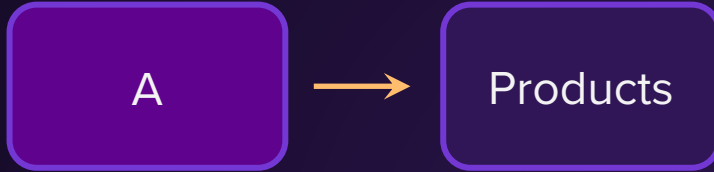
n : Order = 1
 k : Rate constant
 $[A]$: Concentration of reactant A

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

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



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

Time = 0

a

0

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

Time = 't'

a - x

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

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

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

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

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

First-Order Reaction



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

k

$$\log[A]_0 - \log[A] =$$

$$\frac{kt}{2.303}$$

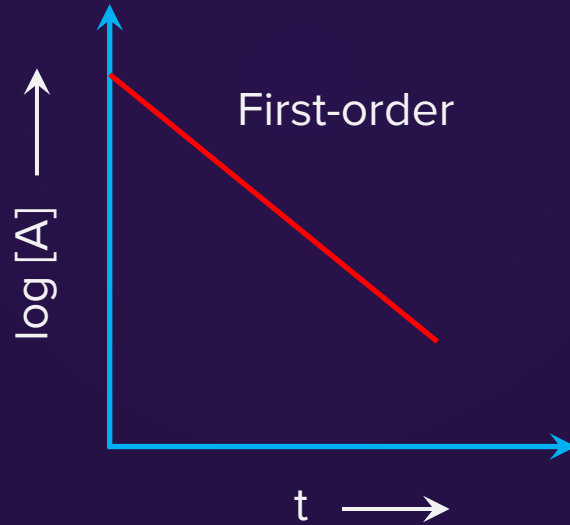
$$\log [A] =$$

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

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,

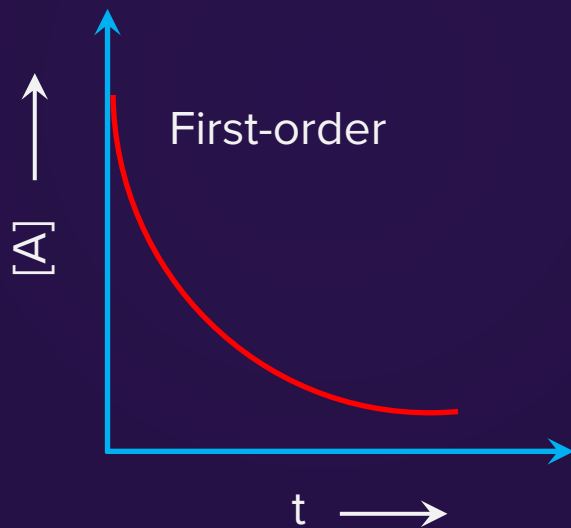
$$[A] = [A]_0 e^{-kt}$$

... (3)

Plot of [A] vs Time



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



Half-Life Period for First-Order Reaction



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

Reaction will be half-completed.

At
 $t = t_{1/2}$

x

=

$$\frac{a}{2}$$

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

$$\ln \frac{a}{a - \left[\frac{a}{2} \right]}$$

=

$$kt_{1/2}$$

$$t_{1/2}$$

=

$$\frac{1}{k} \ln 2$$

$$t_{1/2}$$

=

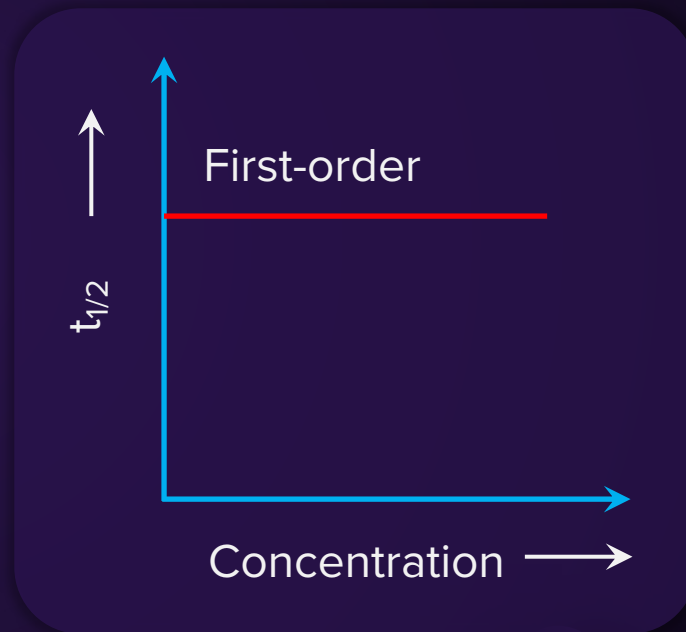
$$\frac{0.693}{k}$$

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



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

Does not depend
on the concentration
of reactants



Unit of Rate Constant (k)



Rate

=

$k [\text{Conc.}]$

Unit of rate



$\text{mole L}^{-1} \text{sec}^{-1}$

Unit of conc.



mole L^{-1}

Unit of k



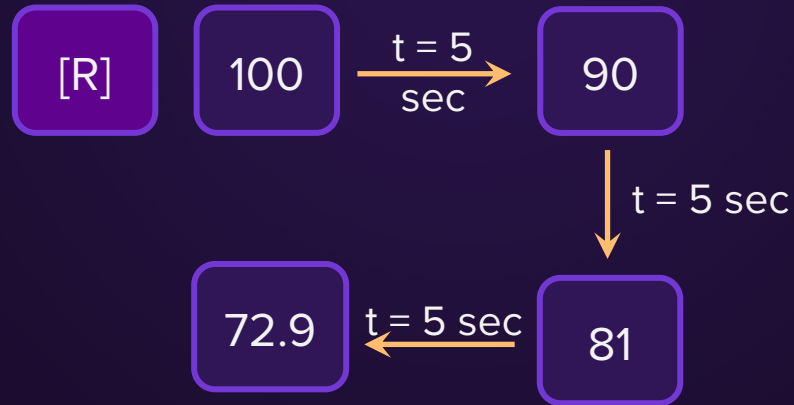
sec^{-1}

Note!



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

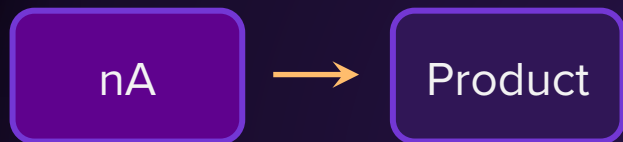
Example



Note!



Generally, for a first-order reaction,



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

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

Replace **k** by **nk** in all the previous formulas.

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

$$[A] = [A]_0 e^{-nkt}$$

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

Examples



1

Decomposition of H_2O_2 takes place.



2

All radioactive decays are always first-order kinetics.



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)



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



At time t,

$a - x$

x

x

$t = 0$

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



In terms of
concentration



At time t,

$$P_0 - P_r \quad P_r \quad P_r$$

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

$P_0 - P_r$

$$\frac{a}{a - x}$$

$=$

$$\frac{P_0}{P_0 - P_r}$$

...(1)

Pressure Measurement



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

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

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 ,

$$kt$$

=

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

Unit of Rate Constant (k)



Rate

=

$k [\text{Concentration}]^n$

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

Unit of
concentration



mol L^{-1}

For zero
order ($n = 0$)



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

Unit of rate



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

For first
order ($n = 1$)



s^{-1}

Unit of k



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

For second
order ($n = 2$)



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

Half-Life Period for n^{th} Order Reaction



So, $t_{1/2} \propto \frac{1}{a^{n-1}}$

Any reaction of any order
will follow this relation.

Half-Life Period for n^{th} Order Reaction



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

For first-order reaction,

$t_{1/2}$ is independent
of $[A]_0$

For zero-order reaction,

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

For second-order reaction,

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

Pseudo Order Reactions



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

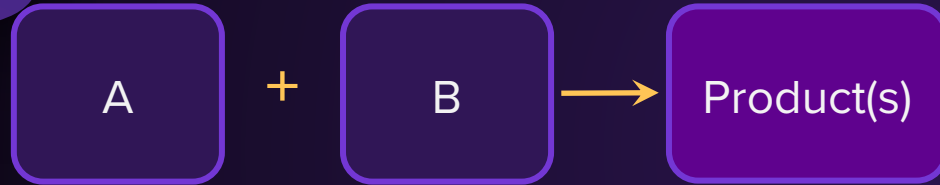
A reaction whose **order** is **different from the actual order** due to **excess** concentration of **one** of the reactants is known as pseudo order reaction.

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

Pseudo First-Order Reaction



For a second-order reaction,



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

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**.

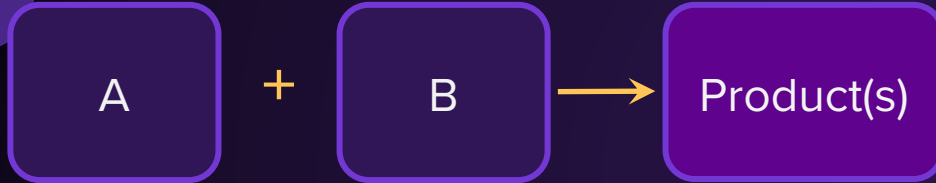


The reaction becomes
a **first-order** reaction.

Pseudo First-Order Reaction



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



$$\text{Rate} = k' [B]$$

$$\text{Where } k' = k[A]$$

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

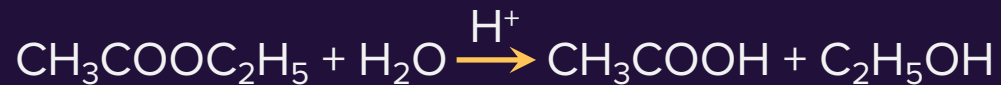
Pseudo first-order reactions

Examples of Pseudo First Order Reaction



Hydrolysis of Ethyl Acetate

0.01 mol of ethyl
acetate + 10 mol H_2O



$t = 0$

0.01

10

0

0

$t = t$

$0.01 - x$

$10 - x$

x

x

Hydrolysis of Ethyl Acetate



Rate

=

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

Rate

=

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

As the change of $[\text{H}_2\text{O}]$ during the reaction is negligible (≈ 0.01 mol out of 10 mol consumed),

Pseudo first-order reaction

$$k [\text{H}_2\text{O}]$$

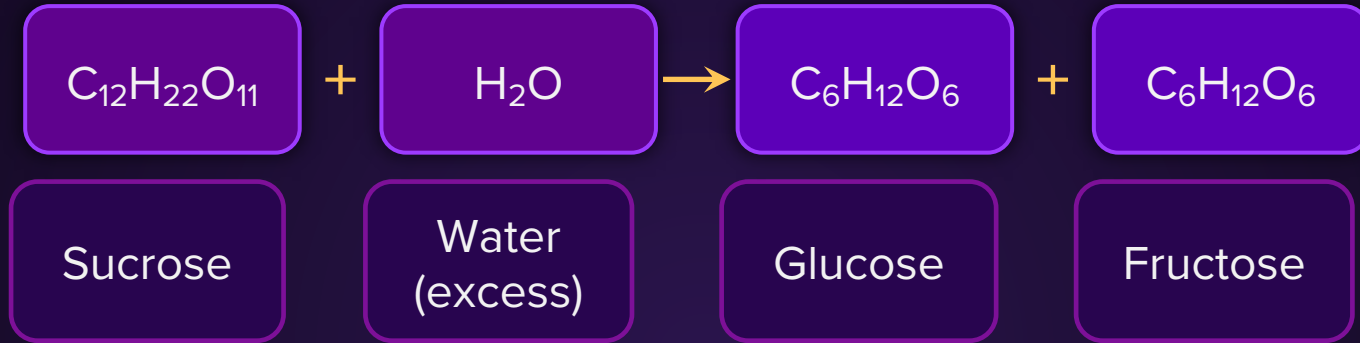
=

Constant

=

k'

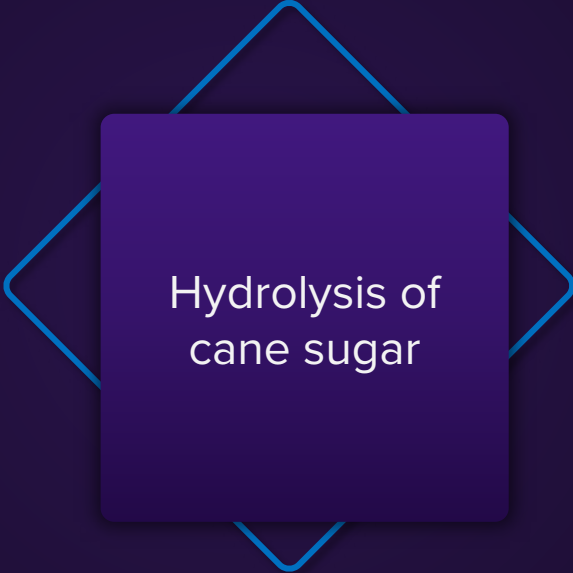
Hydrolysis of Ethyl Acetate



$$\text{Rate} = k [\text{sucrose}] [\text{water}]$$

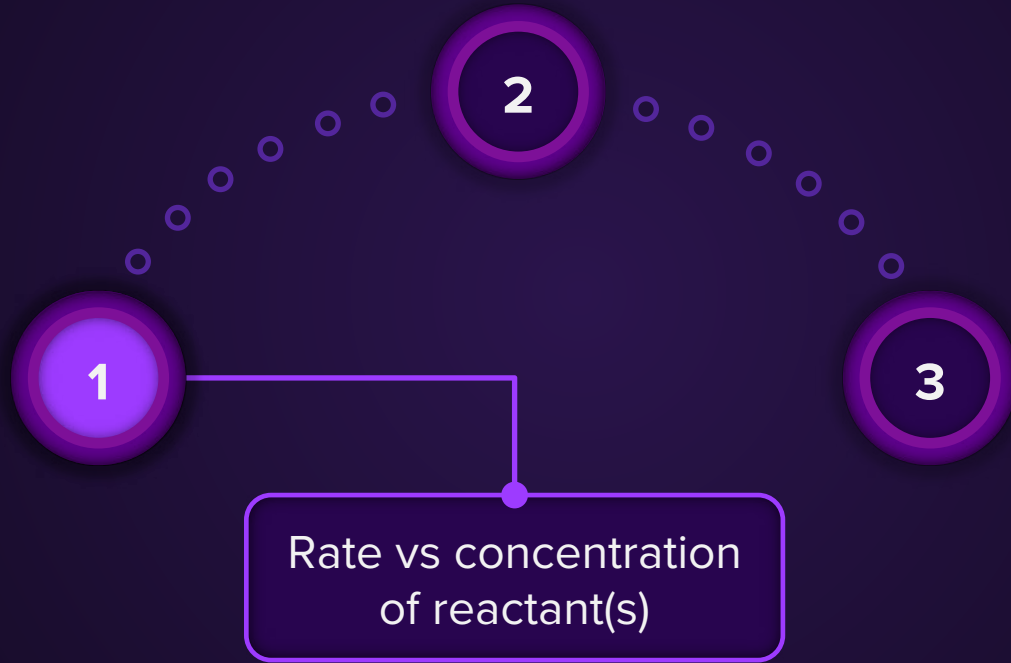
$$\text{Rate} = k' [\text{sucrose}]$$

Hydrolysis of Ethyl Acetate



Hydrolysis of
cane sugar

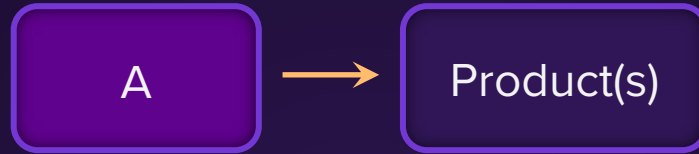
Graphical Representation



Rate vs Concentration of Reactant(s)



For a general reaction,



Rate law,

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

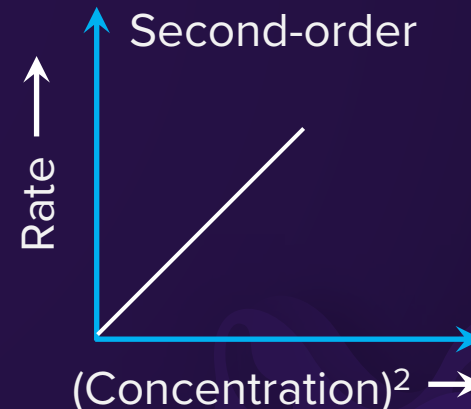
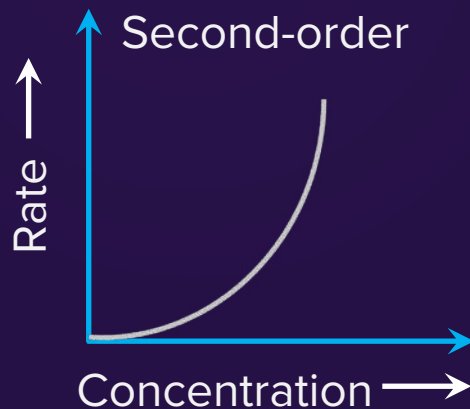
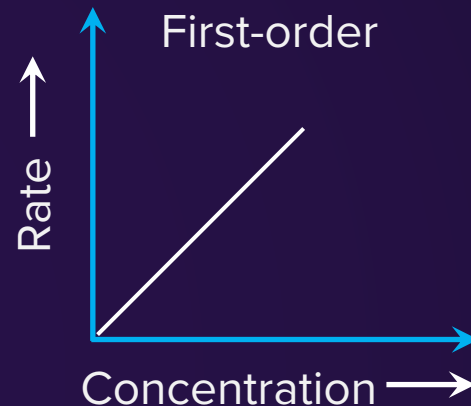
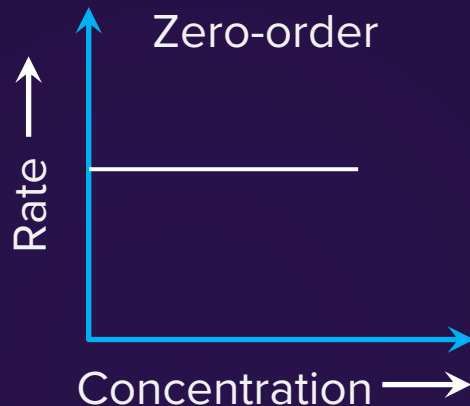
$$\boxed{-\frac{d[A]}{dt}} = \boxed{k [A]^n}$$

Rate vs Concentration of Reactant(s)



For n^{th} order reaction

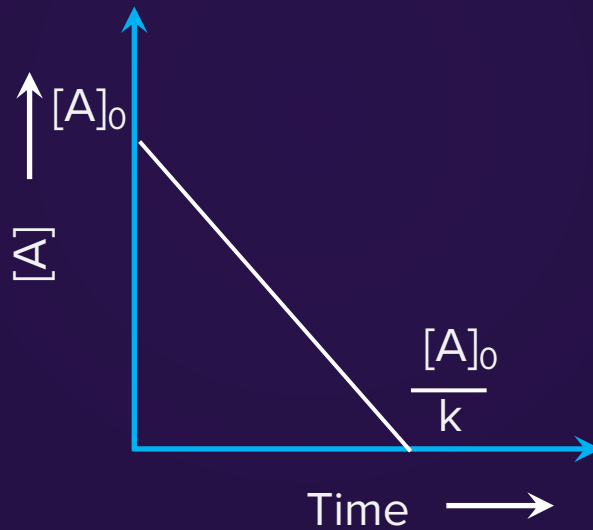
$$\text{Rate} = k [A]^n$$



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



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

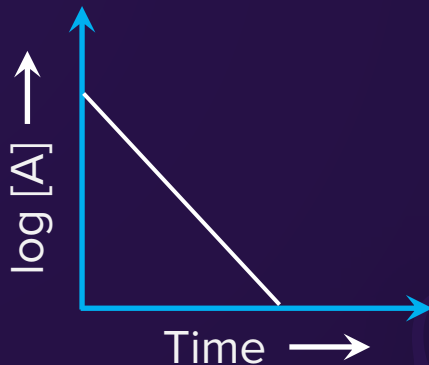
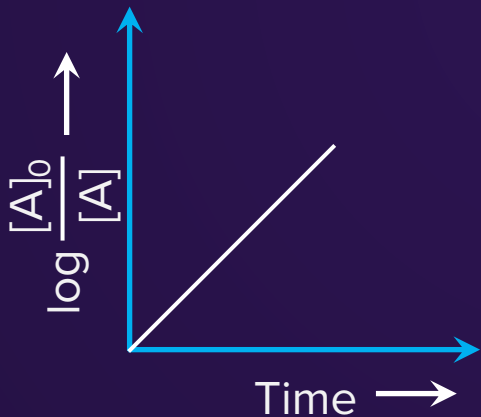


Concentration of Reactant(s) vs Time (For First-Order)



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

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



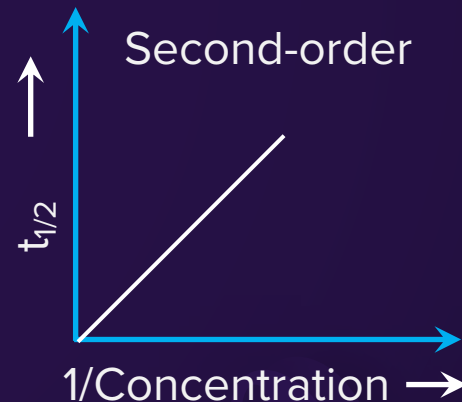
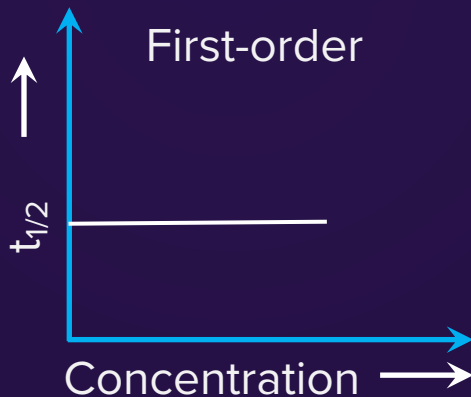
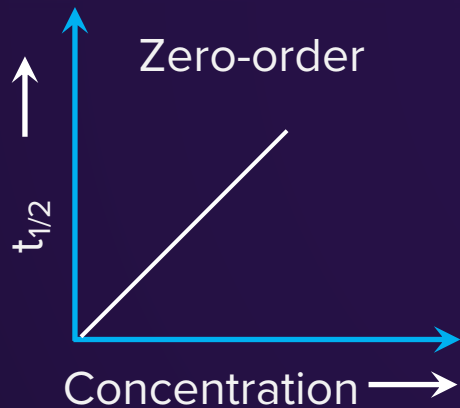
$t_{1/2}$ vs Concentration of Reactant(s)



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

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

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



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 ($n = 1$)



$$\text{s}^{-1}$$

For second
order ($n = 2$)



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

Effect of the Temperature on Rate of Reaction



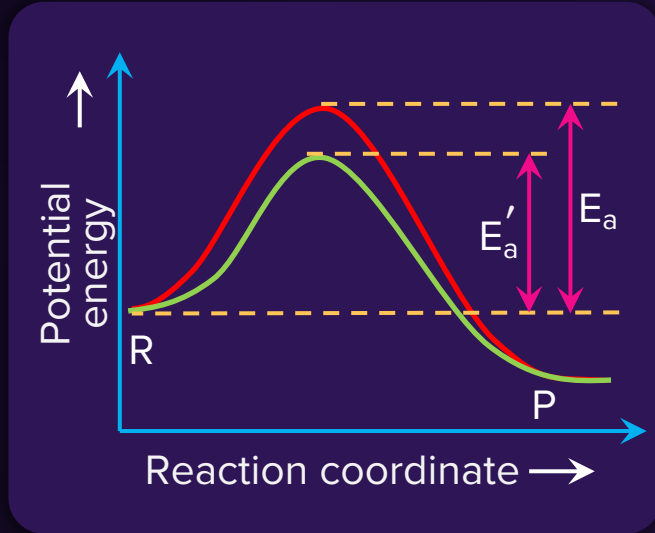
Generally, for a chemical reaction with rise in temperature by **10°**, the **rate constant** is nearly **doubled**.

The **effect** of temperature on reaction rate

Can be **mathematically** expressed using

Temperature coefficient

Arrhenius Equation (With and Without Catalyst)



Without catalyst

k

$=$

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

... (1)

With catalyst

k_{cat}

$=$

$$Ae^{-E'_a/RT}$$

... (2)

k : Rate constant without catalyst

k_{cat} : Rate constant with catalyst

E_a : Activation energy without catalyst

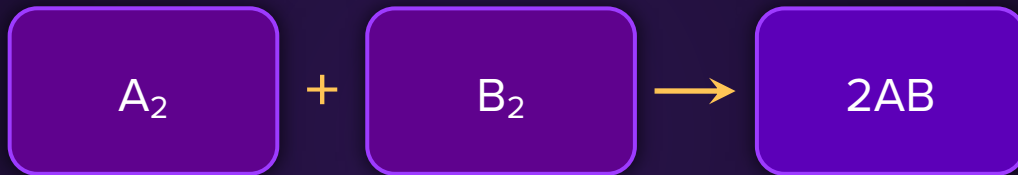
E'_a : Activation energy with catalyst

Trying to Interpret Arrhenius Theory



Example

Elementary reaction

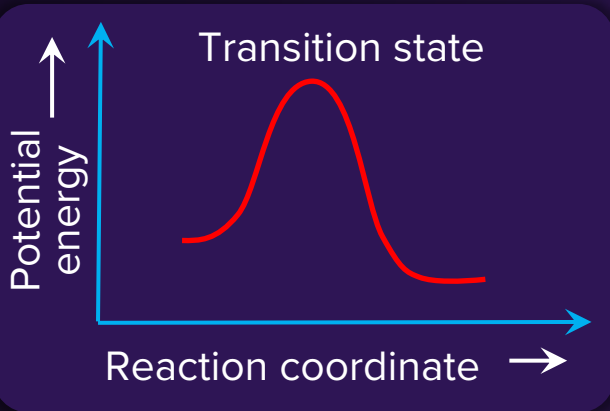


According to Transition state theory,

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



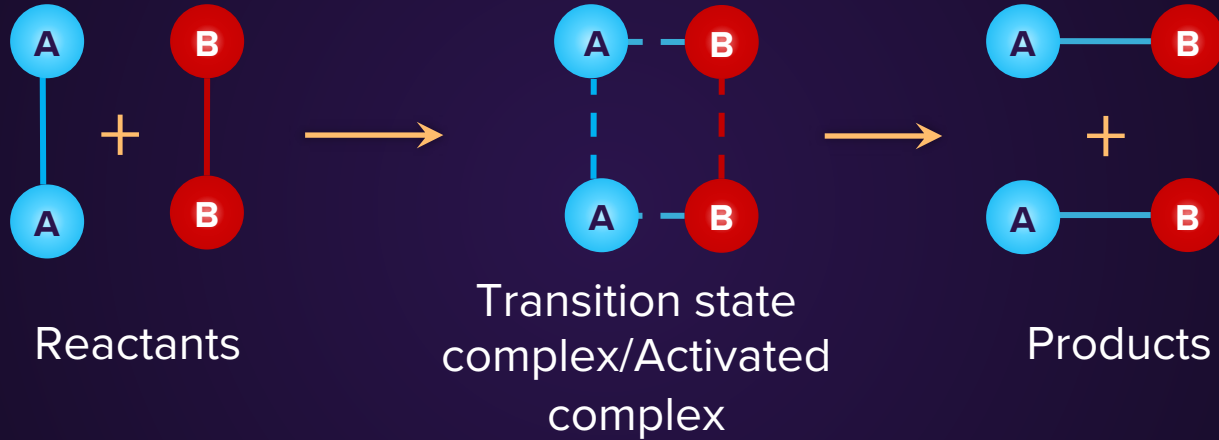
2

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

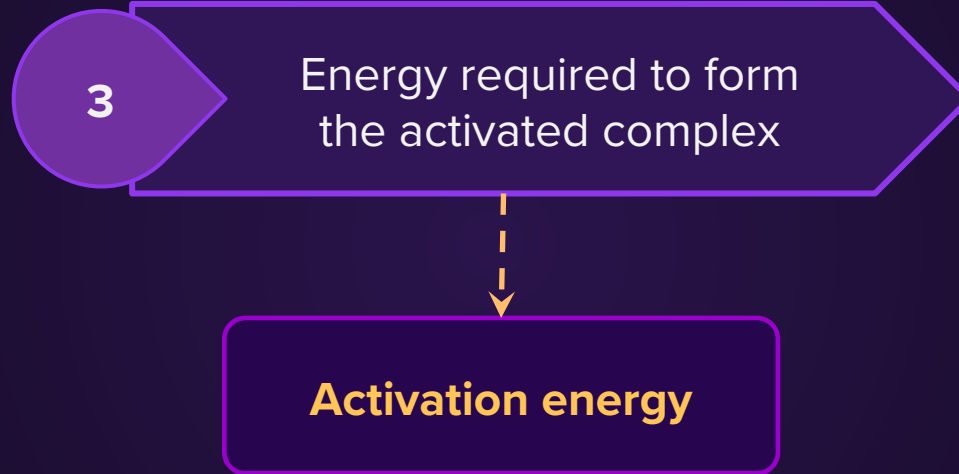
It exists for a very **short time** and gradually a product is formed from this.

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

Reaction and Transition State Complex



Trying to Interpret Arrhenius Theory

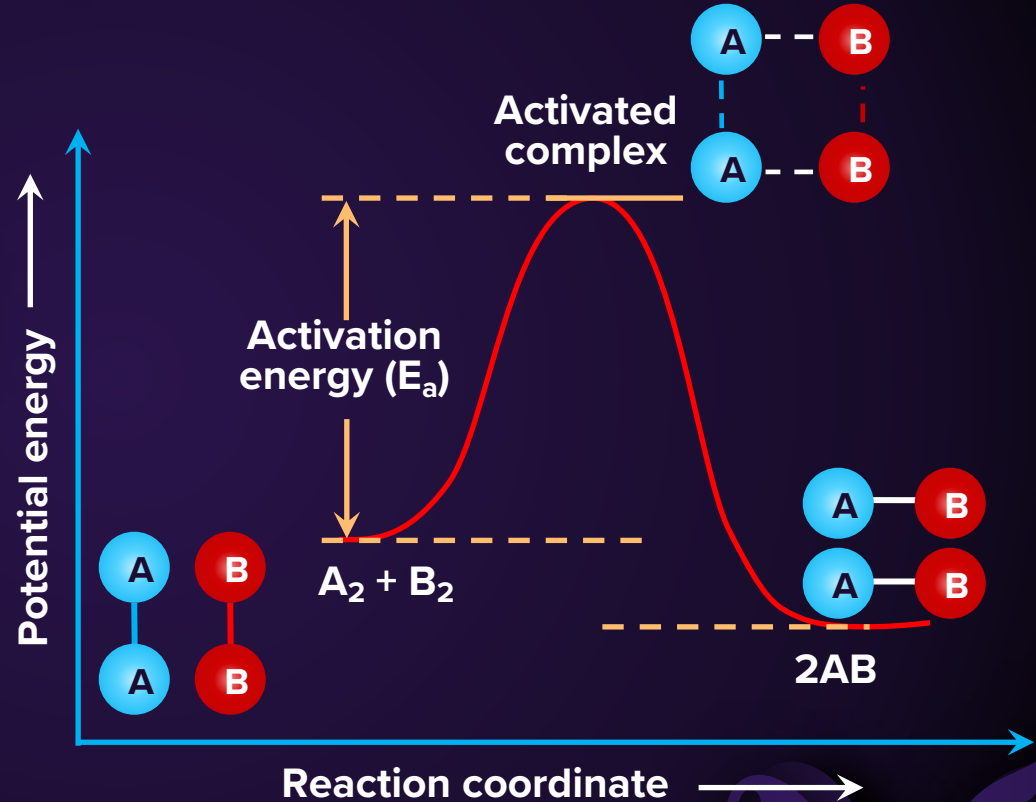


Plot of Potential Energy vs Reaction Coordinate



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



For exothermic reaction

$$\Delta H < 0$$

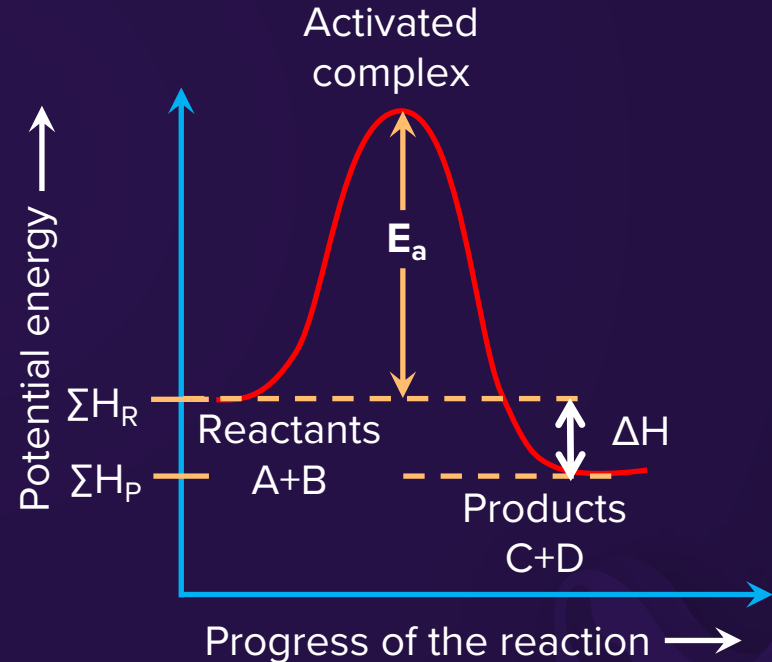
$$\Delta H$$

=

$$\Sigma H_P - \Sigma H_R$$

ΣH_P = Summation of enthalpies of product(s)

ΣH_R = Summation of enthalpies of reactant(s)

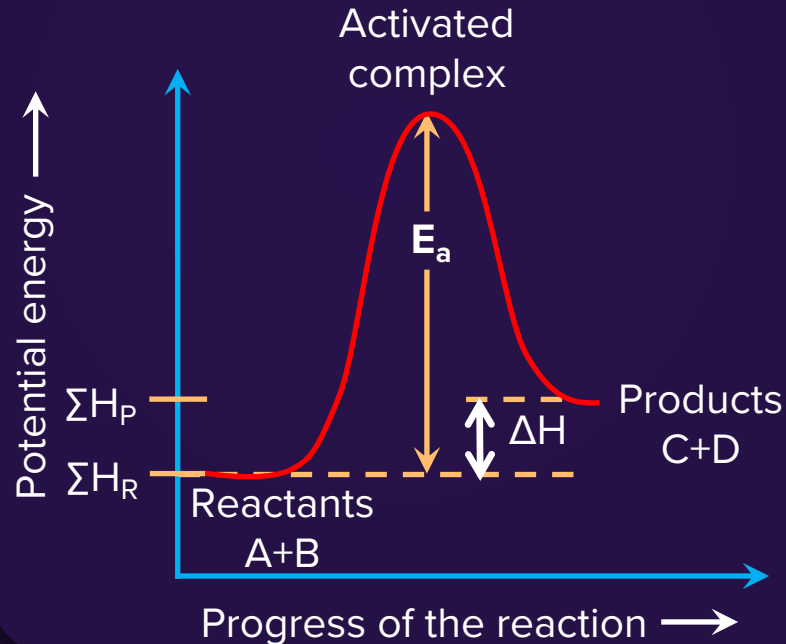


Enthalpy Change During a Reaction



For endothermic
reaction

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



Enthalpy Change During a Reaction



For a **reversible**
exothermic reaction

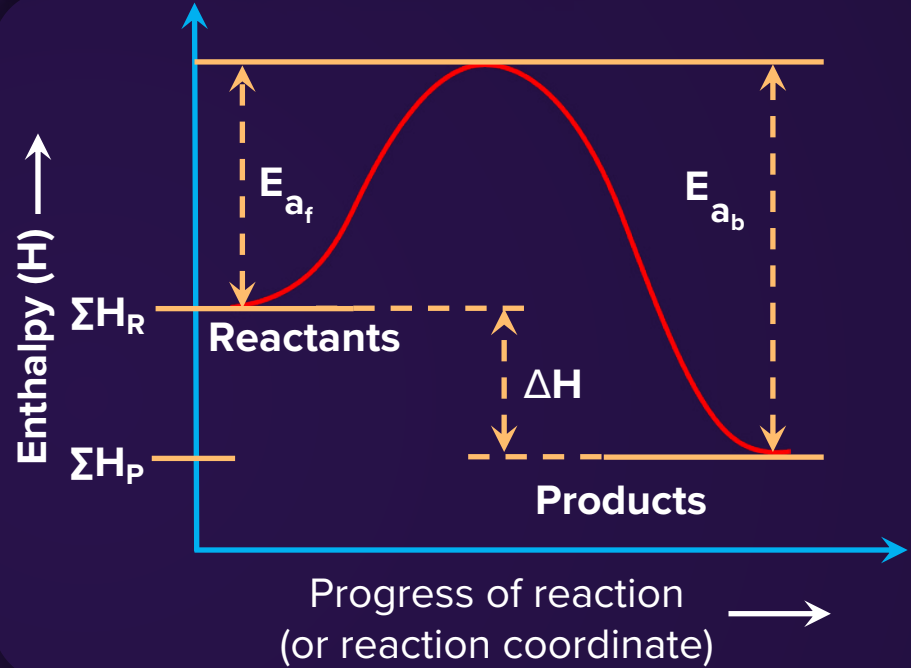
Reactants \rightleftharpoons Products

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

ΔH

=

$E_{a_f} - E_{a_b}$



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

Enthalpy Change During a Reaction



For a **reversible**
exothermic reaction

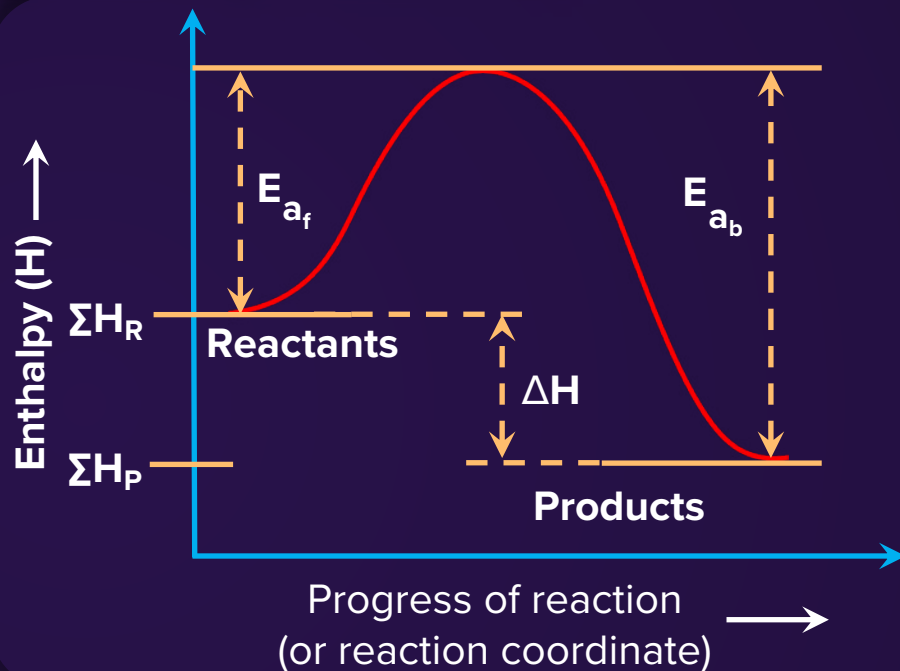
Reactants \rightleftharpoons Products

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

ΔH

=

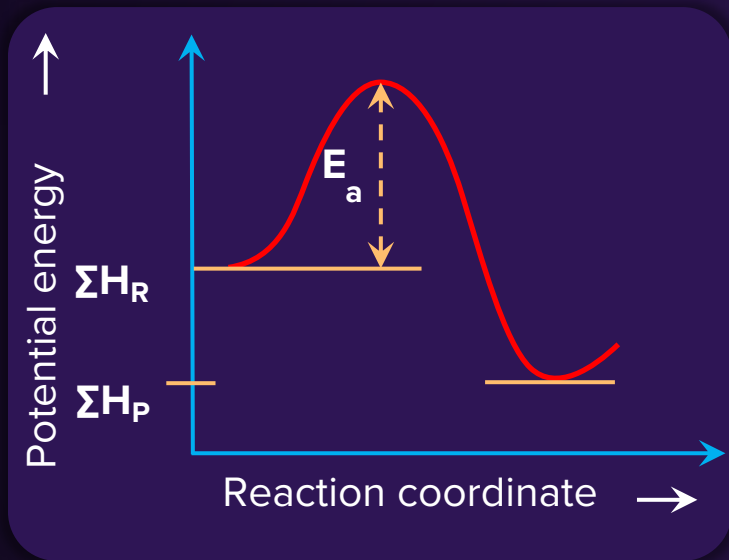
$E_{a_f} - E_{a_b}$



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**

Decrement in Energy After Transition State



Endothermic
or exothermic

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

Activation Energy vs Threshold Energy

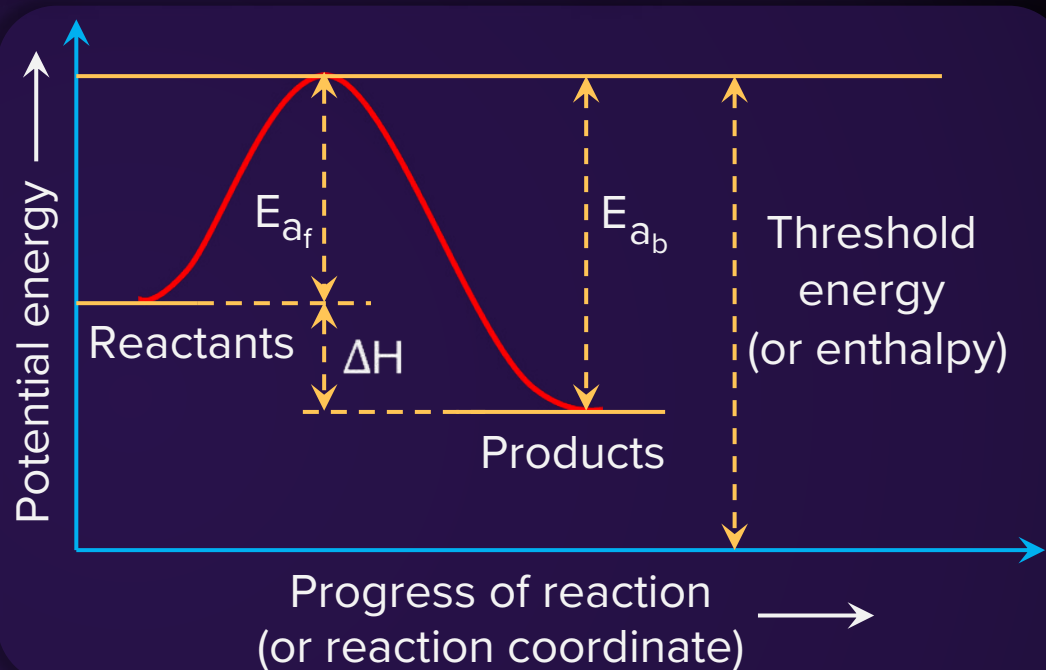


Threshold energy

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

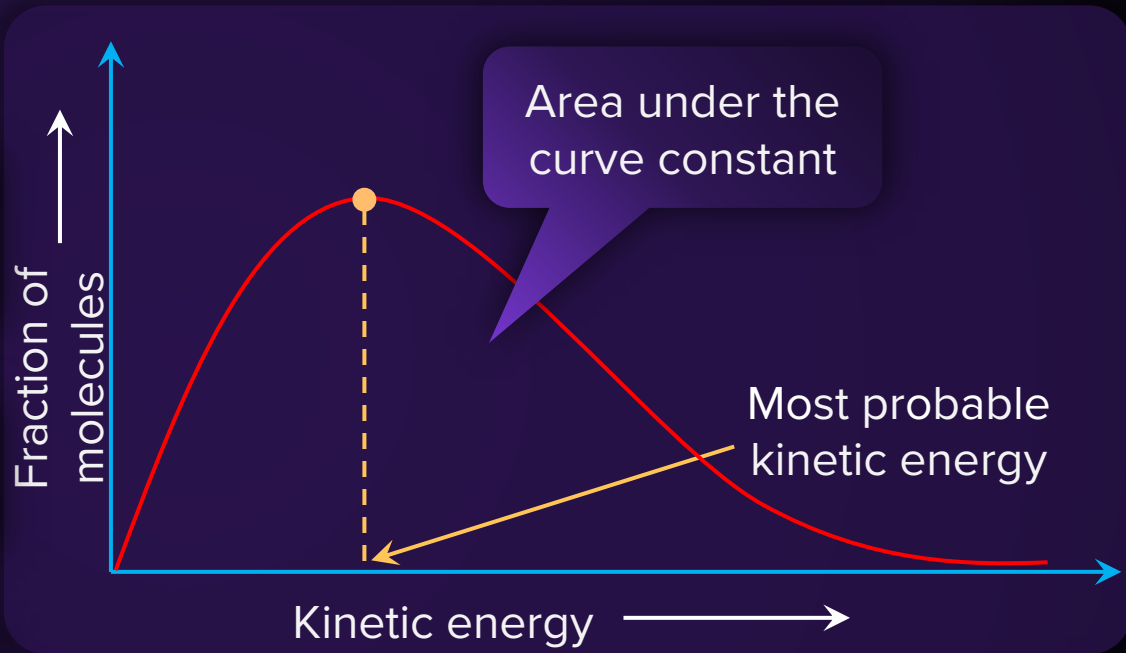
The **maxima** of the curve moves to the higher energy value



Curve **broadens out**



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



Maxwell–Boltzmann Statistics and Arrhenius Theory



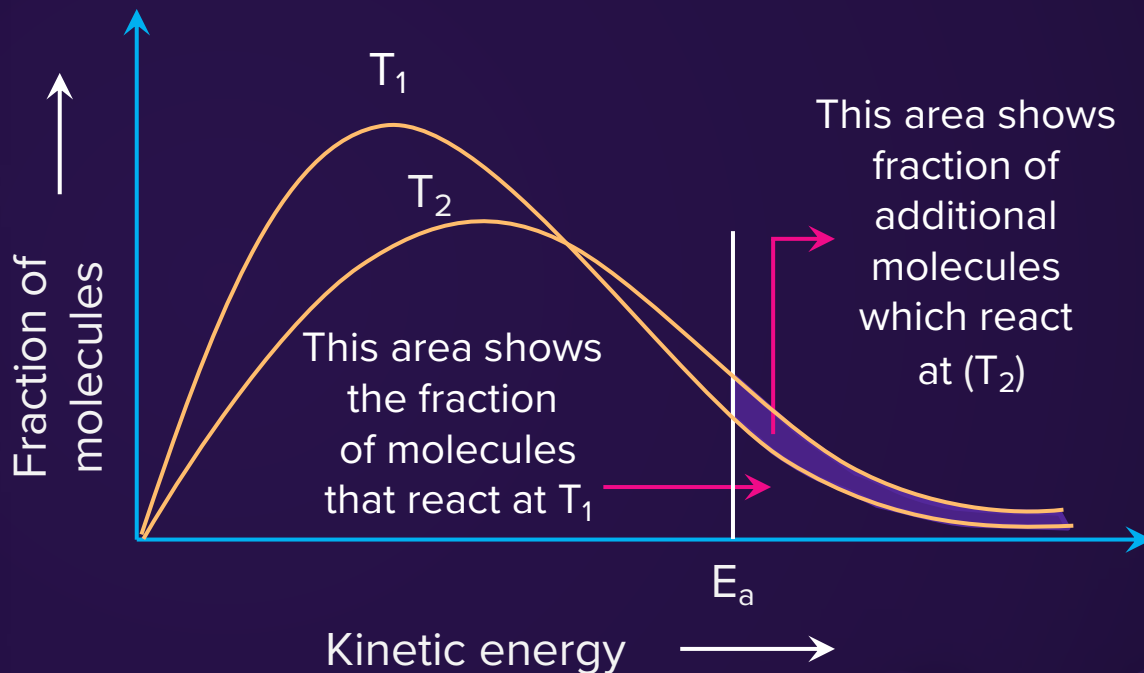
Increasing temperature



Increases the fraction of molecules



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



Maxwell–Boltzmann Statistics and Arrhenius Theory



k

$=$

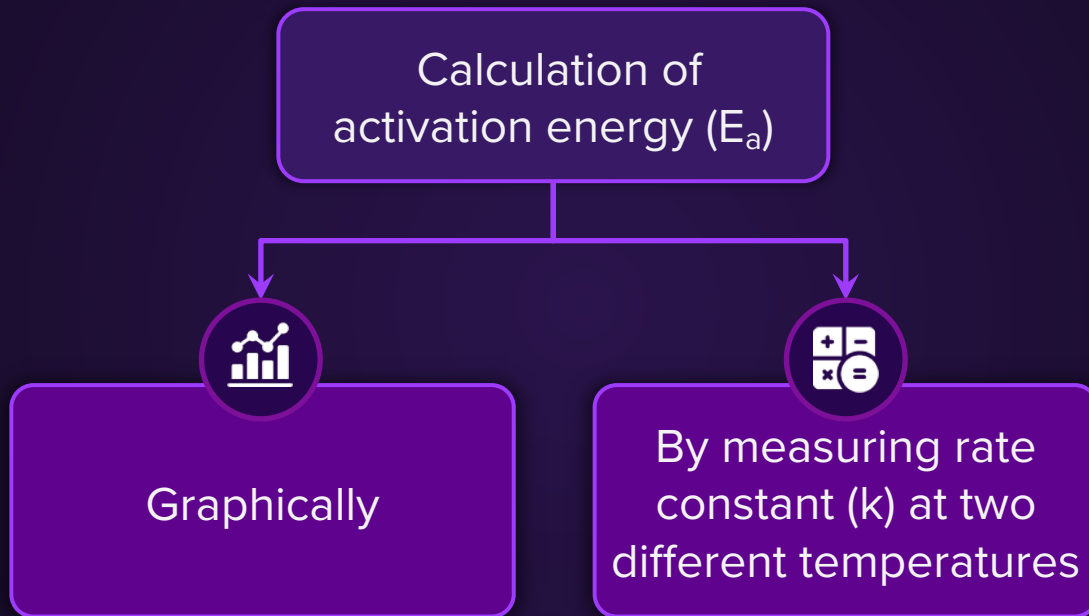
$$A \left[e^{-E_a/RT} \right]$$



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)



Graphically



Arrhenius equation

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

Taking natural logarithm on both sides

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

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

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 $1/T$



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

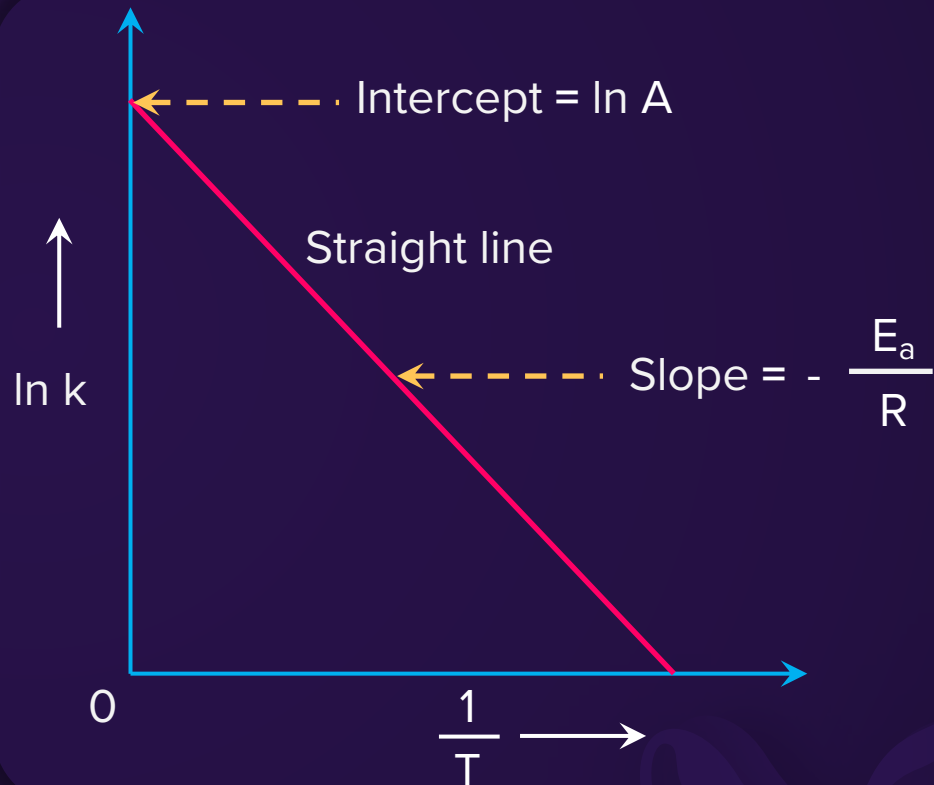
Slope

=

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

From the
graph

E_a can be
calculated



Rate Constant at Different Temperatures



At temperature T_1 , Arrhenius equation:

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

k_1 : Rate constant at temperature T_1

At temperature T_2 , Arrhenius equation:

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

k_2 : Rate constant at temperature T_2

Rate Constant at Different Temperatures



Subtracting eq (1) from eq (2)

$$\ln k_2$$

-

$$\ln k_1$$

=

$$\frac{E_a}{RT_1}$$

-

$$\frac{E_a}{RT_2}$$

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

... (1)

$$\ln \frac{k_2}{k_1}$$

=

$$\frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

... (3)

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

... (2)

$$\log \frac{k_2}{k_1}$$

=

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

... (4)

Rate Constant at Different Temperatures



If the rate constant k_1 and k_2 and the corresponding temperatures T_1 and T_2 are known.



E_a can be calculated

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



Example

Thermal decomposition of H_2O_2 is **accelerated**



By the presence of MnO_2

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



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



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**

4

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

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

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

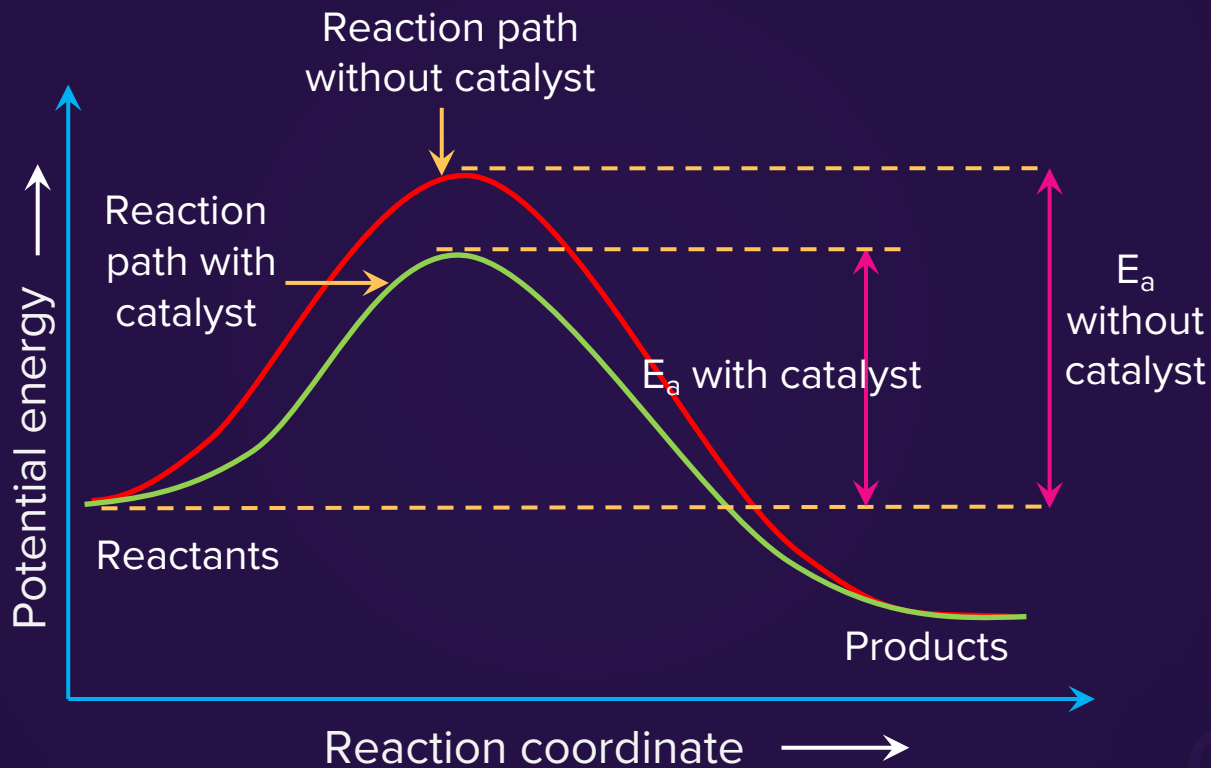
Activation energy decreases

Positive catalyst

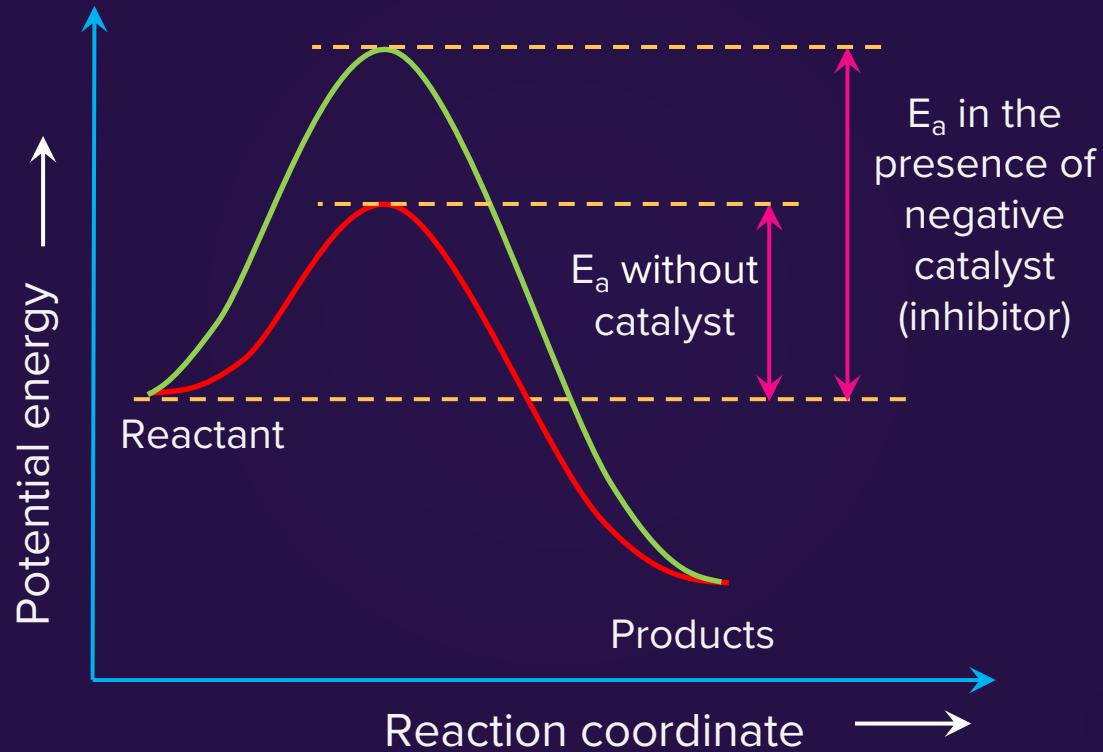
Activation energy increases

Negative catalyst (inhibitor)

Positive Catalyst



Negative Catalyst



Collision Theory



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

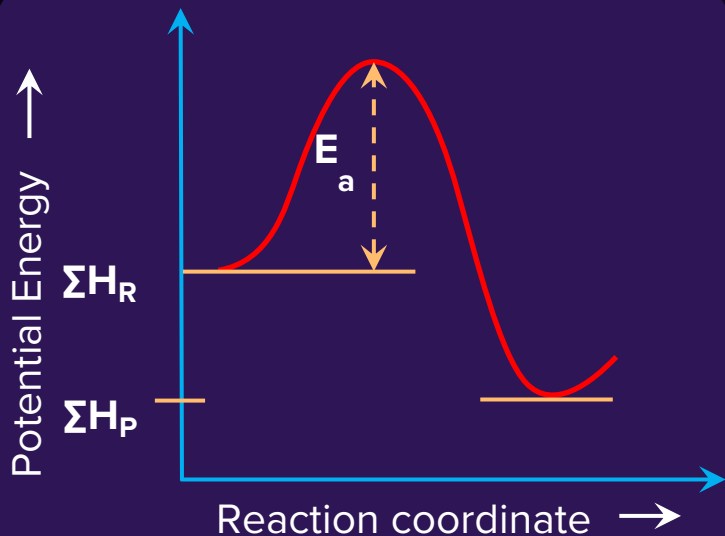
Rate of reaction

Collision frequency

Activation energy

Orientation factor

Activation Energy



Not all collisions result
in **product** formation



A few reactant molecules
acquire **activation** energy

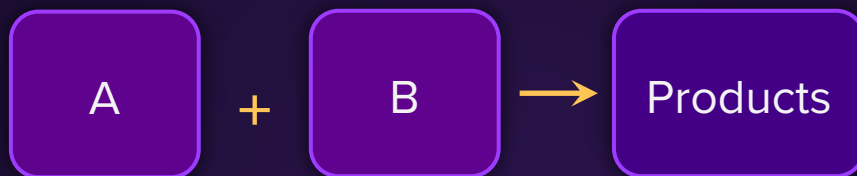


Activation energy is
inversely related to
the **rate** of a reaction

Collision Theory



For a **bimolecular elementary** reaction



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

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



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

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

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

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

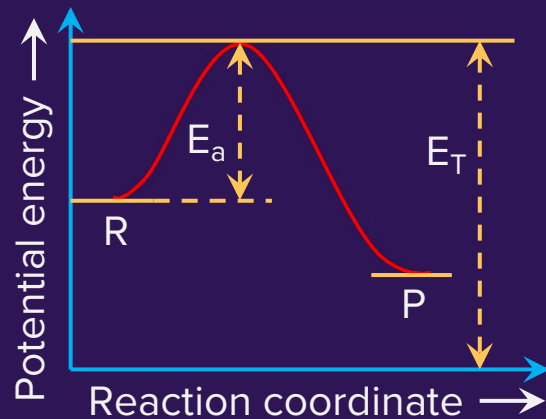
So, if

Energy of
colliding
molecule

\geq

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

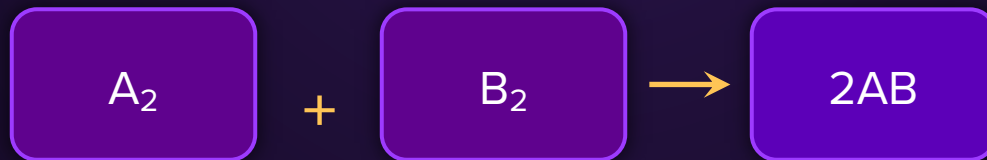
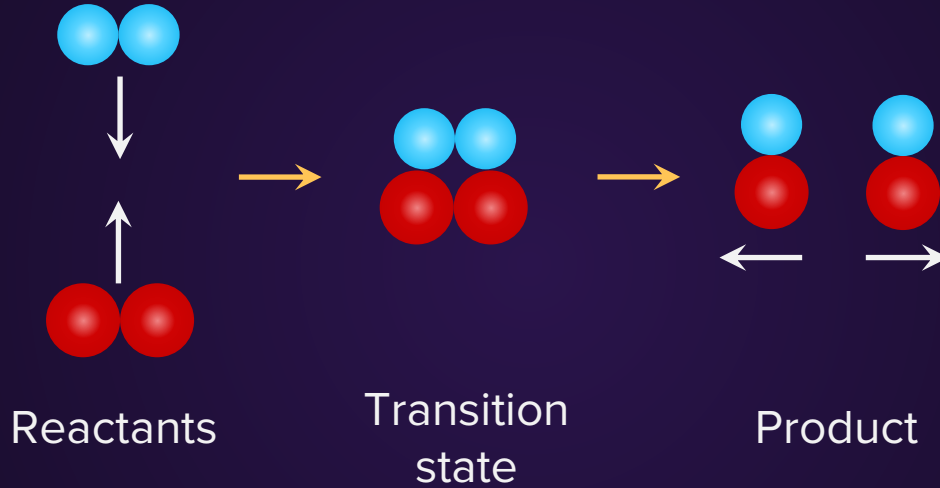


The reacting molecules
must **collide** in a
proper **orientation** to make
the collision **effective**.

Proper Orientation



Proper collision



Proper Orientation

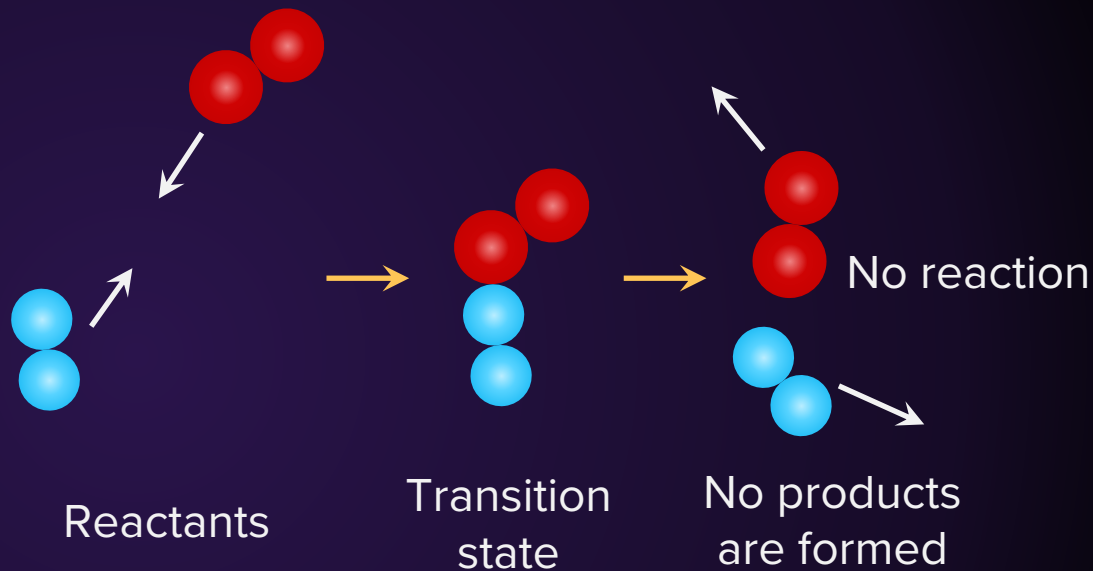


Improper collision

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

Rate

=

$$P Z_{AB} e^{-E_a/RT}$$

Orientation factor