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**
- **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.
Thermodynamics vs Chemical Kinetics

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

However, **chemical kinetics** tells about the **speed** with which it proceeds.
Some reactions are rapid.
Some reactions proceed with moderate Speed

**Inversion of cane sugar**

\[ \text{C}_{12}\text{H}_{22}\text{O}_{11} + \text{H}_2\text{O} \rightarrow \text{C}_6\text{H}_{12}\text{O}_6 + \text{C}_6\text{H}_{12}\text{O}_6 \]

Sucrose \(\rightarrow\) Glucose \(\rightarrow\) Fructose

**Decomposition of hydrogen peroxide**

\[ 2\text{H}_2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{O}_2 \]
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.

The rate of decrease in concentration (disappearance) of reactants.

The rate of increase in concentration (appearance) of products.

Rate can be expressed as

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

For a gaseous reaction at constant temperature,

\[
\text{Concentration} \propto \text{Partial pressure of species}
\]

Rate is expressed as the \textit{rate of change in partial pressure} of a reactant or a product.
Types of Rate

- Average rate
- Instantaneous rate
Average Rate of Reaction

For the reaction, 

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

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

$$= \frac{\Delta C}{\Delta t}$$
Average Rate of Reaction

Rate of disappearance of reactant (R)

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

\[ \begin{align*}
[R]_{\text{initial}} &= \text{Initial concentration of reactant at } t_{\text{initial}} \\
[R]_{\text{final}} &= \text{Final concentration of reactant at } t_{\text{final}} \\
[R]_{\text{final}} &< [R]_{\text{initial}}
\end{align*} \]
Average Rate of Reaction

Rate of appearance of product (P)

\[ [P]_{\text{initial}} = \text{Initial concentration of product at } t_{\text{initial}} \]
\[ [P]_{\text{final}} = \text{Final concentration of product at } t_{\text{final}} \]
\[ [R]_{\text{final}} < [R]_{\text{initial}} \]

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

Average rate \( = \frac{[P]_{\text{final}} - [P]_{\text{initial}}}{t_{\text{final}} - t_{\text{initial}}} \)
As we know,

During a reaction

- The concentration of the reactant decreases.
  \[ [R]_f < [R]_i \]

- The concentration of the product increases.
  \[ [P]_f > [P]_i \]
The **rate** is defined in a manner so that it is always a **positive quantity**.

**Average Rate of Reaction**

For reactant R,

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

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

\[ \text{Rate of disappearance of R} = \text{Rate of appearance of P} \]

\[ \text{Average rate of reaction, } r_{\text{avg}} = -\frac{\Delta[R]}{\Delta t} = \frac{\Delta[P]}{\Delta t} \]
Average Rate of Reaction (Graph)

Concentration of R vs time

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

Concentration of reactants

\[ [R_0] \quad [R_1] \quad [R_2] \]

Time

\[ t_1 \quad t_2 \]
Average Rate of Reaction (Graph)

Concentration of P vs time

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

Rate of Reaction Graph:
- Concentration of products
- Time
- \( r_{\text{avg}} \)
- \([P_1]\)
- \([P_2]\)
- \(\Delta t\)
- \(\Delta[P]\)
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,\[R \rightarrow P\]

\[R_{\text{Instantaneous}} = \lim_{\Delta t \to 0} \left( \frac{\Delta C}{\Delta t} \right) = \frac{dC}{dt}\]
Instantaneous Rate of Reaction

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

Instantaneous rate of disappearance of \( R \)

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

Instantaneous rate of appearance of \( P \)

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

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

\[ r_{\text{avg}} = - \frac{\Delta[R]}{\Delta t} = - \frac{(C_2 - C_1)}{(t_2 - t_1)} \]
Relation between Rates of Different Species Involved in a Reaction
Rate of Reaction

Example

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

These all are correct rate expressions.

However, they are not equal.

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

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

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

\[ \text{N}_2 (g) + 3\text{H}_2 (g) \rightarrow 2\text{NH}_3 (g) \]

1 mol \( \text{N}_2 \) reacts with 3 mol \( \text{H}_2 \) to produce 2 mol \( \text{NH}_3 \).

\[
\begin{align*}
\text{Rate of consumption of } \text{N}_2 & = \frac{1}{3} \left( \text{Rate of consumption of } \text{H}_2 \right) = \frac{1}{2} \left( \text{Rate of formation of } \text{NH}_3 \right)
\end{align*}
\]
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

\[ \text{Rate of reaction} \]

\[
\begin{align*}
\text{w.r.t. } N_2 &= - \frac{d[N_2]}{dt} \\
\text{w.r.t. } H_2 &= - \frac{d[H_2]}{dt} \\
\text{w.r.t. } NH_3 &= + \frac{d[NH_3]}{dt}
\end{align*}
\]

Overall rate of reaction

\[
\begin{align*}
\text{Overall rate} &= - \frac{d[N_2]}{dt} \\
&= - \frac{1}{3} \frac{d[H_2]}{dt} \\
&= + \frac{1}{2} \frac{d[NH_3]}{dt}
\end{align*}
\]

\[ N_2 (g) + 3H_2 (g) \rightarrow 2NH_3 (g) \]
Rate of a Chemical Reaction

\[ \text{Average rate of reaction, } r_{\text{avg}} = \frac{1}{a} \frac{\Delta[A]}{\Delta t} - \frac{1}{b} \frac{\Delta[B]}{\Delta t} + \frac{1}{c} \frac{\Delta[C]}{\Delta t} + \frac{1}{d} \frac{\Delta[D]}{\Delta t} \]

\[ \text{Instantaneous rate of reaction, } r_{\text{inst}} = -\frac{1}{a} \frac{d[A]}{dt} = -\frac{1}{b} \frac{d[B]}{dt} = +\frac{1}{c} \frac{d[C]}{dt} = +\frac{1}{d} \frac{d[D]}{dt} \]
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 dm³ = 10⁻³ m³ = 10³ cm³

\[ \text{Rate} = \frac{\Delta C}{\Delta t} \]

Where,
\( \Delta C \): Change in concentration of any species
\( \Delta t \): Time change corresponding to the concentration change

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

\[ = \frac{\text{mol L}^{-1} \text{s}^{-1}}{\text{mol dm}^{-3} \text{s}^{-1}} \]
Note!

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

\[ r_{\text{inst}} = \frac{\text{d}p}{\text{d}t} \]

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
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

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

For these reactions,

\[
\text{Rate} \propto (\text{concentration})^{\text{order}}
\]

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 Law or Rate Expression

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

Where \( k \): Proportionality constant (rate constant)
\( x \) and \( y \): May or may not be equal to stoichiometric coefficients (a and b) of reactants

\[ aA + bB \rightarrow cC + dD \]
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 $\rightarrow$ Product

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

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

It is the rate of reaction when the concentration of reactant is \textit{unity}.

It is also known as the \textit{specific reaction rate}

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

Where \( n \) is the order of the reaction.
The rate constant (k) depends on **only** temperature and not on concentration.

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

\[
\text{Rate} = \frac{dC}{dt}
\]

- **Unit of rate**: \((\text{Concentration})^1 \text{ time}^{-1}\)
- **Unit of k**: \(\text{mol}^{1-n} \text{ L}^{-n} \text{ s}^{-1}\)
- **Unit of concentration**: \(\text{mol} \text{ L}^{-1}\)
Order of a Reaction

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

Experimentally,

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

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.

The reaction is of the form:

\[ aA + bB + cC \rightarrow \text{Products} \]
Order of a Reaction:

It is the sum of powers of the concentration of the reactants in the rate law of a chemical reaction.

\[ aA + bB + cC \rightarrow \text{Products} \]

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

Thus \( p, q, \) and \( r \) indicate how sensitive the rate is to change in concentration of A, B, and C, respectively.
Remember!

\[ aA + bB + cC \rightarrow \text{Products} \]

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:

\[ 2\text{N}_2\text{O}_5 (g) \rightarrow 4\text{NO}_2 (g) + \text{O}_2 (g) \]

Rate law: \[ k [\text{N}_2\text{O}_5]^1 \]

Overall order: \[ 1 \]
Order of a Reaction

Example:

\[ 5\text{Br}^- (aq) + \text{BrO}_3^- (aq) + 6\text{H}^+ (aq) \rightarrow 3\text{Br}_2 (l) + 3\text{H}_2\text{O} (l) \]

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

Overall order
\[ 1 + 1 + 2 = 4 \]
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 $= \text{Order of the reaction}$
Remember!

For the elementary reaction, 

\[ \text{H}_2 (g) + \text{I}_2 (g) \rightarrow 2\text{HI} (g) \]

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

Overall order = 2
Remember!

For a complex reaction,

The reaction involves more than one step.

The order is experimentally calculated.

Steps involved:

Step 1: $2\text{NO} \rightleftharpoons \text{N}_2\text{O}_2$

Step 2: $\text{N}_2\text{O}_2 + \text{H}_2 \rightarrow \text{N}_2\text{O} + \text{H}_2\text{O}$

Step 3: $\text{N}_2\text{O} + \text{H}_2 \rightarrow \text{N}_2 + \text{H}_2\text{O}$

For example:

$2\text{NO} + 2\text{H}_2 \rightarrow \text{N}_2 + 2\text{H}_2\text{O}$

Rate $= k [\text{NO}]^2 [\text{H}_2]$
Methods to Analyse Rate of a Reaction

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

\[
aA + bB + cC \rightarrow \text{Products} \\
\text{Rate} = k [A]^p [B]^q [C]^r
\]

The concentration of A **is changed**, by keeping the concentrations of B and C **same as before**.
Two different initial concentrations of A, \([A_0]_1\), and \([A_0]_2\) are taken.

The initial rates of the reaction are determined as,

\[
\begin{align*}
r_1 &= k' [A_0]_1^p \\
r_2 &= k' [A_0]_2^p
\end{align*}
\]

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
For a general reaction

A $\rightarrow$ Product(s)

According to the rate law,

Rate of reaction $= k [A]^n$

For a zero-order reaction

Where,

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

Rate $= k$
For a zero-order reaction

Rate = \( k[A]^0 \)

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

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

\[
\frac{d[A]}{dt} = k
\]
Zero-Order Reaction

Rate = \( k [A]^0 \)

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

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

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

When \(time = 0\)

Concentration of \(A\) = \([A]_0\)

Initial concentration

When \(time = t\)

Concentration of \(A\) = \([A]_t\)

When \(Concentration\ of\ A = \[A\]_t\)

When \(Concentration\ of\ A = \[A\]_0\)
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

$$[A]_t = [A]_0 - kt$$  ... (1)
Rate Constant for Zero-Order Reaction

Unit of \( k \) = mol\(^{1-n} \) L\(^{n-1} \) s\(^{-1} \)

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

Unit of \( k \) = Concentration\(^1 \) time\(^{-1} \)

So, Unit of \( k \) = mol L\(^{-1} \) s\(^{-1} \)
At this time, the reactants are consumed completely.

At this time, \( t_c \), the reactants are consumed completely. So, at \( t_c \),

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

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

\[
So, at t_c,
\]

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

\[
t_c = \frac{[A]_0}{k}
\]
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.

At $t = t_{1/2}$

$$[A]_t = \frac{[A]_0}{2}$$
Half-Life Period \((t_{1/2})\)

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

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

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

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

\[
t_{1/2} \propto [A]_0
\]
Plot of $t_{1/2}$ vs Concentration

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

Zero-order

Concentration

$t_{1/2}$
Examples of Zero-Order Reaction

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

**i**  
2NH₃ (g) → Pt → N₂ (g) + 3H₂ (g)

**ii**  
2HI (g) → Au → H₂ (g) + I₂ (g)

**iii**  
2PH₃ (g) → Ni → 2P (g) + 3H₂ (g)

**iv**  
H₂ (g) + Cl₂ (g) → hv → 2HCl (g)
In a zero-order reaction equal concentration of reactants get consumed in equal time.

Zero-Order Reaction

Example

- Initial concentration $A_0$.
- After time $t_{1/2}$, concentration becomes $A_0/2$.
- After another $t_{1/2}$, concentration becomes 0.

Example:

- Initial concentration $[R] = 100$.
- After $t = 10$ s, $[R] = 90$.
- After another $t = 5$ s, $[R] = 85$.
- After another $t = 2.5$ s, $[R] = 82.5$. 

$t_c$ represents the time for a complete reaction.
Generally, in a zero-order reaction, replace $k$ by $nk$ in all the previous formulas.

\[
\text{Rate} = nk \quad \Rightarrow \quad nA \rightarrow \text{Product}
\]

\[
\text{Rate} = k[A]^o \quad \Rightarrow \quad \frac{-d[A]}{n \, dt} = k
\]

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

\[
t_c = \frac{[A]_0}{nk}
\]
First-Order Reaction

For a general reaction,

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

According to the rate law,

For a first-order reaction,

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

Where,

- \( n \) : Order = 1
- \( k \) : Rate constant
- \([A]\) : Concentration of reactant A

A \rightarrow \text{Product}
First-order

\[ R = k[A] \]

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

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

Plot of Rate vs Time

- Rate vs Concentration
- First-order relationship

Diagram:
- Graph showing rate increasing linearly with concentration
- Equation: \[ R = k[A] \]
- Equation: \[ \text{Rate} = k [A]^n \]
- Equation: \[ \frac{d[A]}{dt} = k[A] \]
First-Order Reaction

\[ k[A] = -\frac{d[A]}{dt} = k(a - x) \]
First-Order Reaction

\[
\frac{dx}{dt} = k(a - x)
\]

Integrating both sides,

\[
\int_{0}^{x} \frac{dx}{a - x} = k \int_{0}^{t} dx
\]

As ‘a’ is a constant value,

\[
\frac{dx}{a - x} = k \ dt
\]

\[
\ln \left( \frac{a}{a - x} \right) = kt
\]

\[
2.303 \log \left( \frac{a}{a - x} \right) = kt
\]
The integrated rate law of first-order reaction

\[
\ln \left( \frac{a}{a - x} \right) = kt \quad \ldots \ (1)
\]

\[
\ln \left( \frac{[A]_0}{[A]} \right) = \frac{1}{t} \ln \left( \frac{[A]_0}{[A]} \right) = k
\]

\[
\ln \left( \frac{[A]_0}{[A]} \right) = kt \quad \ldots \ (2)
\]

\[
\frac{2.303}{t} \log \left( \frac{[A]_0}{[A]} \right) = k
\]
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 $[A] \text{ vs Time}$

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

First-order
First-Order Reaction

\[ \ln \left( \frac{[A]_0}{[A]} \right) = kt \] ... (2)

Multiplying eq. (2) by -1,

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

Eliminating natural log from both the sides,

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

\[ [A] = [A]_0 e^{-kt} \] ... (3)
Plot of $[A]$ vs Time

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

First-order
Half-Life Period for First-Order Reaction

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

$$\ln \left( \frac{a}{a-x} \right) = kt$$

$$(1)$$

Reaction will be half-completed.

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

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

$$t_{1/2} = \frac{0.693}{k}$$
Plot of $t_{1/2}$ vs Concentration

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

Does not depend on the concentration of reactants
Average Life for First-Order Reaction

There is another important parameter $t_{av}$

Average life ($t_{av}$)

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

$k$: Rate constant of a reaction
From the first-order rate expression,

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

At completion,
The reactant concentration will be zero. So, \([A] = 0\)

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

\[
\begin{align*}
0 &= [A]_0 e^{-kt} \\
\text{e}^{-kt} &= 0 \\
\text{t}_c &= \infty
\end{align*}
\]

It will happen when,
Unit of Rate Constant (k)

Rate = \( k \text{ [Conc.]} \)

Unit of rate → mole L\(^{-1}\) sec\(^{-1}\)

Unit of conc. → mole L\(^{-1}\)

Unit of k → sec\(^{-1}\)
Generally, for a first-order reaction,

\[ \text{Rate} = \frac{d[A]}{n \, dt} = k \, [A] \]
Note!

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

**Example**

\[
\begin{align*}
[R] & \quad 100 & \quad t = 5 \text{ sec} & \quad 90 \\
\quad & \quad 72.9 & \quad t = 5 \text{ sec} & \quad 81
\end{align*}
\]
1. Decomposition of \( \text{H}_2\text{O}_2 \) takes place.

\[
2\text{H}_2\text{O}_2 (\text{aq}) \rightarrow 2\text{H}_2\text{O} (\text{l}) + \text{O}_2 (\text{g})
\]

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

\[
^{226}\text{Ra}_{88} \rightarrow ^{222}\text{Rn}_{86} + ^{4}\text{He}_2
\]
Second-Order Reaction

For a general reaction,

\[ A + A \rightarrow \text{Product(s)} \]

According to the rate law,

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

Where,

- \( n \) : Order = 2
- \( k \) : Rate constant
- \([A]\) : Concentration of reactant A

For a second-order reaction

\[ \text{Rate} = k [A]^2 \]
Second-Order Reaction

Rate = $k [A]^2$

A + A → Products

Rate = $k [A]^2$

Rate vs. (conc.)$^2$ graph
Second-Order Reaction

\[ \frac{dx}{dt} = k(a-x)^2 \]

\[ \int_{0}^{x} \frac{dx}{(a-x)^2} = \int kdt \]

\[ \left( \frac{1}{a-x} \right)_{0}^{x} = kt \]

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

or

\[ \int kdt = kt \]
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 ($t_{1/2}$)

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

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

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

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

$$t_{1/2} \propto \frac{1}{[A]_0}$$
Second-Order Reaction

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

Graph:
- Vertical axis: \( t_{1/2} \)
- Horizontal axis: \( \frac{1}{\text{(conc.)}} \)
- Linear relationship between \( t_{1/2} \) and \( \frac{1}{\text{(conc.)}} \)
Unit of Rate Constant (k)

Rate = \( k \ [\text{Concentration}]^n \)

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

- For zero order (n = 0): \( \text{mol} \ \text{L}^{-1} \ \text{s}^{-1} \)
- For first order (n = 1): \( \text{s}^{-1} \)
- For second order (n = 2): \( \text{mol}^{-1} \ \text{L}^{1} \ \text{s}^{-1} \)
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,

\[ A + B \rightarrow \text{Product(s)} \]

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)

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 H₂O

\[
\begin{align*}
\text{CH}_3\text{COOC}_2\text{H}_5 + \text{H}_2\text{O} & \xrightarrow{\text{H}^+} \text{CH}_3\text{COOH} + \text{C}_2\text{H}_5\text{OH} \\
\end{align*}
\]

<table>
<thead>
<tr>
<th>t = 0</th>
<th>0.01</th>
<th>10</th>
<th>0</th>
<th>0</th>
</tr>
</thead>
<tbody>
<tr>
<td>t = t</td>
<td>0.01-x</td>
<td>10-x</td>
<td>x</td>
<td>x</td>
</tr>
</tbody>
</table>
Hydrolysis of Ethyl Acetate

\[ \text{CH}_3\text{COOC}_2\text{H}_5 + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{COOH} + \text{C}_2\text{H}_5\text{OH} \]

- Rate = \( k \left[ \text{CH}_3\text{COOC}_2\text{H}_5 \right] \left[ \text{H}_2\text{O} \right] \)
- 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 (\(\approx 0.01\) mol out of 10 mol consumed),

\[ k[\text{H}_2\text{O}] = \text{Constant} = k' \]

**Pseudo first-order reaction**
Hydrolysis of Ethyl Acetate

\[ \text{Sucrose} + \text{H}_2\text{O} \rightarrow \text{Glucose} + \text{Fructose} \]

\[ C_{12}H_{22}O_{11} + \text{H}_2\text{O} \rightarrow C_6H_{12}O_6 + C_6H_{12}O_6 \]

Rate = \( k \ [\text{sucrose}] \ [\text{water}] \)

Rate = \( k' \ [\text{sucrose}] \)
Rate vs Concentration of Reactant(s)

For \( n^{\text{th}} \) order reaction

\[
\text{Rate} = k [A]^n
\]
Concentration of Reactant(s) vs Time (For Zero-Order)

\[ [A] = [A]_0 - kt \]

Diagram showing the relationship between concentration ([A]) and time, with the initial concentration ([A]_0) and rate constant (k) illustrated.
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)

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

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

$1/2$ vs Concentration of Reactant(s)

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

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

- Zero-order:
  - $t_{1/2}$ vs Concentration
  - $t_{1/2} = \frac{[A]_0}{2k}$

- First-order:
  - $t_{1/2}$ vs Concentration
  - $t_{1/2} = 0.693k$

- Second-order:
  - $t_{1/2}$ vs (1/Concentration)
  - $t_{1/2} = \frac{1}{k[A]_0}$
For an $n^{th}$ order reaction, we know that,

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

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

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

For first order ($n = 1$) -> $\text{s}^{-1}$

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

In this method, the **order** of a reaction can be determined by observing the **unit** of the **rate constant**.
For a reaction, half-life can be determined at **two different initial concentrations** and related to the **order of the reaction**.

For a general \( n \text{th order} \) reaction,

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

For the reaction,\[ \text{A} \rightarrow \text{Product (s)} \]

If, \[ \text{Initial concentration of A} = [A]_0 \]

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

At a different initial concentration \([A]_0',\]

\[ \text{Initial concentration of A} = [A]_0' \]

\[ \text{New half-life,} \quad t'_{1/2} \propto \frac{1}{[A]_0'^{n-1}} \quad \text{...(2)} \]
Half-Life Method

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

\[ \frac{t_{1/2}}{t'} = \frac{1}{\frac{[A]_0^{n-1}}{[A]_0}} \] \hspace{2cm} \ldots(3)

‘\(n\)’ can be calculated by measuring \(t_{1/2}, t', [A]_0, \text{and } [A]'_0\) 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,

\[ PV = nRT \]

So,

\[ P \propto \frac{n}{V} RT \]

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

P \propto \frac{n}{V}

Concentration
Pressure Measurement

Progress of a reaction involving gaseous reactants/products can be monitored by measuring the total pressure at a fixed volume and temperature.

So, for the reactions involving gaseous reactants and products, Pressure is considered to monitor the reaction instead of concentration.

\[
\begin{align*}
A (g) & \rightarrow B (g) \\
+ & \\
& C (g)
\end{align*}
\]
Pressure Measurement

In terms of concentration:

\[ A \rightarrow B + C \]

At time \( t \),

\[ a - x \quad x \quad x \]

\[ \begin{align*}
  t = 0 & : P_0 \\
  t = t & : P_0 - P_r
\end{align*} \]

\[ \begin{align*}
  A (g) & \rightarrow B (g) + C (g) \\
  P_0 & \\
  0 & \\
  P_r & \\
  P_r & \\
\end{align*} \]

\( P_0 \): 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
In terms of concentration
At time t,

\[ A \rightarrow B + C \]

\[ P_0 - P_r \quad P_r \quad P_r \]

Total pressure at time ‘t’

\[ P_t \]

According to Dalton’s law,

\[ P_t = (P_0 - P_r) + P_r + P_r \]

\[ P_t = P_0 + P_r \]

\[ P_r = P_t - P_0 \]
As, Concentration $\propto$ Pressure

$\propto P_0$

$\propto P_0 - P_r$

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

...(1)
Pressure Measurement

For the first-order reaction,

\[
\frac{a}{a - x} = \frac{P_0}{P_0 - P_r} \quad \text{(1)}
\]

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

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

Substituting the value of \(P_r\),

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

\[
kt = \ln \frac{P_0}{2P_0 - P_t}
\]
**Volume Measurement**

In terms of concentration:

\[ A \rightarrow B + C \]

At time = \( t \):

\[ a - x \quad x \quad x \]

At time = \( t_\infty \):

\[ 0 \quad a \quad a \]

Monitoring the **progress** of a reaction

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

\[ V_t: \text{The volume of } C \text{ collected at time } 't' \]

\[ V_\infty: \text{The volume of } C \text{ collected at the end of the reaction} \]
Volume Measurement

First-order integrated rate law,

\[ \begin{align*}
\text{kt} &= \ln \frac{a}{a-x} \quad \text{...(1)} \\
\text{Volume of gas collected at infinite time } V_\infty \\
\text{Volume of gas collected at any time } V_t
\end{align*} \]

In terms of concentration

\[
\begin{align*}
\text{A} & \rightarrow \text{B} + \text{C} \\
\text{At time } t, & \quad a - x \quad x \quad x \\
\text{At time } t_\infty, & \quad 0 \quad a \quad a
\end{align*}
\]

\[ a \quad (\text{amount of solid taken initially}) \]

\[ \text{Amount of solid decomposed } (x) \]

\[ \propto \]

\[ \propto \]
Volume Measurement

\[ \text{Putting these values in eq. (1),} \]

\[ \begin{align*}
\frac{\alpha}{V_{\infty} - V_t} &= \ln \frac{V_{\infty}}{V_{\infty} - V_t} \\
\alpha - x \propto V_{\infty} - V_t \\
\end{align*} \]
The volume of KMnO₄ used corresponds to the undecomposed hydrogen peroxide.

The progress of a reactant is monitored by titrating a fixed volume of H₂O₂ solution in a KMnO₄ solution in an acidic medium.

Decomposition reaction

\[
2\text{H}_2\text{O}_2 (\text{l}) \xrightleftharpoons[\Delta]{\rightarrow} 2\text{H}_2\text{O} (\text{l}) + \text{O}_2 (\text{g})
\]
Titration Method

Assuming it as a first-order reaction,

\[ V_0 \propto \text{Initial concentration of } \text{H}_2\text{O}_2 \text{ (a)} \]

\[ V_t \propto \text{Concentration of } \text{H}_2\text{O}_2 \text{ at that instant (a} - x) \]

The volume of KMnO₄ used initially

The volume of KMnO₄ used after time ‘t’
The integrated rate law for a first-order reaction,

\[ \text{kt} = \ln \left( \frac{a}{a - x} \right) \]

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

\[ \text{kt} = \ln \left( \frac{V_0}{V_t} \right) \]
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)

\[
C_{12}H_{22}O_{11} + \text{H}_2\text{O} \xrightarrow{\text{H}^+} C_6H_{12}O_6 + C_6H_{12}O_6
\]

Sucrose \hspace{1cm} (dextro-rotatory) \hspace{1cm} + \hspace{1cm} 66.5°

Glucose \hspace{1cm} (dextro-rotatory) \hspace{1cm} + \hspace{1cm} 52.5°

Fructose \hspace{1cm} (laevo-rotatory) \hspace{1cm} − \hspace{1cm} 92°

(laevo-rotatory)
Inversion of Cane Sugar (Sucrose)

\[ C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+} C_{6}H_{12}O_{6} + C_{6}H_{12}O_{6} \]

\begin{align*}
\text{t = 0} & \quad a & \quad 0 & \quad 0 \\
\text{t = t} & \quad a - x & \quad x & \quad x \\
\text{t = t_c} & \quad 0 & \quad a & \quad a 
\end{align*}
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 $t = t$
$r_\infty$: Optical rotation at $t = \infty$
The integrated rate law for first-order reaction is given by:

\[ kt = \ln \left( \frac{a}{a-x} \right) \]

\[ kt = \ln \left( \frac{r_0 - r_\infty}{r_t - r_\infty} \right) \]

The integrated rate law for first-order reaction is:

\[ a - x \propto (r_0 - r_\infty) - (r_0 - r_t) \]

\[ a - x \propto r_t - r_\infty \]

Inversion of Cane Sugar (Sucrose)
Molecularity of a Reaction

Elementary reaction:

\[ aA + bB \rightarrow \text{Product} \]

Molecularity = \((a + b)\)

1, 2, or 3

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.

Molecularity is simply the sum of the stoichiometric coefficients of the different reactants.
Elementary reactions involving more than three molecules are not known.

So, Molecularity ≤ 3
# Comparison Between Order and Molecularity

<table>
<thead>
<tr>
<th></th>
<th>Molecularity of reaction</th>
<th>Order of reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>It is defined as the number of reactants taking part in a chemical reaction. ( \ce{NH_4NO_2 \rightarrow N_2 + 2H_2O} ) Molecularity = 1</td>
<td>It is defined as the sum of the power of concentration terms that appear in rate law. ( \ce{NH_4NO_2 \rightarrow N_2 + 2H_2O} ) Rate = ( k[\ce{NH_4NO_2}] ) Order = 1</td>
</tr>
<tr>
<td>2</td>
<td>It is always a whole number. It can neither be zero nor be fractional.</td>
<td>It may be zero, fractional, or integer.</td>
</tr>
<tr>
<td></td>
<td>Molecularity of reaction</td>
<td>Order of reaction</td>
</tr>
<tr>
<td>-----------------------</td>
<td>--------------------------------------------------------------</td>
<td>--------------------------------------------------------</td>
</tr>
<tr>
<td><strong>3</strong></td>
<td>It is defined <em>only for elementary</em> reactions.</td>
<td>It is defined for <em>elementary as well as complex</em> reactions.</td>
</tr>
<tr>
<td><strong>4</strong></td>
<td>It is a <em>theoretical</em> value.</td>
<td>It is an <em>experimental</em> value.</td>
</tr>
</tbody>
</table>
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,

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

\[
H_2 (g) + I_2 (g) \rightarrow 2HI (g)
\]
Elementary/Simple/Single Step Reaction

AB + C → AC + B

The state corresponding to the highest P.E.

Energy of reactants

Energy of products

Transition state

P.E.

Reaction coordinate
Elementary/Simple/Single Step Reaction

For these type of reactions:

- **Molecularity** = **Order of a reaction**
- **Stoichiometric coefficient of any reactant** = **Order with respect to that reactant**

Example:

Elementary reaction:

\[ aA + bB \rightarrow \text{Product} \]

**Rate** = \( k[A]^a[B]^b \)

**Molecularity/Order** = \( a + b \)
For the complex reaction,

\[
2\text{NO} + 2\text{H}_2 \rightarrow \text{N}_2 + 2\text{H}_2\text{O}
\]

**Step 1**

\[
2\text{NO} \rightleftharpoons \text{N}_2\text{O}_2
\]

**Step 2**

\[
\text{N}_2\text{O}_2 + \text{H}_2 \rightarrow \text{N}_2\text{O} + \text{H}_2\text{O}
\]

**Step 3**

\[
\text{N}_2\text{O} + \text{H}_2 \rightarrow \text{N}_2 + \text{H}_2\text{O}
\]
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

Transition states

Intermediate

Reaction coordinate

P.E.
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.
The rate of flow of sand is decided only by the narrow opening.
The step of a complex reaction that is the slowest and on which, the overall reaction rate is dependent.

The order of any reaction (complex) has to be always determined experimentally.
Effect of the Temperature on Rate of Reaction

The effect of temperature on reaction rate can be mathematically expressed using the temperature coefficient. Generally, for a chemical reaction with rise in temperature by 10°, the rate constant is nearly doubled.
Temperature Coefficient

The ratio of the rate of reaction at two different temperatures differing by 10°C is given by:

\[
\text{Temperature coefficient (T.C.)} = \frac{k_t + 10}{k_t}
\]

Approximately:

\[
\approx 2 \text{ to } 3
\]
Arrhenius Theory

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

\[ k = \text{A} \text{e}^{-\frac{E_a}{RT}} \]

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

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.

Example

Elementary reaction

$$A_2 + B_2 \rightarrow 2AB$$
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 $\rightarrow$ Transition state complex/Activated complex $\rightarrow$ Products
Energy required to form the activated complex

Activation energy
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

\[ \Delta H = \Sigma H_P - \Sigma H_R \]

\[ \Sigma H_P = \text{Summation of enthalpies of product(s)} \]
\[ \Sigma H_R = \text{Summation of enthalpies of reactant(s)} \]

For exothermic reaction \( \Delta H < 0 \)
Enthalpy Change During a Reaction

For endothermic reaction

\[ \Delta H = \Sigma H_P - \Sigma H_R > 0 \]

\[ A + B \rightarrow C + D \]

 activated complex

Potential energy

\[ \Sigma H_P \]

\[ \Sigma H_R \]

Reactants A+B

Progress of the reaction

Products C+D

{\[
\begin{align*}
\Delta H &= \Sigma H_P - \Sigma H_R > 0 \\
A + B &\rightarrow C + D
\end{align*}
\]
Enthalpy Change During a Reaction

For a **reversible** exothermic reaction

Reactants $\rightleftharpoons$ Products

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

$$\Delta H = E_{af} - E_{ab}$$

$E_{af}$ = Activation energy of the forward reaction

$E_{ab}$ = 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.

\[
E_T = E_a + \text{Energy of reactant molecule}
\]

\[
E_a = E_a^f + E_a^b
\]

Threshold energy (or enthalpy)

Progress of reaction (or reaction coordinate)

\[
\Delta H = E_a^f - E_a^b
\]
The distribution of kinetic energy may be described by plotting the fraction of molecules (\( \frac{N_E}{N_T} \)) 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**

Area under the curve constant

Most probable kinetic energy

Kinetic energy

Fraction of molecules
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 fraction of additional molecules which react at ($T_2$)

This area shows the fraction of molecules that react at $T_1$

Increasing temperature increases the fraction of molecules which collide with energies greater than activation energy ($E_a$).
Maxwell–Boltzmann Statistics and Arrhenius Theory

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

The fraction of molecules that have kinetic energy greater than $E_a$ is given by:

$$k = A e^{-E_a/RT}$$
Calculation of Activation Energy (Eₐ)

Calculation of activation energy (Eₐ)

- Graphically
- By measuring rate constant (k) at two different temperatures
Plotting \( \ln k \) versus \( (1/T) \), can give a straight line

Graphically

Arrhenius equation

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

Taking natural logarithm on both sides

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

\[
 \ln k = \ln A - \frac{E_a}{RT}
\]

\( \text{....(1)} \)

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

\[
 \ln k = \ln A - \frac{E_a}{RT} \times \frac{1}{T}
\]
\[ \ln k = \ln A - \frac{E_a}{R} \times \frac{1}{T} \quad \text{...(1)} \]

**Slope**

\[ \text{Slope} = - \frac{E_a}{R} \]

**From the graph**

\( E_a \) can be calculated

**Straight line**

- Intercept = \( \ln A \)
- Slope = \( -\frac{E_a}{R} \)
At temperature $T_1$, Arrhenius equation:

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

$k_1$: Rate constant at temperature $T_1$

At temperature $T_2$, Arrhenius equation:

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

$k_2$: Rate constant at temperature $T_2$
Rate Constant at Different Temperatures

Subtracting eq (1) from eq (2)

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

\[ \ln k_1 = \ln A - \frac{E_a}{RT_1} \quad \ldots (1) \]

\[ \ln k_2 = \ln A - \frac{E_a}{RT_2} \quad \ldots (2) \]

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

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

Thermal decomposition of $\text{H}_2\text{O}_2$ is accelerated by the presence of MnO$_2$.

By the presence of MnO$_2$:

$$2\text{H}_2\text{O}_2 + \text{MnO}_2 \rightarrow 2\text{H}_2\text{O} + \text{O}_2 + \text{MnO}_2$$

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

4. It does **not alter** the Gibbs energy ($\Delta G$) of a reaction. Catalyses **spontaneous** reactions but **not non-spontaneous** reactions.
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

Potential energy

Reaction path without catalyst

Reaction path with catalyst

Reactants

Products

$E_a$ with catalyst

$E_a$ without catalyst

Reaction coordinate
Potential energy

Reaction coordinate

$E_a$ in the presence of negative catalyst (inhibitor)

$E_a$ without catalyst

Reactant

Products
Arrhenius Equation (With and Without Catalyst)

Without catalyst

\[ k = Ae^{-\frac{E_a}{RT}} \]  

... (1)

With catalyst

\[ k_{\text{cat}} = Ae^{-\frac{E_a'}{RT}} \]  

... (2)

\[ \begin{align*}
  k & : \text{Rate constant without catalyst} \\
  k_{\text{cat}} & : \text{Rate constant with catalyst} \\
  E_a & : \text{Activation energy without catalyst} \\
  E_a' & : \text{Activation energy with catalyst}
\end{align*} \]
Comparing eq. (1) and eq. (2)

\[ k = Ae^{-\frac{E_a}{RT}} \quad \ldots (1) \]

\[ k_{cat} = Ae^{-\frac{E'_a}{RT}} \quad \ldots (2) \]

\[ \frac{k_{cat}}{k} = \frac{e^{-\frac{E'_a}{RT}}}{e^{-\frac{E_a}{RT}}} \]

\[ \frac{k_{cat}}{k} = \frac{(E_a - E'_a)/RT}{e} \]
Arrhenius Equation (With and Without Catalyst)

We know,

\[ k_{\text{cat}} > k \]

\[ \frac{k_{\text{cat}}}{k} = e^{\frac{(E_a - E_{a'})}{RT}} > 1 \]

Rate of catalysed reaction

Rate of uncatalysed reaction
The temperature of the uncatalysed reaction is more than the catalysed reaction.

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

\[ k = Ae^{-\frac{E_a}{RT}} \]
Arrhenius Equation Variation With $E_a$ and Temperature

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

$k_{\text{cat}} = Ae^{-E_a'/RT_2}$ \hspace{1cm} \text{... (2)}

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

$e^{-E_a/RT_1} = e^{-E_a'/RT_2}$ \hspace{1cm} \text{... (3)}

$T_1$ : Temperature at which uncatalysed reaction occurs

$T_2$ : Temperature at which catalysed reaction occurs
Arrhenius Equation Variation With $E_a$ and Temperature

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

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

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.

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

\[
\text{A} + \text{B} \rightarrow \text{Products} \\
\text{Rate} = Z_{AB} e^{-E_a/RT} \quad \ldots \ (1)
\]

- \(Z_{AB}\): 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

Rate = \( Z_{AB} e^{-\frac{E_a}{RT}} \) ... (1)

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

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

For complex molecules, significant deviations are observed.
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?

- Sufficient kinetic energy
- Proper orientation
So, if the colliding molecules must possess the minimum amount of energy (Threshold energy) to participate in a chemical reaction, the molecule that satisfies this condition can cross the energy barrier.
Proper Orientation

The reacting molecules must collide in a proper orientation to make the collision effective. Energy alone does not determine the effectiveness of a collision. 

Conditions:

1. Sufficient kinetic energy
2. Proper orientation
Proper Orientation

Proper collision

Reactants → Transition state → Product

\[ A_2 + B_2 \rightarrow 2AB \]
Proper Orientation

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

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

Improper collision

Reactants → Transition state → No products are formed

No reaction
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 $\alpha$, $\beta$, $\gamma$ is called radioactivity.

Radioactivity is independent of external conditions like temperature, pressure etc. and physical state of substance.
## Properties of $\alpha$, $\beta$ and $\gamma$ Radiations

<table>
<thead>
<tr>
<th>Property</th>
<th>$\alpha$-rays</th>
<th>$\beta$-rays</th>
<th>$\gamma$-rays</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nature</td>
<td>$^2\text{He}^4$ (nucleus of He atom)</td>
<td>$^-1\text{e}^0$</td>
<td>EM radiation</td>
</tr>
<tr>
<td>Velocity</td>
<td>Relatively low (depends on the source)</td>
<td>Greater than $\alpha$ - particles</td>
<td>Very high (3 x10^8 m/sec)</td>
</tr>
<tr>
<td>Ionising power</td>
<td>Very high</td>
<td>Less than $\alpha$ - particles</td>
<td>Very low</td>
</tr>
<tr>
<td>Penetrating power</td>
<td>Low</td>
<td>Intermediate (much greater than $\alpha$ - particles)</td>
<td>Very high</td>
</tr>
</tbody>
</table>
Group Displacement Law

1. When one $\alpha$ emission takes place from a nuclei, the newly formed nuclei occupies two positions left in the periodic table.

2. When one $\beta$ 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

\[ ^{238}\text{U}_{\text{92}} \rightarrow ^{234}\text{Th}_{\text{90}} + _{\text{2}}^\text{He} \]

f-Block element (Group-3)

f-Block element (Group-3)
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

Number of protons (Z)

Number of neutrons

Stability belt

Last stable nucleus

$^{209}_{83}Bi$

$(N = Z)$
Isotopes which lie in the **band of stability** (stability belt) are found to be stable (non-radioactive).
Nuclear Stability

Z

- Upto 20
  - Stable nuclei with n/p ratio nearly 1:1
- > 20
  - n/p ratio increases with Z in stable nuclei region

More number of neutrons are required to reduce repulsion between protons.
For heavier isotopes, the 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.
Case 1

If n/p ratio is high

Stability will be gained by losing β-particle.

\[ _{0}n^{1} \rightarrow _{1}H^{1} + _{-1}e^{0} \]

(β-particle)
Example

\[ _6^1 \text{C}^{12} \text{ (stable)} \]

\[ \frac{n}{p} = \frac{6}{6} \]

\[ _6^1 \text{C}^{14} \text{ (radioactive)} \]

\[ \frac{n}{p} = \frac{8}{6} \] (High)
Example

$^{14}_6 \text{C} \rightarrow ^{14}_7 \text{N} + ^0_- \text{e}$

$^{14}_6 \text{C}$

$\frac{n}{p} = \frac{8}{6}$

$^{14}_7 \text{N}$

$\frac{n}{p} = \frac{7}{7}$
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 $\alpha$-particle emission

Generally observed in heavier isotopes

$Z_X^A \rightarrow Z-2X^{A-4} + 2\text{He}^4$

$^{92}\text{U}^{238} \rightarrow ^{90}\text{Th}^{234} + 2\text{He}^4$
Nuclear Stability

By emission of **positron**

Generally observed in lighter isotopes

1. \( \text{Na}^{22} \rightarrow \text{Ne}^{22} + e^0 \)

2. \( p^1 \rightarrow n^1 + e^0 \)

(From nucleus)
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.

\[ {}_{80}^{197}\text{Hg} + {}_{-1}^{0}\text{e} \rightarrow {}_{79}^{197}\text{Au} \]
Mass Defect and Binding Energy

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**.

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

- Oxygen atom: $8p, 8n, 8e^-$
- Observed mass of O$^{16}$ atom: $\approx 15.99 \text{ amu}$
- Mass sum of $8p, 8n, 8e^-$: $\approx 16.13 \text{ amu}$
Mass Defect and Binding Energy

Where,

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

1 amu $= 931.5 \text{ MeV}$

Higher the binding energy per nucleon, greater will be the stability of nucleus.
Mass Defect and Binding Energy

B.E. per nucleon vs. Mass No. (A)
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

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**

\[ ^{235}\text{U} + _0^1\text{n} \rightarrow ^{236}\text{U}^* \]  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

\[ ^1\text{H}^2 + ^1\text{H}^3 \rightarrow ^2\text{He}^4 + ^0\text{n}^1 \]

Hydrogen bomb is based on fusion.

Very high temperature is required.
Rate of Radioactive Decay

All radioactive disintegrations follow 1st order kinetics.

\[
-\frac{dN}{dt} = \lambda N
\]

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)
\(\lambda\) is decay constant
### Units Of Activity

<table>
<thead>
<tr>
<th>Unit</th>
<th>Conversion</th>
<th>dps</th>
</tr>
</thead>
<tbody>
<tr>
<td>Curie (Ci)</td>
<td>$= \ 3.7 \times 10^{10}$</td>
<td>$3.7 \times 10^{10}$</td>
</tr>
<tr>
<td>Millicurie (mCi)</td>
<td>$= \ 3.7 \times 10^{7}$</td>
<td>$3.7 \times 10^{7}$</td>
</tr>
<tr>
<td>Microcurie (μCi)</td>
<td>$= \ 3.7 \times 10^{4}$</td>
<td>$3.7 \times 10^{4}$</td>
</tr>
<tr>
<td>Rutherford (1 Rd)</td>
<td>$= \ 1 \times 10^{6}$</td>
<td>$1 \times 10^{6}$</td>
</tr>
</tbody>
</table>

Where dps = disintegration per second
Rate of Radioactive Decay

Number of nuclei $N_0$ vs. time $t$.
Rate of Radioactive Decay

\[ \frac{-dN}{N} = \lambda dt \]

\[ \int \frac{-dN}{N} = \int \lambda dt \]

\[ N = N_0 e^{-\lambda t} \]

\[ \lambda = \frac{1}{t} \ln \left( \frac{N_0}{N} \right) \]
Half Life of Radioactive Decay

\[ t = t_{1/2}; \quad N = \frac{N_0}{2} \]

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

\[
t_{1/2} = \frac{\ln 2}{\lambda}
\]

\[
\frac{\ln 2}{\lambda} = \frac{0.693}{\lambda}
\]
Average Life of Radioactive Decay

\[ t_{\text{avg}} = \frac{\int_0^{\infty} dN \cdot t}{N_0} = \frac{1}{\lambda} \]

\[ t_{\text{avg}} = \frac{1}{\lambda} = 1.44 \cdot t_{1/2} \]
Carbon Dating

In living matter existing in nature

Radioactive

$\text{^{14}C} : \text{^{12}C} = 1 : 10^{12}$

Stable

In upper atmosphere

$7\text{N}^{14} + 0\text{n}^{1} \rightarrow \text{^{14}C} + 1\text{p}^{1}$

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