

CHEMICAL KINETICS

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Syllabus

- Rate of reactions
- Rate laws of multi- step reactions (steady state approximation).
- Parallel reactions
- Opposing reactions
- Consecutive reactions
- Theory of reaction rate: Collision theory, Lindemann modification,
Absolute reaction rate theory.
- Catalysis: types, theories.
- Kinetics of enzyme catalysis: Michaelis-Menten mechanism

Rate of reactions

Slow reactions, take years or months



Fast reactions, takes seconds or minutes

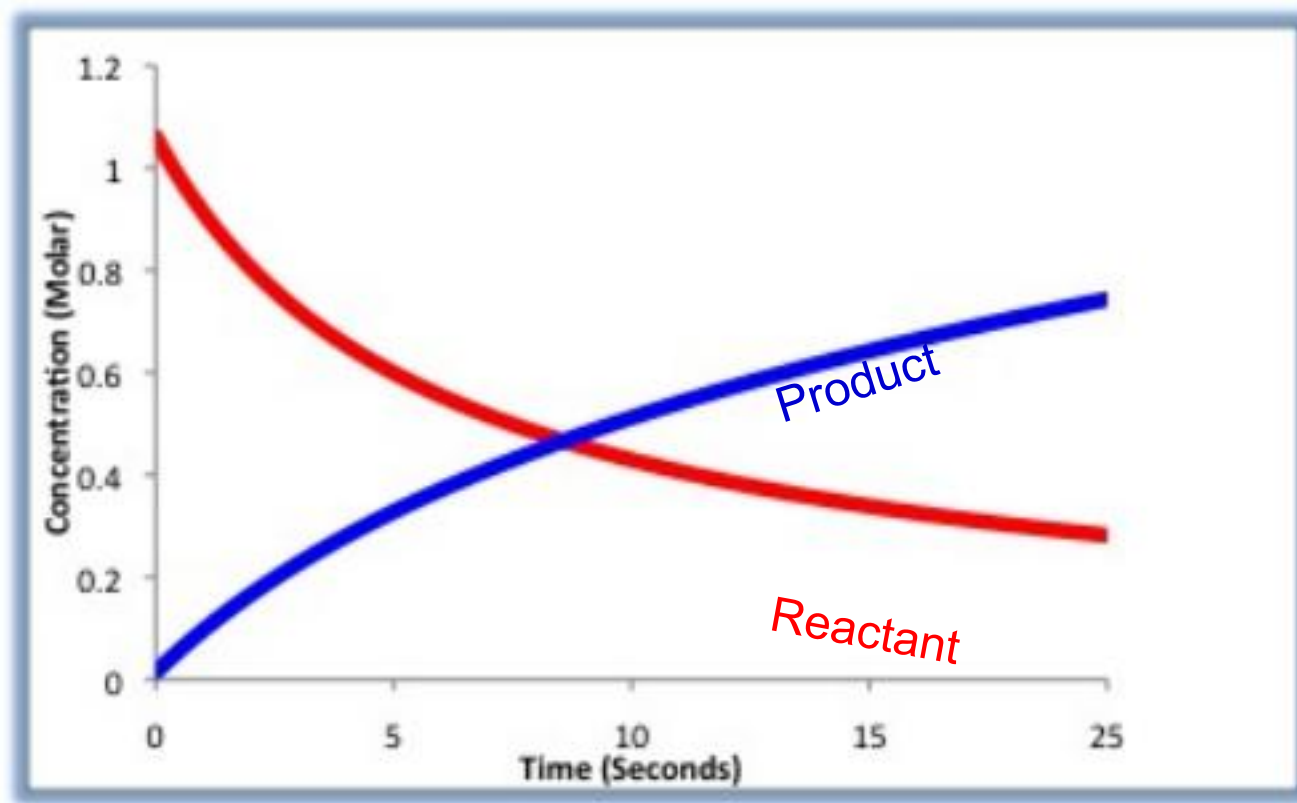


Chemical Kinetics

Chemical kinetics deals with the study of the rate of chemical reactions and their mechanism.

- **Studies the rate of a chemical reactions & rate laws**
 - Shows time needed for a given amount of the product
 - Shows amount of product in a given amount of time
 - Shows how to control the reaction
 - Guide towards the mechanism of a reaction
- **Factors affecting the rate of a reaction**
 - (Temperature, pressure, concentration and catalyst)
- **Studies the mechanism of a chemical reaction**
 - Predict products of similar reactions
 - Better understand the reaction
 - Accurately manipulate the reaction for a desired result
 - Organize and simplify the study of chemistry

Rate of Reaction



“The rate of reactions is defined as the change in concentration of any of reactant or products per unit time”

Rate of Reaction

$$\text{Rate of reaction (r)} = \frac{\text{Amount of A consumed}}{\text{Time taken}}$$



$$\text{Rate of reaction (r)} = \frac{\text{Amount of B produced}}{\text{Time taken}}$$



$$\text{Rate of reaction (r)} = \frac{dx}{dt}$$

Rate of Reaction



Rate of Reaction (r) = Rate of disappearance of A

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

= Rate of appearance of B

$$= \frac{+d[B]}{dt} = \frac{+\Delta[B]}{dt}$$

Unit of Rate

Concentration/Time

(Mole/litre)/sec

mol l⁻¹ s⁻¹

Rate of Reaction



$$\text{Rate of Reaction (r)} = \text{Rate of disappearance of A} = \frac{-d[A]}{dt}$$

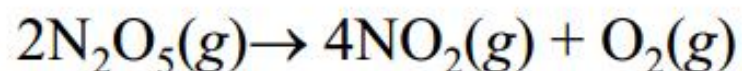
$$= \text{Rate of disappearance of B} = \frac{-d[B]}{dt}$$

$$= \text{Rate of appearance of C} = \frac{+d[C]}{dt}$$

$$= \text{Rate of appearance of D} = \frac{+d[D]}{dt}$$

An Example

Consider the decomposition of N_2O_5 to give NO_2 and O_2 :

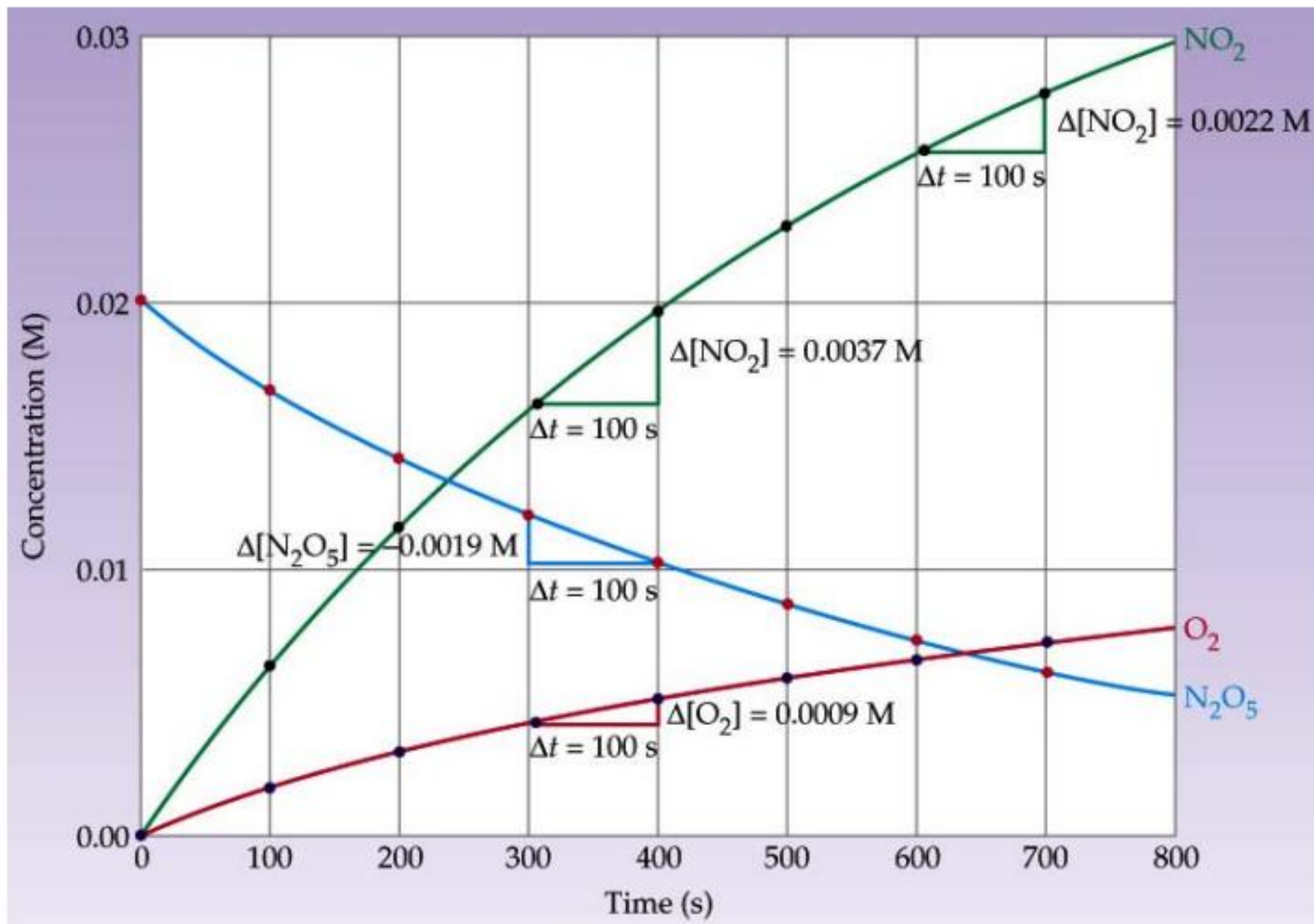


| Time (s) | Concentration (M) | | |
|-------------|------------------------|---------------|--------------|
| | N_2O_5 | NO_2 | O_2 |
| 0 | 0.0200 | 0 | 0 |
| 100 | 0.0169 | 0.0063 | 0.0016 |
| 200 | 0.0142 | 0.0115 | 0.0029 |
| 300 | 0.0120 | 0.0160 | 0.0040 |
| 400 | 0.0101 | 0.0197 | 0.0049 |
| 500 | 0.0086 | 0.0229 | 0.0057 |
| 600 | 0.0072 | 0.0256 | 0.0064 |
| 700 | 0.0061 | 0.0278 | 0.0070 |

reactants
decrease with
time

products
increase with
time

Determination of Rate



Determination of Rate

From the graph looking at $t = 300$ to 400 s

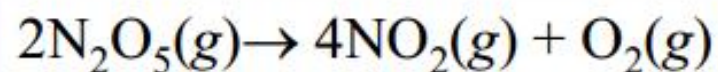
$$\text{Rate O}_2 = \frac{0.0009\text{M}}{100\text{s}} = 9 \times 10^{-6} \text{Ms}^{-1}$$

Why do they differ?

$$\text{Rate NO}_2 = \frac{0.0037\text{M}}{100\text{s}} = 3.7 \times 10^{-5} \text{Ms}^{-1}$$

Recall:

$$\text{Rate N}_2\text{O}_5 = \frac{0.0019\text{M}}{100\text{s}} = 1.9 \times 10^{-5} \text{Ms}^{-1}$$



To compare the rates one must account for the *stoichiometry*.

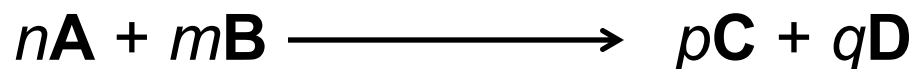
$$\text{Rate O}_2 = \frac{1}{1} \times 9 \times 10^{-6} \text{Ms}^{-1} = 9 \times 10^{-6} \text{Ms}^{-1}$$

$$\text{Rate NO}_2 = \frac{1}{4} \times 3.7 \times 10^{-5} \text{Ms}^{-1} = 9.2 \times 10^{-6} \text{Ms}^{-1}$$

$$\text{Rate N}_2\text{O}_5 = \frac{1}{2} \times 1.9 \times 10^{-5} \text{Ms}^{-1} = 9.5 \times 10^{-6} \text{Ms}^{-1}$$

Now they agree!

Rate of Reaction & Stoichiometry



$$\text{Rate of Reaction (r)} = \text{Rate of disappearance of A} = \frac{-1}{n} \frac{d[A]}{dt}$$

$$= \text{Rate of disappearance of B} = \frac{-1}{m} \frac{d[B]}{dt}$$

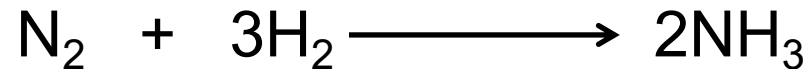
$$= \text{Rate of appearance of C} = \frac{+1}{p} \frac{d[C]}{dt}$$

$$= \text{Rate of appearance of D} = \frac{+1}{q} \frac{d[D]}{dt}$$

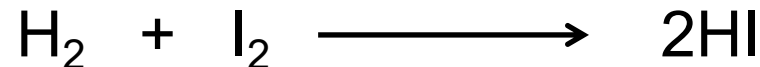
Determination of Rate



$$\text{rate} = -\frac{d[\text{Zn}]}{dt} = -\frac{d[\text{H}_2\text{SO}_4]}{dt} = \frac{d[\text{ZnSO}_4]}{dt} = \frac{d[\text{H}_2]}{dt}$$

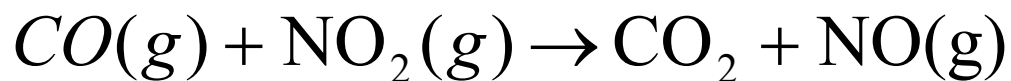


$$\text{rate} = -\frac{d[\text{N}_2]}{dt} = -\frac{1}{3} \frac{d[\text{H}_2]}{dt} = \frac{1}{2} \frac{d[\text{NH}_3]}{dt}$$



$$\text{rate} = -\frac{d[\text{H}_2]}{dt} = -\frac{d[\text{I}_2]}{dt} = \frac{1}{2} \frac{d[\text{HI}]}{dt}$$

Average Rate & Instantaneous Rate



$$\text{Average rate} = \frac{-\Delta[\text{CO}]}{\Delta t} = \frac{-d[\text{CO}]}{dt}$$

| | | | | | |
|------------------|-------|-------|-------|-------|-------|
| [CO] (mol/liter) | 0.100 | 0.067 | 0.050 | 0.040 | 0.033 |
| Time (sec) | 0 | 10 | 20 | 30 | 40 |

$$\text{Instantaneous rate} = \frac{-d[\text{CO}]_t}{dt}$$

At any time the instantaneous rate is equal to the slope of a straight line drawn tangent to the curve at that time

Average Rate & Instantaneous Rate

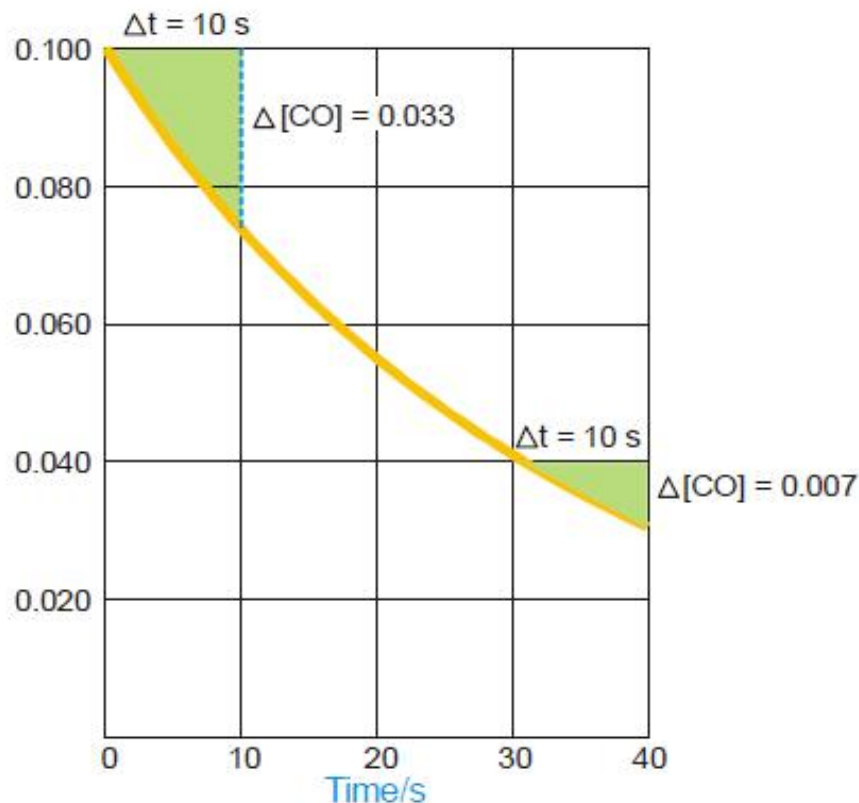


Figure 20.1

Graph of CO concentrations *versus* time. The average rate is equal to the slope of the curve. The average rates for the first 10 and the last 10 seconds are shown.

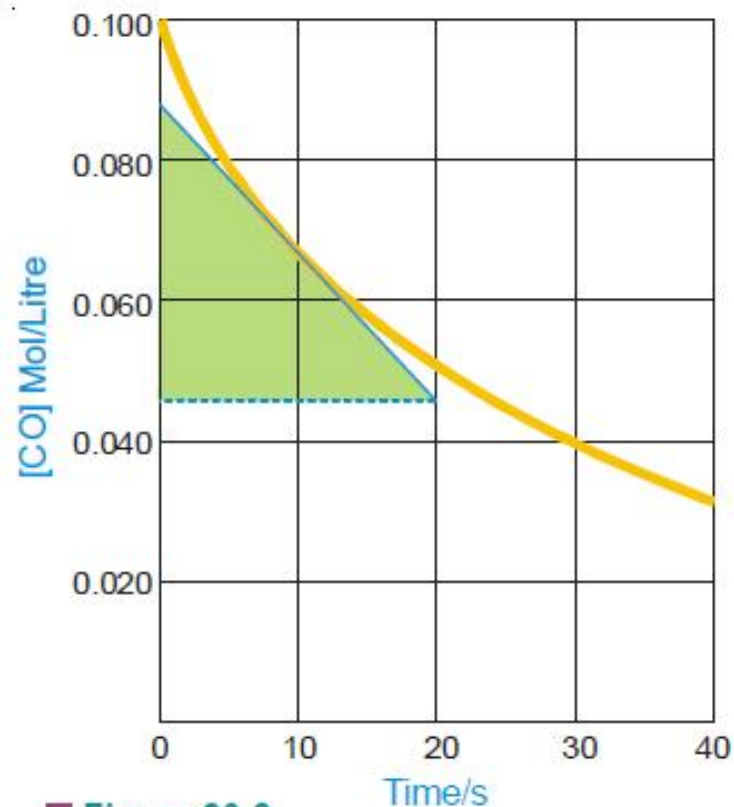


Figure 20.2

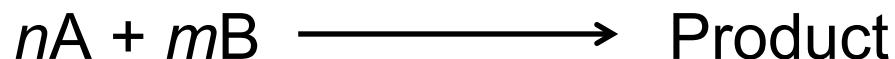
The slope of tangent at 10 seconds is equal to the instantaneous rate.

Factors influencing the rate of reaction

- **Nature of reactants & products**
e.g., solution vs gas phase
- **Concentration**
Usually increase as reactant increases.
- **Temperature**
Usually faster at higher temperature
- **Pressure**
Increases as pressure increases
- **Solvent**
- **Light**
- **Catalyst**
Speed chemical reactions

Law Mass Action & Rate of Reaction

Law of mass action states that the rate at which a substance reacts is proportional to its active mass, i.e., molar concentration and the rate of a chemical reaction is directly proportional to the product of the active masses or molar concentrations of the reactants.



$$\text{Rate} \propto [A]^n [B]^m$$

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

K is the rate constant

(Velocity constant, Velocity co-efficient or Specific reaction rate)

Rate Laws/Rate Equation

It is an expression showing the relationship between the reaction rate and the concentrations of reactants



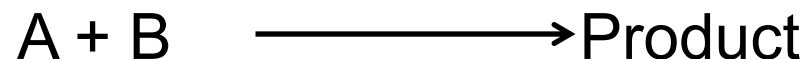
$$\text{Rate} \propto [A]^n [B]^m$$

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

K is the rate constant

(Velocity constant, Velocity co-efficient or Specific reaction rate)

Rate Constant



$$\text{Rate} \propto [A] [B]$$

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

If $[A] = [B] = 1$, then

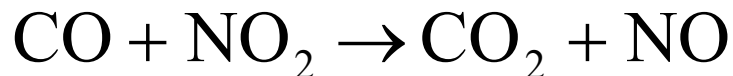
$$\text{Rate} = k \times 1 \times 1 = k$$

Thus, rate constant of a reaction may be defined as the rate of reaction when the concentration of each of the reactants is unity at a given temperature

Characteristics of k

- Different value for different reactions.
- A measure of rate of reaction.
- Independent of reactant concentration.
- Varies with change in temperature.

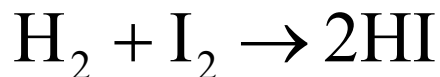
More Examples



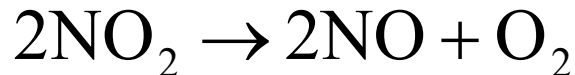
$$\text{Rate} = k[\text{CO}][\text{NO}_2]$$



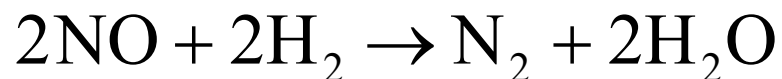
$$\text{Rate} = k[\text{N}_2\text{O}_5]$$



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



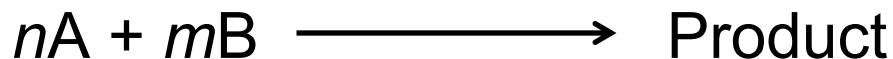
$$\text{Rate} = k[\text{NO}_2]^2$$



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

Order of a Reaction

The sum of the powers of concentrations in the rate law



$$\text{Rate} \propto [A]^m [B]^n$$

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

$$\text{Order of the reaction} = m + n$$

$m + n = 0$, a zero order reaction

$m + n = 1$, a first order reaction

$m + n = 2$, a second order reaction

$m + n = 3$, a third order reaction

Molecularity of a Reaction

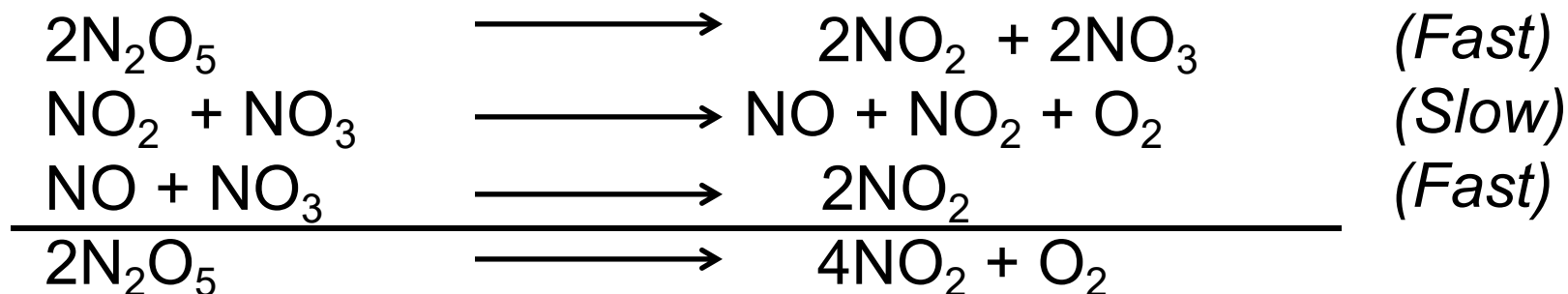
The number of reactant molecules involved in a reaction

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

Bimolecular reactions $A + B \longrightarrow \text{Product}$

Termolecular reactions $A + B + C \longrightarrow \text{Product}$

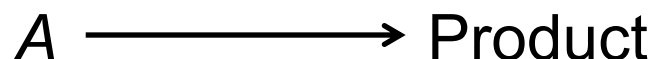
The decomposition of N_2O_5



| <u>Order of a reaction</u> | <u>Molecularity of a reaction</u> |
|--|---|
| Sum of the power of the concentration terms in the rate law. | Number of reacting species involved in a simple reaction. |
| Experimentally determined. | A theoretical concept |
| Can have fractional value. | Always a whole number |
| Can have zero value. | Do not have zero value |
| Can be changed with reaction conditions. | Can not be changed with reaction conditions. |
| For a complex reaction, the slowest step gives the order of the reaction | For a complex reaction, each step has its own molecularity. |

Zero Order Reaction

The rate is independent of reactant concentrations.



Initial conc. a 0

Final conc. a-x x

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

$$\frac{dx}{dt} = \frac{-d(a-x)}{dt} = k(a-x)^0 = k$$

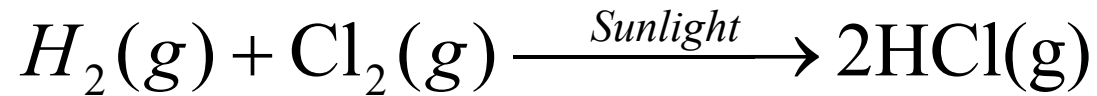
$$\int dx = \int k dt$$

$$x = kt \quad \text{or} \quad k = \frac{x}{t}$$

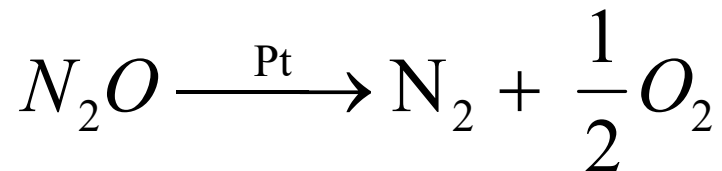
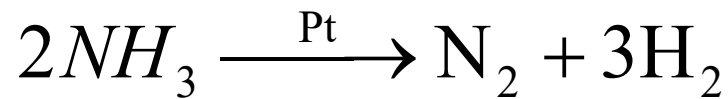
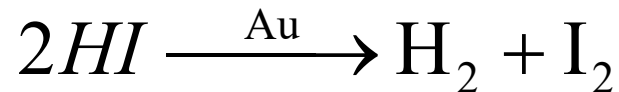
Unit of k = concentration per unit time

Examples of Zero Order Reaction

Photochemical reactions:

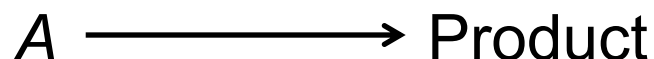


Heterogeneous reactions:



First Order Reaction

Rate is determined by the change of only one concentration term



| | | |
|---------------|-----|---|
| Initial conc. | a | 0 |
| Final conc. | a-x | x |

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

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

$$\frac{dx}{a-x} = kdt$$

First Order Reaction

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

$-\ln (a-x) = kt + I$, I is the constant of integration

If $t = 0$ and $x = 0$
 $I = -\ln a$

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

$$k = \frac{1}{t} \ln \frac{a}{a-x}$$

$$k = \frac{2.303}{t} \log \frac{a}{a-x}$$

Unit of k = (time)⁻¹

Examples of First Order Reaction

Decomposition of N_2O_5 in CCl_4 solution:



$$k = \frac{2.303}{t} \log_{10} \frac{V_{\infty}}{V_{\infty} - V_t}$$

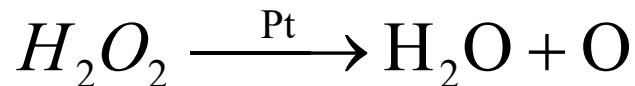
Problem:

From the following data for the decomposition of N_2O_5 in CCl_4 solution at 48 °C, show that it is a first order reaction.

| | | | | | |
|-----------|------|------|-------|------|----------|
| t (mins) | 10 | 15 | 20 | 25 | ∞ |
| V_{O_2} | 6.30 | 8.95 | 11.40 | 13.5 | 34.75 |

Examples of First Order Reaction

Decomposition of H_2O_2 in aqueous solution:



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

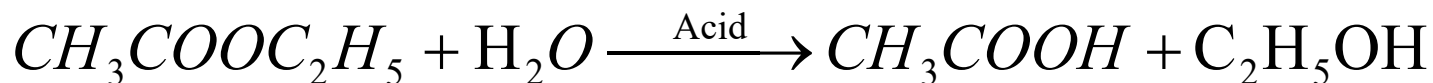
Problem:

The catalysed decomposition of H_2O_2 in aqueous solution is followed by titrating equal volume of sample solutions with KMnO_4 solution at different time interval give the following results. Show that the reaction is a first order reaction.

| | | | | | |
|---------------------|----|------|------|------|-----|
| t (mins) | 0 | 5 | 15 | 25 | 45 |
| V_{KMnO_4} | 37 | 29.8 | 19.6 | 12.3 | 5.0 |

Examples of First Order Reaction

Acid Hydrolysis of a Ester:



$$k = \frac{2.303}{t} \log_{10} \frac{V_{\infty} - V_0}{V_{\infty} - V_t}$$

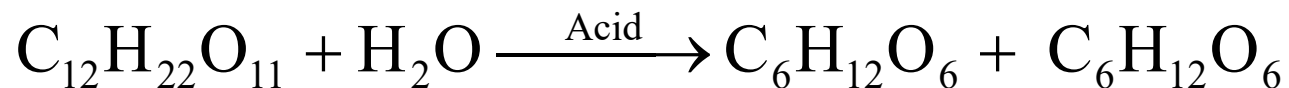
Problem:

The following data was obtained on hydrolysis of methyl acetate at 25 °C in 0.2N HCl. Show that it is a first order reaction.

| | | | | | |
|---------------------|-------|-------|-------|-------|----------|
| t (mins) | 0 | 75 | 119 | 180 | ∞ |
| V _{alkali} | 19.24 | 24.20 | 26.60 | 29.32 | 42.03 |

Examples of First Order Reaction

Inversion of Cane sugar:



$$k = \frac{2.303}{t} \log_{10} \frac{r_0 - r_\infty}{r_t - r_\infty}$$

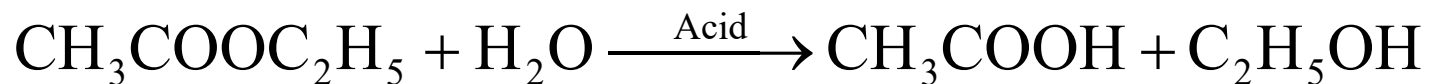
Problem:

The optical rotation of sucrose in 0.9N HCl at different time interval is given in the following table. Show that it is first order reaction.

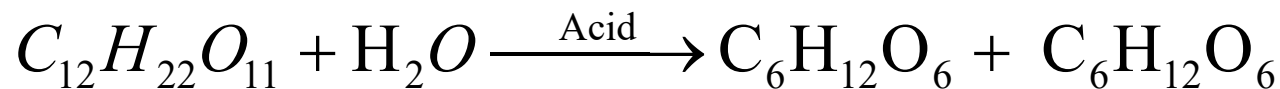
| | | | | | |
|----------|--------|-------|-------|-------|----------|
| t (mins) | 0 | 7.18 | 18 | 27.05 | ∞ |
| Rotation | +24.09 | +21.4 | +17.7 | +15 | -10.74 |

Pseudo-Order Reaction

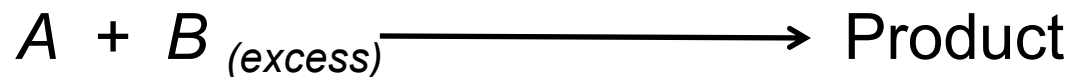
Acid Hydrolysis of a Ester:



Inversion of Cane sugar:



The experimental order which is not the actual one observed.

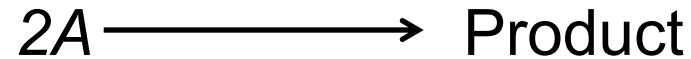


$$\text{Rate} = k [A] [B]$$

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

Second Order Reaction

Rate is determined by the change of two concentration term



Initial conc. a 0

Final conc. a-x x

$$Rate = \frac{-d[A]}{dt} = k[A]^2$$

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

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

Second Order Reaction

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

$$\frac{1}{a-x} = kt + I$$

If $t = 0$ and $x = 0$
 $I = 1/a$

$$\frac{1}{a-x} = kt + \frac{1}{a}$$

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

Unit of k = (conc.)⁻¹ (time)⁻¹

Second Order Reaction



| | | | |
|---------------|-----|-----|---|
| Initial conc. | a | b | 0 |
| Final conc. | a-x | b-x | x |

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

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

$$\Rightarrow \frac{dx}{(a-x)(b-x)} = kdt$$

Integrating,

$$k = \frac{2.303}{t(a-b)} \log \frac{b(a-x)}{a(b-x)}$$

Second Order Reaction



| | | | |
|---------------|-----|-----|---|
| Initial conc. | a | a | 0 |
| Final conc. | a-x | a-x | x |

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

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

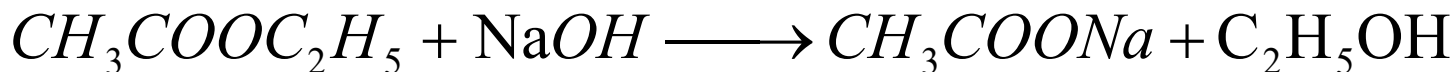
$$\Rightarrow \frac{dx}{(a-x)^2} = kdt$$

Integrating,

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

Examples of Second Order Reaction

Alkali Hydrolysis of Ester:



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

Problem:

A gram mole of ethyl acetate was hydrolysed with a gram mole of NaOH and was studied by titrating 25ml of the reaction mixture at different time interval against a standard acid. Show that the reaction is of the second order.

| | | | | | | |
|-------------------|------|-----|------|-----|------|------|
| t (mins) | 0 | 4 | 6 | 10 | 15 | 20 |
| V _{acid} | 8.04 | 5.3 | 4.58 | 3.5 | 2.74 | 2.22 |

Third Order Reaction

Let us consider a simple third order reaction of the type



Let the initial concentration of A be a moles litre⁻¹ and after time t , x , moles have reacted. Therefore, the concentration of A becomes $(a - x)$. The rate law may be written as :

$$\frac{dx}{dt} = k(a - x)^3 \quad \dots(1)$$

Rearranging equation (1), we have

$$\frac{dx}{(a - x)^3} = k dt \quad \dots(2)$$

On integration, it gives

$$\frac{1}{2(a - x)^2} = kt + I \quad \dots(3)$$

where I is the integration constant. I can be evaluated by putting $x = 0$ and $t = 0$. Thus,

$$I = \frac{1}{2a^2}$$

By substituting the value of I in (3), we can write

$$kt = \frac{1}{2(a - x)^2} - \frac{1}{2a^2}$$

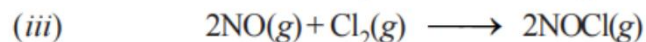
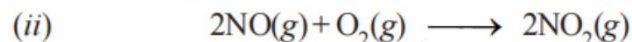
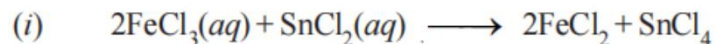
Therefore,

$$k = \frac{1}{t} \cdot \frac{x(2a - x)}{2a^2(a - x)^2}$$

This is the integrated rate equation for a third order reaction.

Examples of Third order Reactions

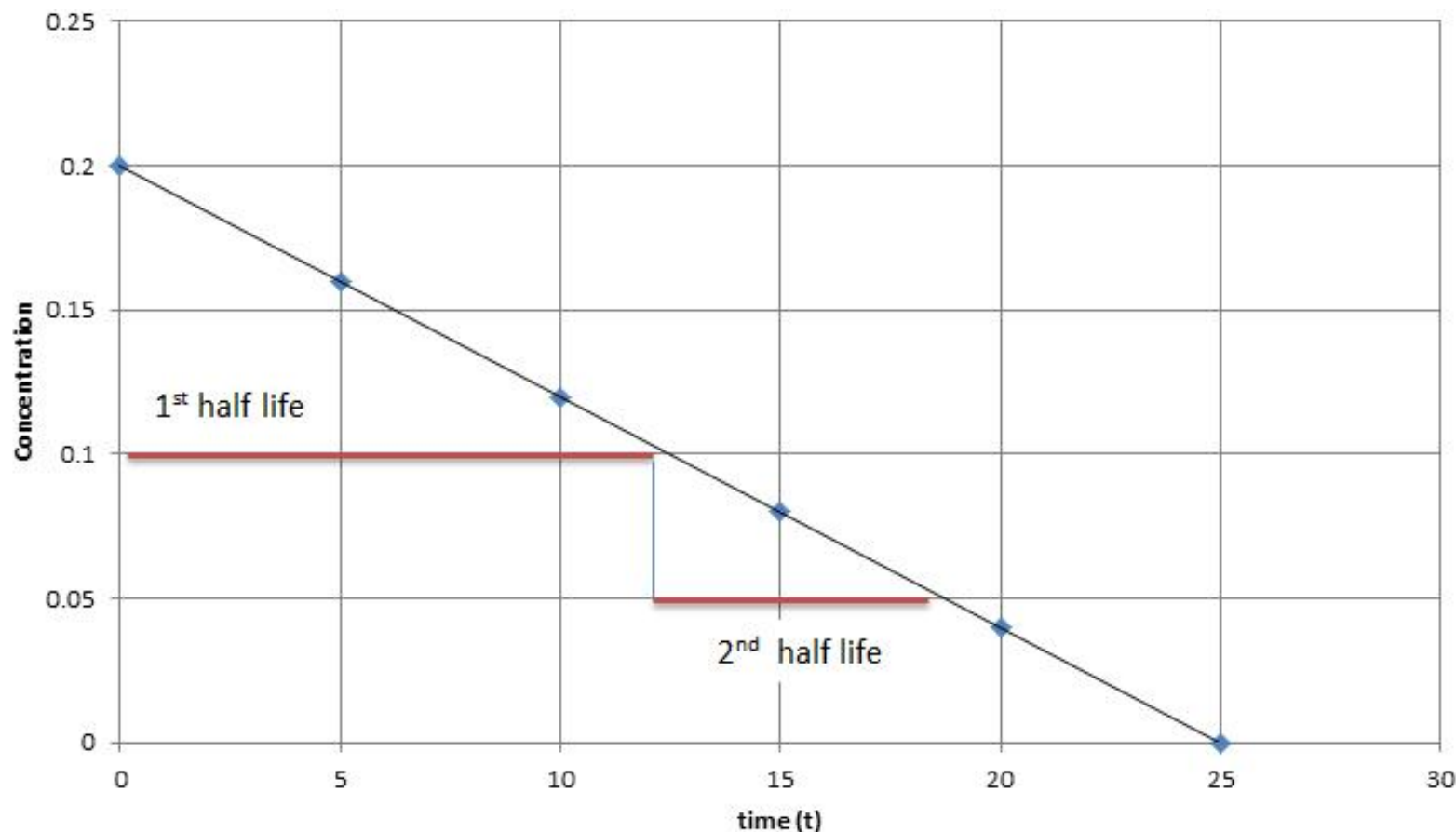
There are not many reactions showing third order kinetics.



$$\text{Unit of } k = (\text{conc.})^{-2} (\text{time})^{-1} \\ \text{mol}^{-2} \text{l}^2 \text{time}^{-1}$$

Half-Life of a Reaction ($t_{1/2}$ or $t_{0.5}$)

Half-life is another expression for reaction rate and is defined as the time required for the concentration of a reactant to decrease to half its initial value



Half-Life of a Zero-Order Reaction

As, $[A]$ at $t_{1/2}$ is one-half of the original $[A]$,

$$[A]_t = 0.5 [A]_0.$$

$$k = \frac{x}{t}$$

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

$$\Rightarrow t_{0.5} = \frac{[A]_0 - 0.5[A]_0}{k_0}$$

$$\Rightarrow t_{0.5} = \frac{[A]_0}{2k}$$

Half-Life of a First-Order Reaction

As, $[A]$ at $t_{1/2}$ is one-half of the original $[A]$,

$$[A]_t = 0.5 [A]_0.$$

$$k = \frac{2.303}{t} \log \frac{a}{a-x}$$

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

$$k = \frac{2.303}{t_{1/2}} \log \frac{[A]_0}{0.5[A]_0}$$

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

$$t_{1/2} = \frac{2.303}{k} \log 2 = \frac{2.303}{k} \times 0.3010$$

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

NOTE: For a first-order process, the half-life does not depend on $[A]_0$ and is inversely proportional to k .

Half-Life of a Second-Order Reaction

As, $[A]$ at $t_{1/2}$ is one-half of the original $[A]$,

$$[A]_t = 0.5 [A]_0.$$

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

$$kt = \frac{x}{a(a-x)} = \frac{[A]_0 - [A]}{[A]_0[A]} = \frac{1}{[A]} - \frac{1}{[A]_0}$$

$$kt_{1/2} = \frac{1}{0.5[A]_0} - \frac{1}{[A]_0} = \frac{2}{[A]_0} - \frac{1}{[A]_0}$$

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

NOTE: For a second-order process, the half-life is inversely proportional to both k and $[A]_0$.

Summarising the all.....



At Time = 0, Concentration of reactant = $[A]_0$ or a

At Time = t , Concentration of reactant = $[A]$ or $(a-x)$

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

| Order | Rate Law | Integrated Rate Law | Half-Life | Straight line Plot |
|----------|--------------|---|---|---|
| 0 | $r = k[A]^0$ | $[A] = -kt + [A]_0$ $(a-x) = -kt + a$ | $t_{0.5} = \frac{[A]_0}{2k}$ $t_{0.5} = \frac{a}{2k}$ | $[A] \text{ vs } t$ $(a-x) \text{ vs } t$ |
| 1 | $r = k[A]^1$ | $\ln[A] = -kt + \ln[A]_0$ $\ln(a-x) = -kt + \ln a$ | $t_{0.5} = \frac{0.693}{k}$ | $\ln[A] \text{ vs } t$ $\ln(a-x) \text{ vs } t$ |
| 2 | $r = k[A]^2$ | $\frac{1}{[A]} = kt + \frac{1}{[A]_0}$ $\frac{1}{(a-x)} = kt + \frac{1}{a}$ | $t_{0.5} = \frac{1}{k[A]_0}$ $t_{0.5} = \frac{1}{ka}$ | $\frac{1}{[A]} \text{ vs } t$ $\frac{1}{(a-x)} \text{ vs } t$ |

Determination of the Order of a Reaction

❑ Using integrated rate expression

- A hit-and-trial method
- Calculating the constant k

❑ Using half-life period

$$t \propto \frac{1}{[A]^{n-1}}, \text{ nth - order}$$

$$n = 1 + \frac{\log\left(\frac{t_2}{t_1}\right)}{\log\left(\frac{A_1}{A_2}\right)}$$

❑ Graphical method

Linear Fitting of rate expression:

- Zero-order, $[A]$ vs t
- 1st-order, $\ln[A]$ vs t
- 2nd-order, $1/[A]$ vs t

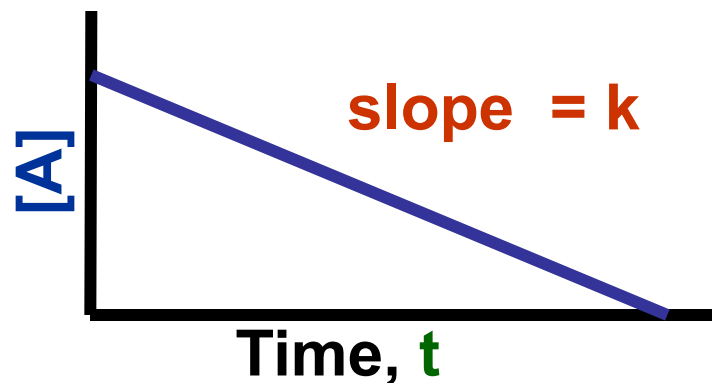
$nA \rightarrow \text{Product}$

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

0th Order $n=0$

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

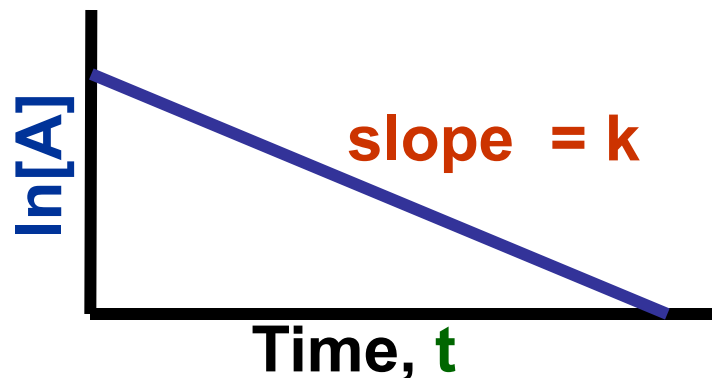
$$[A] = -kt + [A]_0$$



1st Order $n=1$

$$\text{Rate} = k[A]^1$$

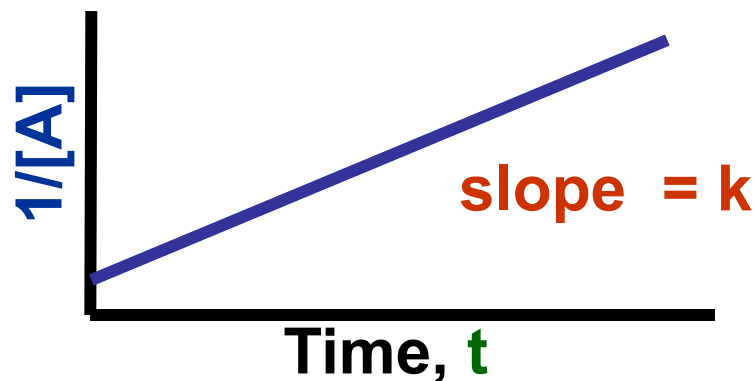
$$\ln[A] = -kt + \ln[A]_0$$



2th Order $n=2$

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

$$1/[A] = kt + 1/[A]_0$$



Determination of the Order of a Reaction

□ Van't Hoff's Differential Method

$$-\frac{dC}{dt} = kC^n$$

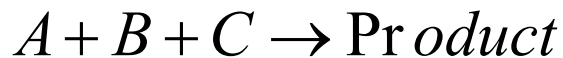
$$-\frac{dC_1}{dt} = kC_1^n \quad -\frac{dC_2}{dt} = kC_2^n$$

$$\log\left(-\frac{dC_1}{dt}\right) = \log k + n \log C_1 \quad \log\left(-\frac{dC_2}{dt}\right) = \log k + n \log C_2$$

$$\log\left(-\frac{dC_1}{dt}\right) - \log\left(-\frac{dC_2}{dt}\right) = n(\log C_1 - \log C_2)$$

$$n = \frac{\log\left(-\frac{dC_1}{dt}\right) - \log\left(-\frac{dC_2}{dt}\right)}{(\log C_1 - \log C_2)}$$

□ Ostwald's Isolation Method



$$n = n_A + n_B + n_C$$

SOLVED PROBLEM 1. Compound A decomposes to form B and C the reaction is first order. At 25°C the rate constant for the reaction is 0.450 s^{-1} . What is the half-life of A at 25°C ?

SOLUTION

We know that for a first order reaction, half-life $t_{1/2}$, is given by the expression

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

where k = rate constant

Substituting the value of $k = 0.450 \text{ s}^{-1}$, we have

$$t_{1/2} = \frac{0.693}{0.450 \text{ s}^{-1}} = \mathbf{1.54 \text{ s}}$$

Thus half-life of the reaction $A \rightarrow B + C$ is 1.54 seconds.

SOLVED PROBLEM 2. The half-life of a substance in a first order reaction is 15 minutes. Calculate the rate constant.

SOLUTION

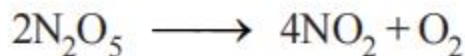
For a first order reaction

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

Putting $t_{1/2} = 15 \text{ min}$ in the expression and solving for k , we have

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{15 \text{ min}} = \mathbf{4.62 \times 10^{-2} \text{ min}^{-1}}$$

SOLVED PROBLEM 3. For the reaction



the rate is directly proportional to $[\text{N}_2\text{O}_5]$. At 45°C , 90% of the N_2O_5 reacts in 3600 seconds. Find the value of the rate constant k .

SOLUTION

Since rate is $\propto [\text{N}_2\text{O}_5]$ it is first order reaction. The integrated rate equation is

$$k = \frac{2.303}{t} \log \frac{[\text{N}_2\text{O}_5]_0}{[\text{N}_2\text{O}_5]}$$

When 90% of N_2O_5 has reacted, the initial concentration is reduced to $\frac{1}{10}$. That is,

$$[\text{N}_2\text{O}_5] = \frac{1}{10}[\text{N}_2\text{O}_5]_0$$

Substituting values in the rate equation,

$$\begin{aligned} k &= \frac{2.303}{3600} \log \frac{[\text{N}_2\text{O}_5]_0}{\frac{1}{10}[\text{N}_2\text{O}_5]_0} \\ &= \frac{2.303}{3600} \log 10 = \frac{2.303}{3600} \times 1 \end{aligned}$$

Thus

$$k = \frac{2.303}{3600} = 6.40 \times 10^{-4} \text{ s}^{-1}$$

SOLVED PROBLEM 4. The rate law for the decomposition of $\text{N}_2\text{O}_5(l)$ is : rate = $k [\text{N}_2\text{O}_5]$ where $k = 6.22 \times 10^{-4} \text{ sec}^{-1}$. Calculate half-life of $\text{N}_2\text{O}_5(l)$ and the number of seconds it will take for an initial concentration of $\text{N}_2\text{O}_5(l)$ of 0.100 M to drop to 0.0100 M.

SOLUTION

Calculation of half-life

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{6.22 \times 10^{-4} \text{ sec}^{-1}} = 1.11 \times 10^3 \text{ sec}$$

Calculation of time in seconds for drop of $[\text{N}_2\text{O}_5]$ from 0.100 M to 0.0100 M

From first order integrated rate equation,

$$t = \frac{2.303}{k} \log \frac{[\text{N}_2\text{O}_5]_0}{[\text{N}_2\text{O}_5]_t}$$

or

$$t = \frac{2.303}{k} \log \frac{[\text{N}_2\text{O}_5]_0}{[\text{N}_2\text{O}_5]_t}$$

Substituting values

$$\begin{aligned} t &= \frac{2.303}{6.22 \times 10^{-4}} \log \frac{0.100}{0.0100} \\ &= \frac{2.303}{6.22 \times 10^{-4}} \times 1 \\ &= 3.70 \times 10^3 \text{ sec} \end{aligned}$$

SOLVED PROBLEM 5. For a certain first order reaction $t_{0.5}$ is 100 sec. How long will it take for the reaction to be completed 75% ?

SOLUTION

Calculation of k

For a first order reaction

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

or
$$100 = \frac{0.693}{k}$$

$\therefore k = \frac{0.693}{100} = 0.00693 \text{ sec}^{-1}$

Calculation of time for 75% completion of reaction

The integrated rate equation for a first order reaction is

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

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

When $\frac{3}{4}$ initial concentration has reacted, it is reduced to $\frac{1}{4}$

Substituting values in the rate equation

$$\begin{aligned} t_{3/4} &= \frac{2.303}{0.00693} \log \frac{[A]_0}{\frac{1}{4}[A]_0} \\ &= \frac{2.303}{0.00693} \log 4 = \mathbf{200 \text{ sec}} \end{aligned}$$

SOLVED PROBLEM 7. 50% of a first order reaction is complete in 23 minutes. Calculate the time required to complete 90% of the reaction.

SOLUTION

Calculation of k

$$t_{0.5} = \frac{0.693}{k}$$

or
$$k = \frac{0.693}{t_{0.5}} = \frac{0.693}{23} = 0.0301304 \text{ min}^{-1}$$

Calculation of time for 90% completion of the reaction

For first order reaction, integrated rate equation is

$$k = \frac{2.303}{t} \log \frac{[A]_0}{[A]} \quad \dots(1)$$

or
$$t = \frac{2.303}{k} \log \frac{[A]_0}{[A]} \quad \dots(2)$$

When 90% of the initial concentration has reacted, 10% of it is left. That is,

$$[A] = \frac{1}{10} [A]_0$$

Substituting values in equation (2)

$$\begin{aligned} t &= \frac{2.303}{0.0301304} \log \frac{[A]_0}{\frac{1}{10}[A]_0} = \frac{2.303}{0.0301304} \log 10 \\ &= \frac{2.303}{0.0301304} = \mathbf{76.4 \text{ min}} \end{aligned}$$

SOLVED PROBLEM. In the reduction of nitric oxide, 50% of reaction was completed in 108 seconds when initial pressure was 336 mm Hg and in 147 seconds initial pressure was 288 mm Hg. Find the order of the reaction.

SOLUTION

We know that

$$\frac{t_2}{t_1} = \left[\frac{A_1}{A_2} \right]^{n-1} \quad \dots(1)$$

where t_1 and t_2 are half-life periods and $[A_1]$ and $[A_2]$ are the corresponding initial concentrations, while n is the order of the reaction.

Taking logs of the expression (1), we have

$$n = 1 + \frac{\log [t_2 / t_1]}{\log [A_1 / A_2]} \quad \dots(2)$$

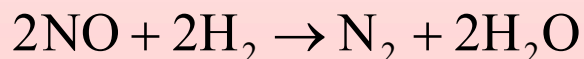
Substituting values in expression (2),

$$\begin{aligned} n &= 1 + \frac{\log 108/147}{\log 288/336} \\ &= 1 + \frac{0.1339}{0.0669} = 1 + 2 = 3 \end{aligned}$$

Therefore, the reaction is of the **third order**.

Problems

Q1. In the reduction of nitric oxide, 50% of reaction was completed in 108 sec when initial pressure was 336 mm Hg and in 147 sec initial pressure was 288 mm Hg. Find the order of the reaction.

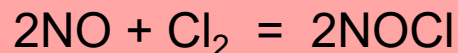


Q2. In the thermal decomposition of a gaseous substance, the time taken for the decomposition of half of the reactant was 105 min when the the initial pressure was 750 mm and 950 min when the initial pressure was 250mm. Find the order of the reaction.

Q3. The half-life for the thermal decomposition of phosphine at three different pressures are given below: Find the order of the reaction.

| | | | |
|-----------|-----|----|-----|
| P (mm Hg) | 707 | 79 | 3.5 |
| $t_{0.5}$ | 84 | 84 | 84 |

Q4. For the reaction between gaseous chlorine and nitric oxide, it is found that doubling the concentration of both reactants increases the rate eight times, but doubling the chlorine concentration alone doubles the rate. What is the order of reaction with respect to nitric oxide and chlorine?



Problems

Q5. The half-life of a chemical reaction at a particular concentration is 50 min. When the concentration is doubled, the half-life become 100 mins. Find out the order of the reaction.

Q6. The half-life of a chemical reaction at a particular concentration is 50 min. When the concentration is doubled, the half-life remains 50 mins. Find out the order of the reaction.

Q7. The half-life of a chemical reaction at a particular concentration is 50 min. When the concentration is doubled, the half-life become 25 mins. Find out the order of the reaction.

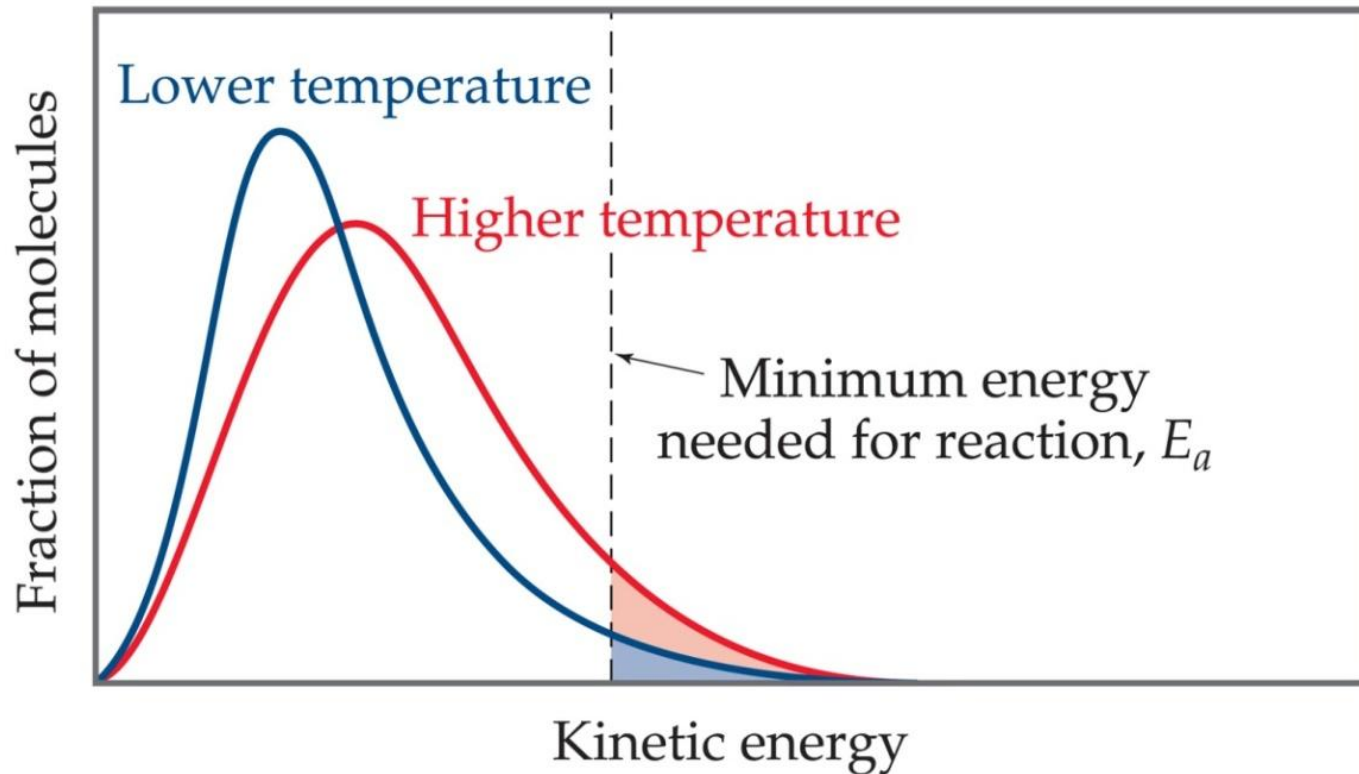
Q8. Compound A decomposes to form B and C is a first order reaction . At 25 °C the rate constant for the reaction is 0.45 s^{-1} . What is the half-life of A at this temperature.

Q9. The half-life of a substance in a first order reaction is 15 minutes. Calculate the rate constant.

Q10. For a certain first order reaction, half-life is 100 sec. How long will it take for the reaction to be completed 75% ?

Q11. 50% of a first order reaction is completed in 23 min. Calculate the time required to complete 90% of the reaction.

Temperature Effect on Reaction Rate



- A measure of the average kinetic energy of the molecules in a sample.
- At any temperature there is a wide distribution of kinetic energies.
- At higher temperatures, a larger population of molecules has higher energy.
- As the temperature increases, the fraction of molecules that can overcome the activation energy barrier increases.
- As a result, the reaction rate increases.

Temperature Effect on Reaction Rate

- Increases the rate of a reaction
- Initiate a reaction

Temperature Coefficient:

The ratio of rate constants of a reaction at two different temperatures differing by 10 degree is known as temperature coefficient. The value of temperature coefficient is generally 2 to 3.

$$\text{Temperature Coefficient} = \frac{k_{35^{\circ}}}{k_{25^{\circ}}} = \frac{k_{308}}{k_{298}} \cong 2 \text{ to } 3$$

Arrhenius Equation

In 1889 Arrhenius developed a mathematical relationship between k , T and E_a , which is known as Arrhenius equation.

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

where, A is an experimentally determined quantity

E_a is the activation energy

R is the gas constant

T is temperature in Kelvin

Taking the natural logarithm of both sides,

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

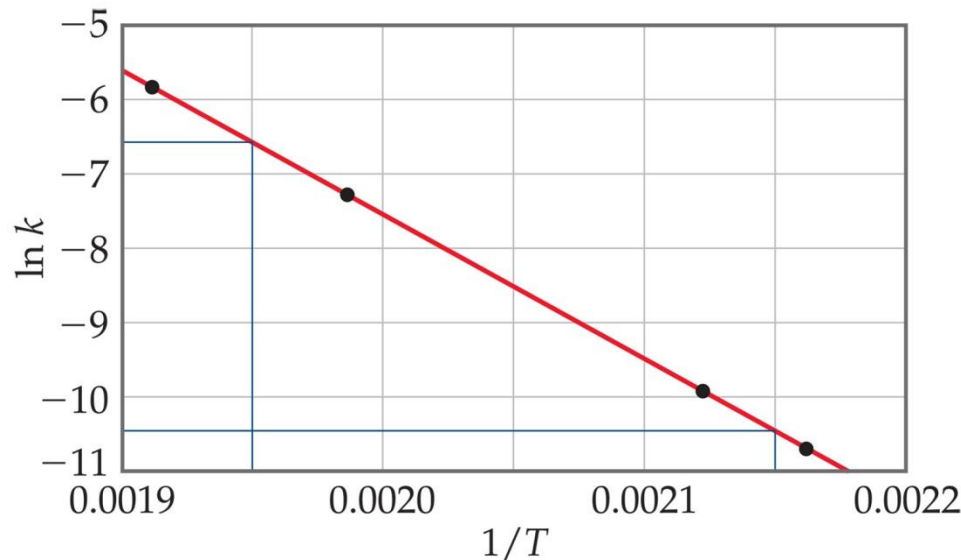
$$y = mx + b$$

k is determined experimentally at several temperatures.

Arrhenius Equation

Calculation of E_a :

E_a can be calculated from the slope of a plot of $(\ln k)$ vs $(1/T)$.



$$\text{Slope} = \frac{\Delta \ln k}{\Delta 1/T} = -\frac{E_a}{R}$$

$$\ln k = -\frac{E_a}{RT} + \ln A$$

$$\log k = -\frac{E_a}{2.303RT} + \log A$$

If k_1 and k_2 corresponds to T_1 and T_2 ,

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

SOLVED PROBLEM. The values of the rate constant (k) for the reaction $2\text{N}_2\text{O}_5(\text{g}) \longrightarrow 4\text{NO}_2(\text{g}) + \text{O}_2(\text{g})$ were determined at several temperatures. A plot of $\ln k$ versus $1/T$ gave a straight line of which the slope was found to be $-1.2 \times 10^4 \text{ K}$. What is the activation energy of the reaction ?

SOLUTION

We know that

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

$$E_a = -R \times (\text{slope})$$

Substituting the values, we have

$$\begin{aligned} E_a &= (-8.314 \text{ JK}^{-1} \text{ mol}^{-1})(-1.2 \times 10^4 \text{ K}) \\ &= 1.0 \times 10^5 \text{ J mol}^{-1} \end{aligned}$$

Thus the activation energy for the reaction is **$1.0 \times 10^5 \text{ J mol}^{-1}$**

SOLVED PROBLEM. The gas-phase reaction between methane (CH_4) and diatomic sulphur (S_2) is given by the equation



At 550°C the rate constant for this reaction is $1.1 \text{ l mol}^{-1} \text{ sec}$ and at 625°C the rate constant is $6.4 \text{ l mol}^{-1} \text{ sec}$. Calculate E_a for this reaction.

SOLUTION

Here

$$k_1 = 1.1 \text{ litre mol}^{-1} \text{ sec.} \quad T_1 = 550 + 273 = 823 \text{ K}$$

$$k_2 = 6.4 \text{ litre mol}^{-1} \text{ sec.} \quad T_2 = 625 + 273 = 898 \text{ K}$$

Substituting the values in the equation

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

$$\ln\left(\frac{6.4}{1.1}\right) = \frac{E_a}{8.3145 \text{ J K}^{-1} \text{ mol}^{-1}} \left(\frac{1}{823 \text{ K}} - \frac{1}{898 \text{ K}}\right)$$

Solving for E_a , gives

$$\begin{aligned} E_a &= \frac{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \ln\left(\frac{6.4}{1.1}\right)}{\left(\frac{1}{823 \text{ K}} - \frac{1}{898 \text{ K}}\right)} \\ &= 1.4 \times 10^5 \text{ J/mol} \end{aligned}$$

Some Problems

Q1. The value of rate constant for the decomposition of N_2O_5 were determined at several temperatures. A plot of $\ln k$ vs $1/T$ gave a straight line of which the slope was found to be $-1.2 \times 10^4 \text{ K}$. Calculate the activation energy of the reaction.

Q2. The value of rate constant for the decomposition of ethyl iodide is $1.6 \times 10^{-5} \text{ s}^{-1}$ at 327°C and $6.36 \times 10^{-3} \text{ s}^{-1}$ at 427°C . Calculate the activation energy for the reaction. ($R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$)

Q3. The rate of a particular reaction quadruples when the temperature changes from 293K to 313K . Calculate the activation energy for the same reaction.

Q4. The activation energy of a non-catalyzed reaction at 37°C is $200 \text{ kcal mol}^{-1}$ and the activation energy of the same reaction when catalyzed by an enzyme is 6 kcal mol^{-1} . Calculate the ratio of the rate constant of the catalysed and the non-catalysed reaction. Assume frequency factor to be same in both cases. ($R = 1.987 \text{ cal}$).

Theories of Reaction Rates

Collision Theory



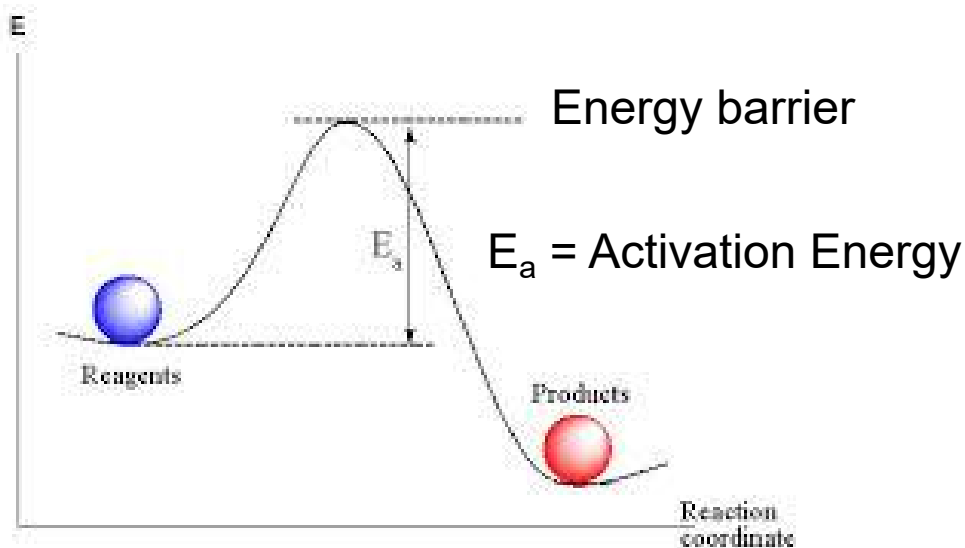
Absolute Reaction Rate Theory Or (Transition State Theory)



Collision Theory

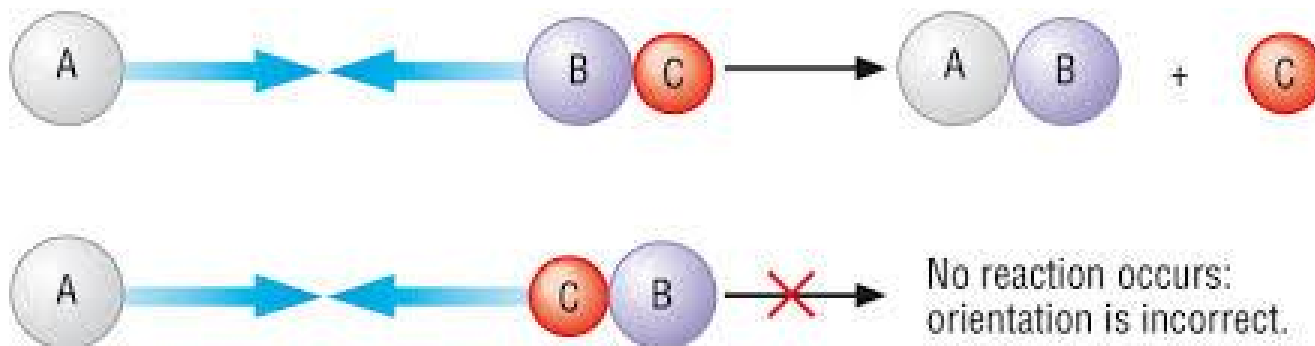
According to this theory, a chemical reaction takes place only by collisions between the reacting molecules.

- The molecules must collide with sufficient kinetic energy.



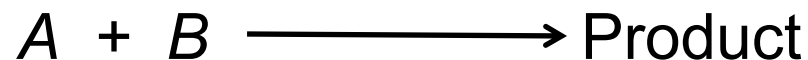
Collision Theory

- The molecules must collide with correct orientation.



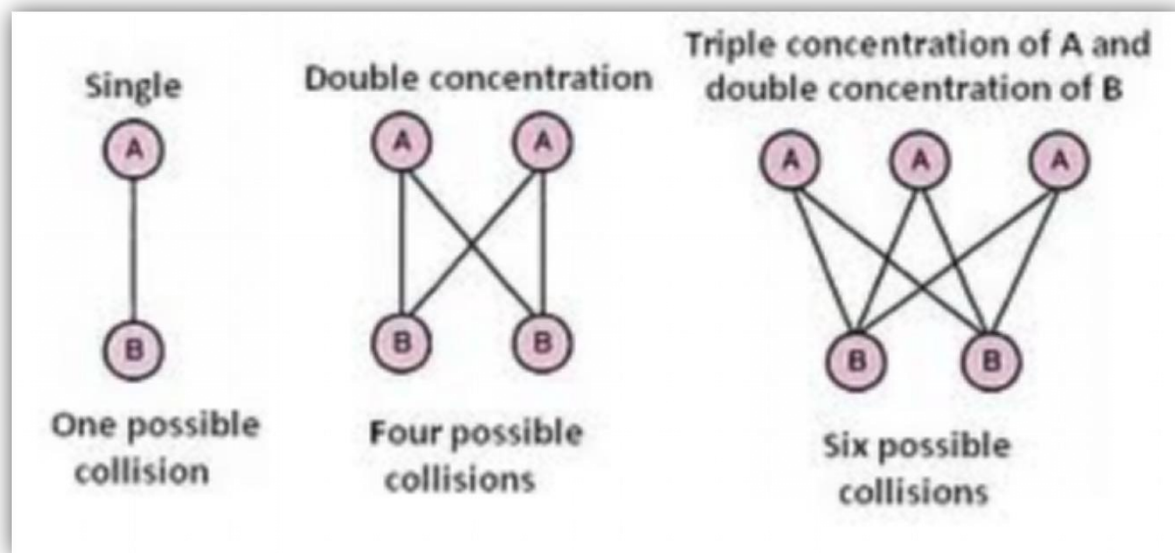
Thus, only molecules collide with kinetic energy greater than activation energy and with correct orientation can cause reaction.

Collision Theory & Reaction Rates:



$$\text{Rate} = f \times p \times z$$

Where, f = fraction molecules having sufficient kinetic energy
 p = probable fraction of molecules with effective orientation
 z = collision frequency



Mathematics Behind Collision Theory

- Collision theory is based on kinetic theory of gases
- It applies to bimolecular gaseous phase reactions
- It assumes colliding atoms are perfect spheres and collision is perfectly elastic
- The molecules must collide with correct orientation.

Lets consider a reaction



The reaction rate is given by

$$\frac{dx}{dt} = Z_{AA} e^{-E/RT} \quad \dots(1)$$

Z_{AA} is the collision frequency and is defined as the number of collision per unit volume per unit second and for 1 ml of the gas, and E is the activation energy

From Kinetic theory of gases

$$\frac{dx}{dt} \propto n_A^2 \quad \text{or} \quad \frac{dx}{dt} = kn_A^2$$

Where k is the rate constant, and n_A is the concentration

Now, comparing eqn (1) and (2)

$$k = \frac{Z_{AA}}{n_A^2} e^{-E/RT} \quad \dots(3)$$

Mathematics Behind Collision Theory

The collision frequency from kinetic theory of gases is given by

$$Z_{AA} = \frac{1}{2} (\pi \sigma_{AA}^2) \left(\frac{16kT}{\pi m_A} \right)^{1/2} n_A^2$$

Where σ_{AA} is the collision cross section

k is the Boltzmann Constant

T is the temperature

n_A is the number of molecules per unit volume

m_A is mass of A

- For simple molecule the Eqn 3 is valid, but not true for complex molecules
- For complex molecules the experimental rate constant is smaller than the theoretical predicted values,
- This is because the kinetic theory considers all the collisions are effective. This is not true as the collisions need to be properly oriented.

$$k = P \frac{Z_{AA}}{n_A^2} e^{-E/RT}$$

The correction suggested to this is

Where p is the probability factor or steric factor that takes care of the orientation

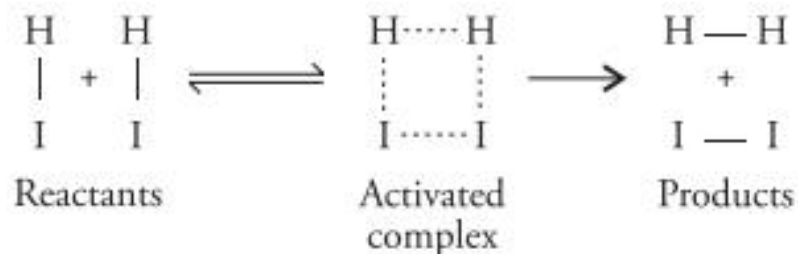
Limitation of the Collision Theory

- Applicable to simple gaseous reaction
- Good for simple bimolecular reaction
- Only kinetic energy is considered
- Silent for bond cleavage and bond formation
- No method to calculate Probability factor or Steric factor

Transition State or Absolute Reaction Rate Theory

This theory proposed by Pelzer and Minger in 1932 and later extensively developed by Eyring and his collaborators (1935) provides a greater insight into the details of a reaction on a molecular scale. It also enables us to calculate the rate.

- (i) The reactant molecules before forming products pass through an intermediate state called the transition state or the activated complex. In this complex, the reactant and the product molecules are weakly linked.

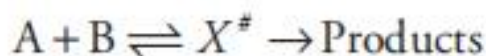


- (ii) The activated complex is an unstable state with potential energy greater than that of the reactants and products. The potential energy of the activated complex is maximum.
- (iii) Fundamental assumption of transition state theory (and one that differentiates it from collision theory) is that the reactants are always in equilibrium with the activated complex.
- $$\text{Reactants} \rightleftharpoons [\text{Activated complex}]$$

- (iv) Activated complex is like a normal molecule in every respect, but, apart from having three translational degrees of freedom, it has an additional fourth degree of freedom along the reaction coordinate. The activated complex decomposes along the fourth degree of freedom to form the products.

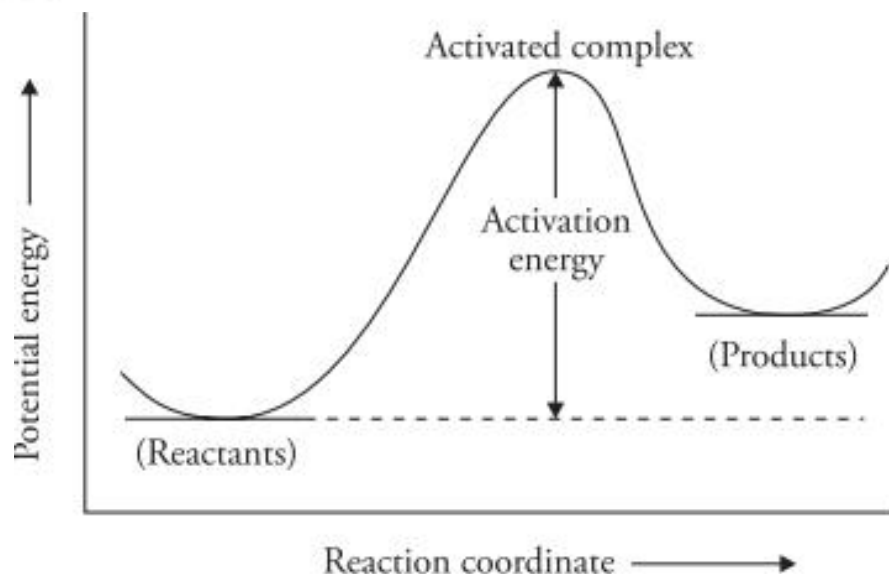
[Activated complex] \rightarrow Products

The above postulates can be put as



A and B are reactants and X^{\ddagger} represent the activated complex.

- (v) The energy changes in the conversion of reactants to products via the activated complex are represented in Figure



The rate of reaction is equal to the concentration of the activated complex at the top of the energy barrier multiplied by the frequency ν of crossing the barrier.

Rate of reaction = number of activated complexes decomposing to form the product

$$\text{Rate of reaction} = \nu [X^\ddagger] \quad (5)$$

The value of $[X^\ddagger]$ can be obtained by considering the equilibrium between the reactants and the activated complex.

$$k^\ddagger = \frac{[X^\ddagger]}{[A][B]} \quad \text{or} \quad [X^\ddagger] = k^\ddagger [A][B]$$

k^\ddagger = equilibrium constant

$[A]$ and $[B]$ = concentration of the reactants

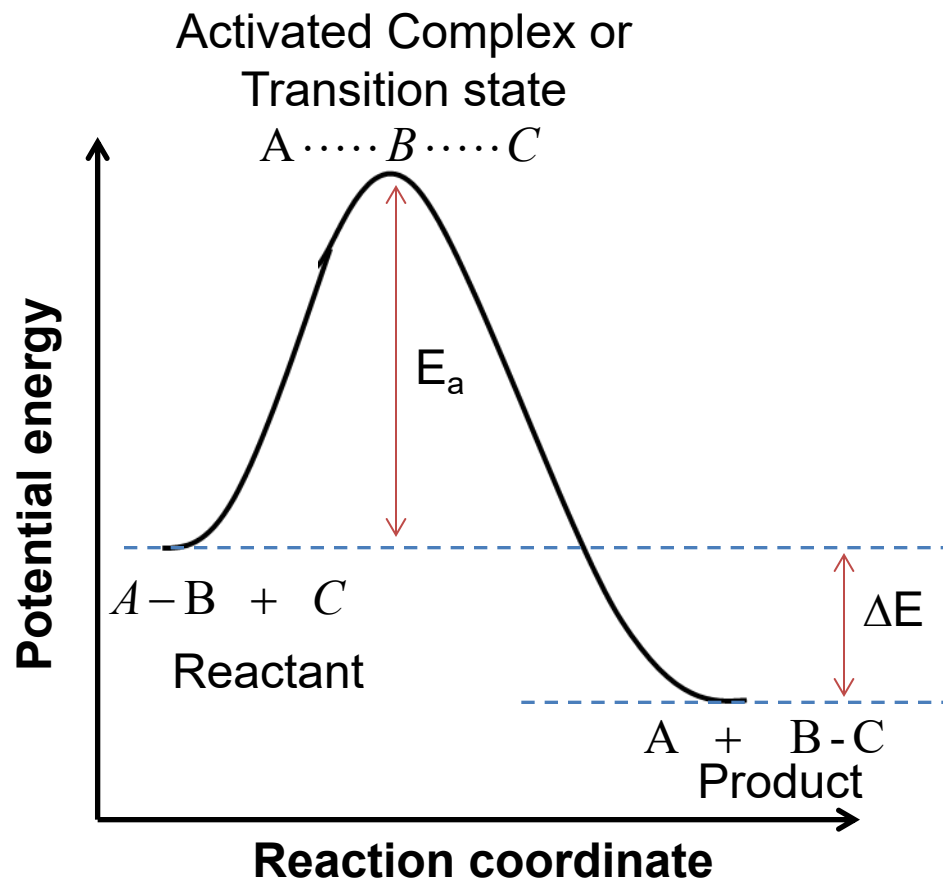
Placing the values of $[X^\ddagger]$ in Eq. (5), we have

$$\begin{aligned} \text{Rate} &= \nu k^\ddagger [A][B] \\ &= k [A][B] \end{aligned}$$

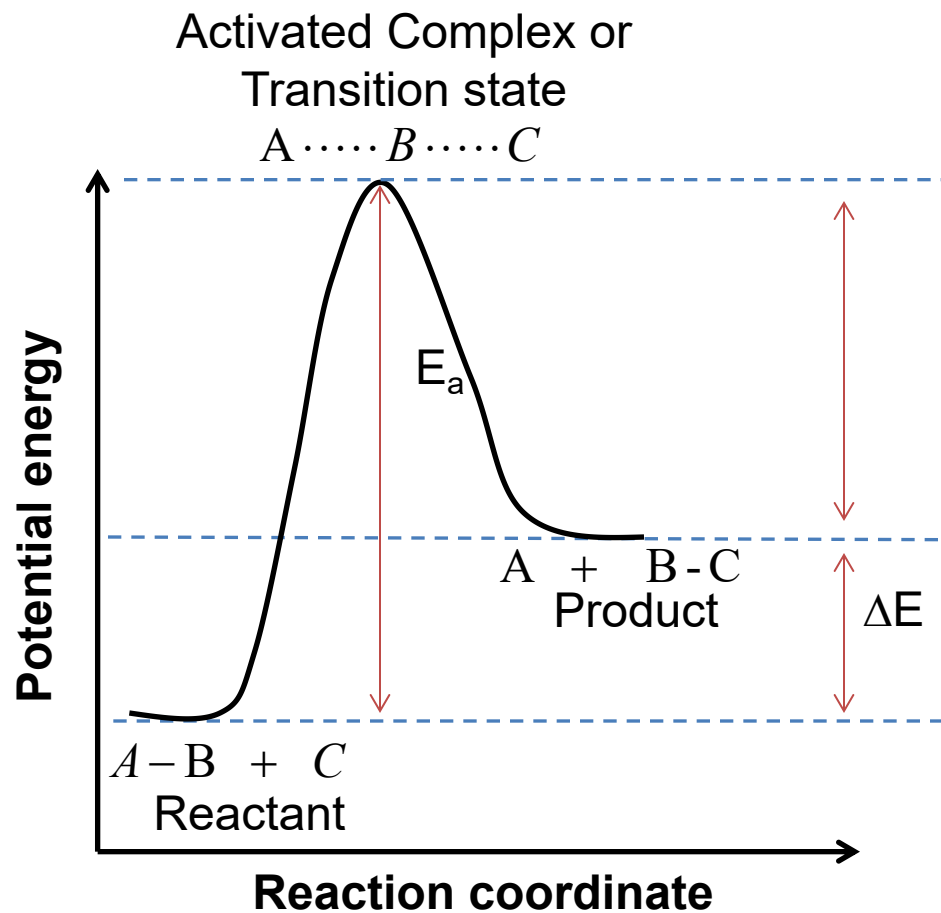
where $k = \nu k^\ddagger$

Thus, the rate can be calculated if the value of ν and k^\ddagger are known.

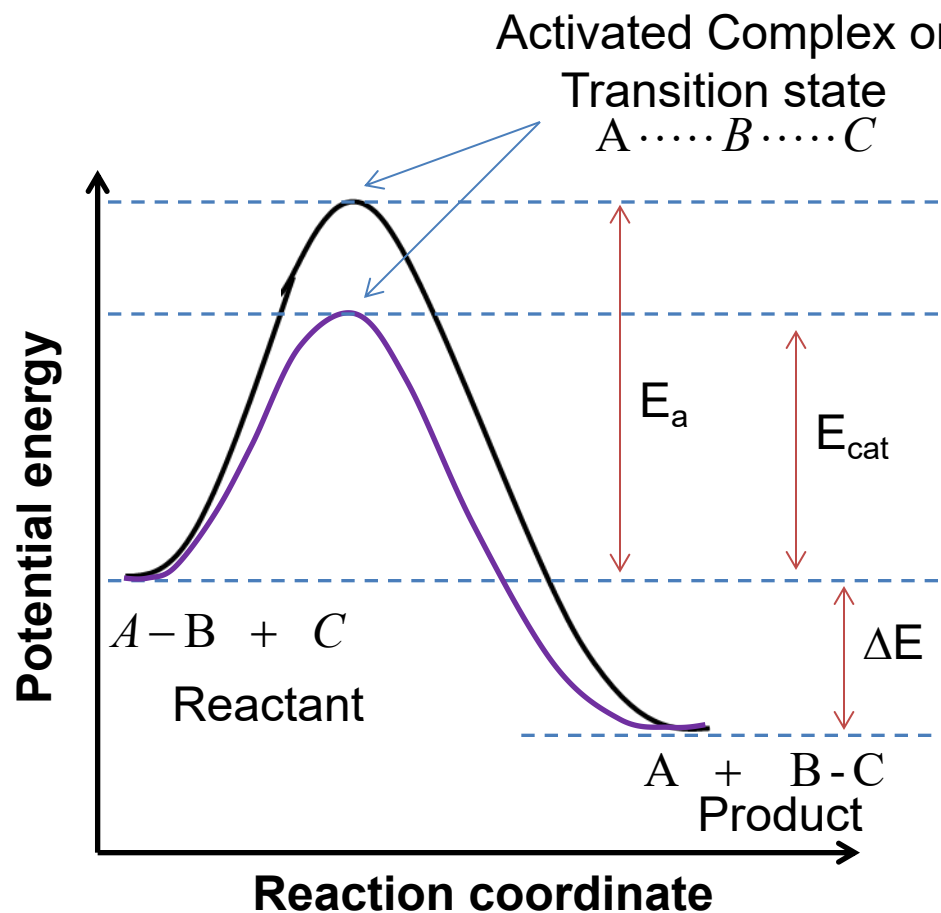
Reaction Energy Diagram for an Exothermic Reaction



Reaction Energy Diagram for an Endothermic Reaction



Activation Energy and Catalysis



Consecutive Reactions



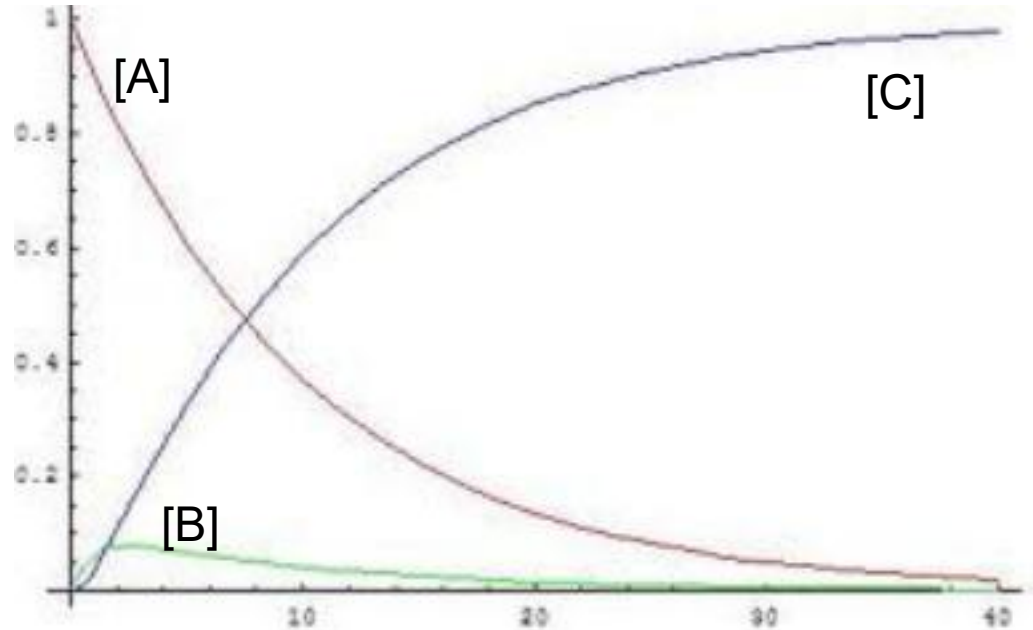
| | | | |
|--------------|---------|-------|-------|
| At $t = 0$, | $[A]_0$ | 0 | 0 |
| At $t = t$, | $[A]$ | $[B]$ | $[C]$ |

$$[A]_0 = [A] + [B] + [C]$$

$$\frac{-d[A]}{dt} = k_1[A]$$

$$\frac{d[B]}{dt} = k_1[A] - k_2[B]$$

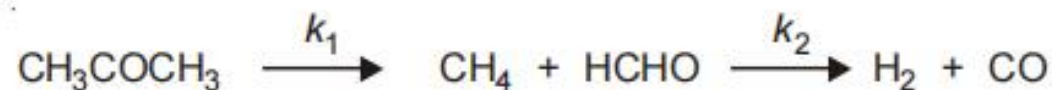
$$\frac{d[C]}{dt} = k_2[B]$$



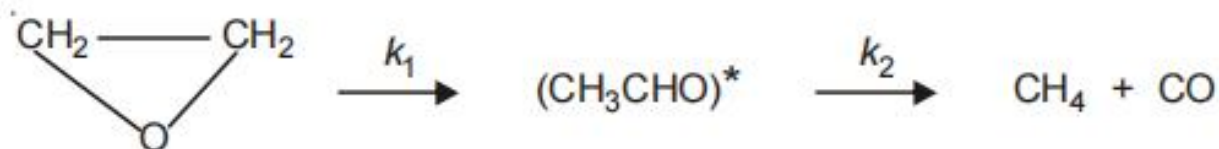
It is clear that the concentration of A decreases exponentially, the concentration of B first increases and then decreases and that of C increases (from zero) with time and finally attains the value equal to $[A]_0$ (initial concentration A) when all A has changed into the final product C.

Examples of First Order Consecutive Reactions

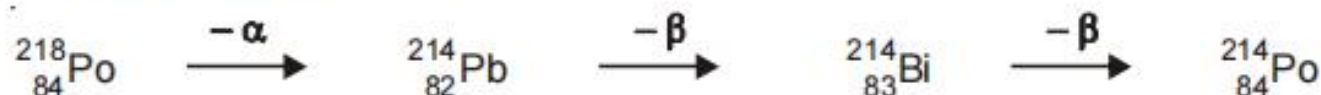
(a) Decomposition of dimethyl ether in gaseous phase



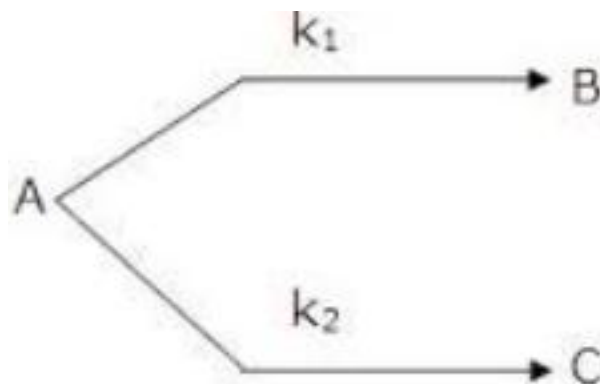
(b) Decomposition of Ethylene oxide



(c) Any radioactive decay of the type



Parallel or Side Reactions



$$r_1 = k_1[A]$$

$$r_2 = k_2[A]$$

$$\frac{-d[A]}{dt} = r_1 + r_2 = k_1[A] + k_2[A]$$

$$\frac{-d[A]}{dt} = (k_1 + k_2)[A]$$

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

$$r_1 = k_1[A]$$

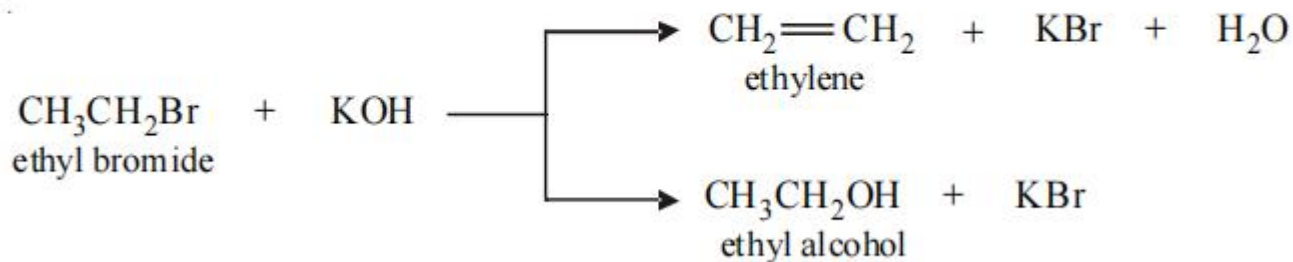
$$r_2 = k_2[A]$$

$$\frac{r_1}{r_2} = \frac{k_1[A]}{k_2[A]} = \frac{k_1}{k_2}$$

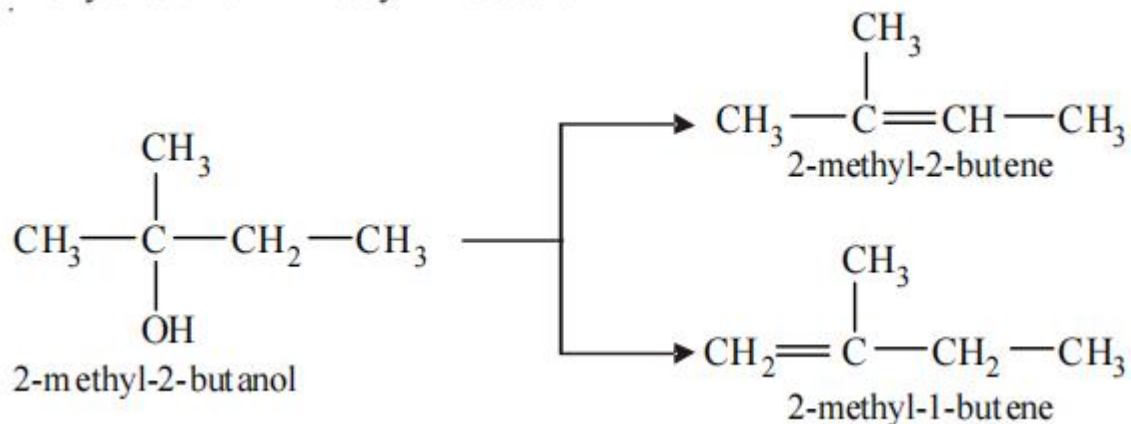
$$\frac{r_1}{r_2} = \frac{k_1}{k_2}$$

Examples of Parallel or Side Reactions

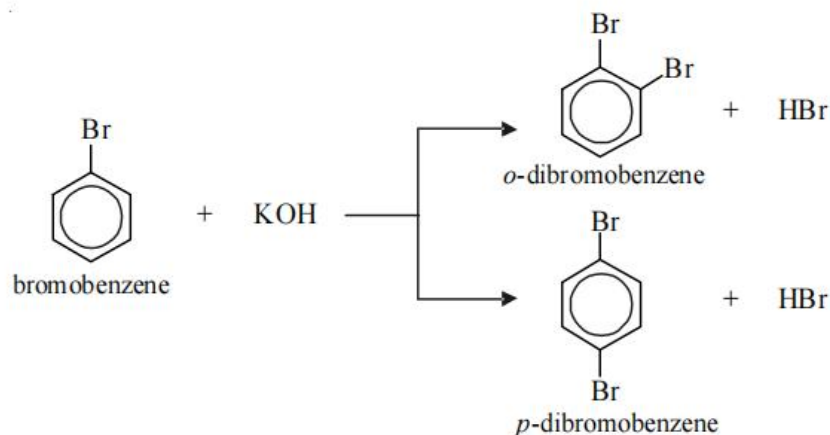
(a) Reaction of ethyl bromide with potassium hydroxide



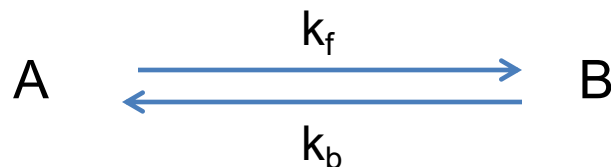
(b) Dehydration of 2-methyl-2-butanol



(c) Bromination of bromobenzene



Riversible or Opposing Reactions



| | | |
|--------------|---------|-------|
| At $t = 0$, | $[A]_0$ | 0 |
| At $t = t$, | $[A]$ | $[B]$ |

$$\frac{-d[A]}{dt} = \frac{d[B]}{dt} = \frac{dx}{dt} = k_f[A] - k_b[B]$$

$$\frac{dx}{dt} = k_f[A] - k_b[B]$$

$$\frac{dx}{dt} = k_f([A]_0 - x) - k_b x$$

$$\text{At equilibrium, } \frac{dx}{dt} = 0 \quad \& \quad x = x_{eq}$$

$$0 = k_f([A]_0 - x_{eq}) - k_b x_{eq}$$

$$\Rightarrow k_b x_{eq} = k_f([A]_0 - x_{eq})$$

$$\Rightarrow k_b = k_f \frac{([A]_0 - x_{eq})}{x_{eq}}$$

$$\frac{dx}{dt} = k_f([A]_0 - x) - k_f \left(\frac{[A]_0 - x_{eq}}{x_{eq}} \right) x$$

Integrating this equation between the limits $t=0, x=0$ and $t=t, x=x_{eq}$, we have

$$\begin{aligned} \int_0^x \frac{dx}{x_{eq} - x} &= k_f \frac{[A]_0}{x_{eq}} \int_0^t dt \\ &= -\ln(x_{eq} - x) + \ln x_{eq} = k_f \frac{[A]_0}{x_{eq}} t \end{aligned}$$

or

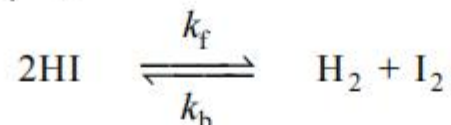
$$\ln \frac{x_{eq}}{x_{eq} - x} = k_f \frac{[A]_0}{x_{eq}} t$$

From this equation we can find the value of k_f from the quantities $[A]_0, x_{eq}$ and x at time t . All these quantities can be measured easily. From the value of k_f the value of k_b can be calculated by using the relation.

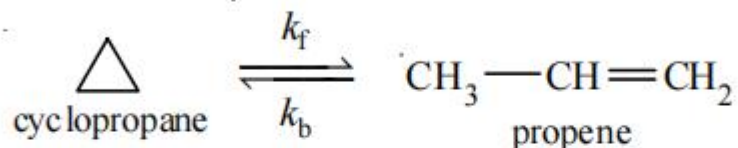
$$k_b = k_f \left(\frac{[A]_0 - x_{eq}}{x_{eq}} \right)$$

Examples of Opposing Reactions

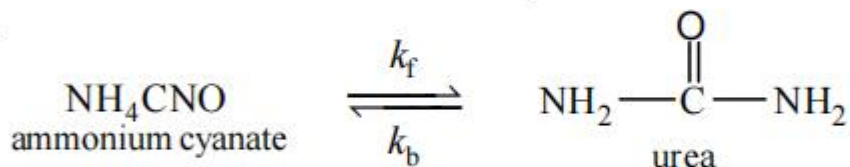
(a) Dissociation of hydrogen iodides



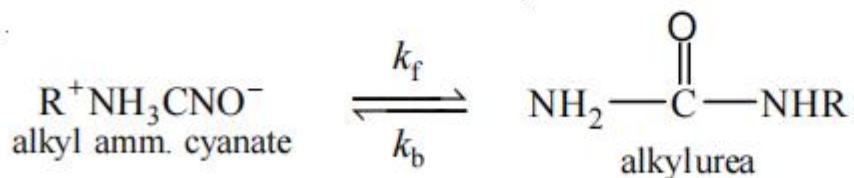
(b) Isomerisation of cyclopropane into propene



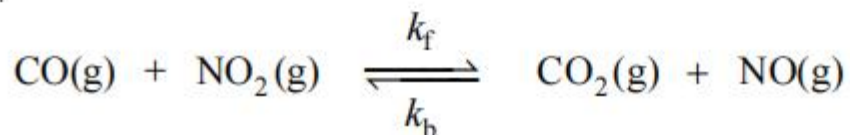
(c) Isomerisation of ammonium cyanate into urea in aqueous solution.



(d) Isomerisation of alkyl ammonium cyanate into substituted urea in aqueous solution

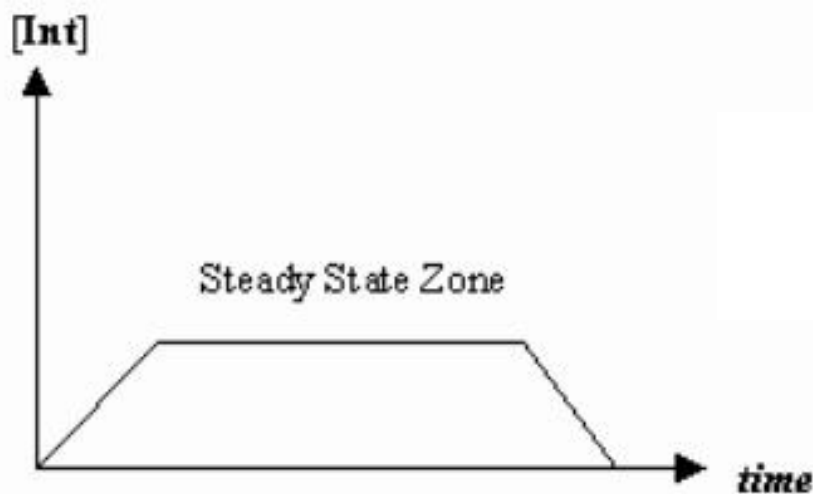


(e) Reaction between gaseous CO and NO₂



The Steady-State Approximation

- The **steady-state approximation** is a method used to derive a rate law.
- The method is based on the assumption that one intermediate in the reaction mechanism is consumed as quickly as it is generated. Its concentration remains the same in a duration of the reaction.
- When a reaction involves one or more intermediates, the concentration of one of the intermediates remains constant at some stage of the reaction. Thus, the system has reached a **steady-state**. The concentration of one of the intermediates, varies with *time* as shown in Figure . At the start and end of the reaction, [Int] does vary with time.
- When a reaction mechanism has several steps with comparable rates, the rate-determining step is not obvious. However, there is an intermediate in some of the steps. The steady-state approximation implies that you select an intermediate in the reaction mechanism, and calculate its concentration by assuming that it is consumed as quickly as it is generated.



$$\frac{d[Int]}{dt} = 0$$

Use the steady-state approximation to derive the rate law for this reaction



assuming it follows the following three-step mechanism:



In these steps, NO and NO₃ are intermediates. You have

$$\begin{aligned}\text{production rate of NO} &= k_2[\text{NO}_3][\text{NO}_2] \\ \text{consumption rate of NO} &= k_3[\text{NO}_3][\text{NO}]\end{aligned}$$

A steady-state approach makes use of the assumption that the rate of production of an intermediate is equal to the rate of its consumption. Thus, we have

$$k_2[\text{NO}_3][\text{NO}_2] = k_3[\text{NO}_3][\text{NO}]$$

and solving for [NO] gives the result,

$$[\text{NO}] = \frac{k_2[\text{NO}_3][\text{NO}_2]}{k_3[\text{NO}_3]} \quad (1)$$

For the other intermediate NO₃,

$$\begin{aligned}\text{production rate of NO}_3 &= k_f[\text{N}_2\text{O}_5] \\ \text{consumption rate of NO}_3 &= k_2[\text{NO}_3][\text{NO}_2] + k_3[\text{NO}_3][\text{NO}] + k_b[\text{NO}_3][\text{NO}_2]\end{aligned}$$

Applying the steady-state assumption gives:

$$k_f[\text{N}_2\text{O}_5] = k_2[\text{NO}_3][\text{NO}_2] + k_3[\text{NO}_3][\text{NO}] + k_b[\text{NO}_3][\text{NO}_2]$$

Thus,

$$[\text{NO}_3] = \frac{k_f[\text{N}_2\text{O}_5]}{k_2[\text{NO}_2] + k_3[\text{NO}] + k_b[\text{NO}_2]} \quad (2)$$

Let's review the three equations (steps) in the mechanism:

Step i. is at equilibrium and thus can not give a rate expression.

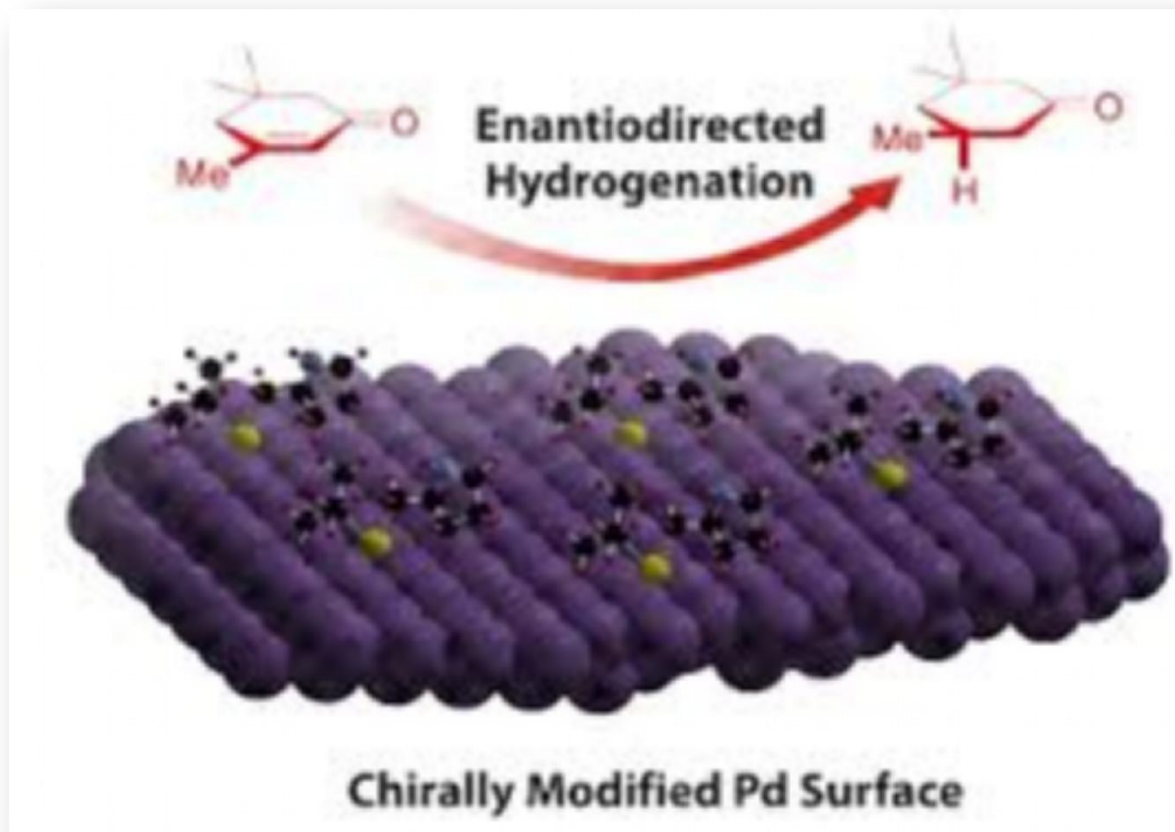
Step ii. leads to the production of some products, and the active species NO causes further reaction in step iii. This consideration led to a rate expression from step ii. as:

$$\frac{d[\text{O}_2]}{dt} = k_2[\text{NO}_3][\text{NO}_2] \quad (3)$$

Substituting (1) in (2) and then in (3) gives

$$\frac{d[\text{O}_2]}{dt} = \frac{k_f k_2 [\text{N}_2\text{O}_5]}{k_b + 2k_2} = k[\text{N}_2\text{O}_5] \quad \text{where } k = \frac{k_f k_2}{k_b + 2k_2}$$

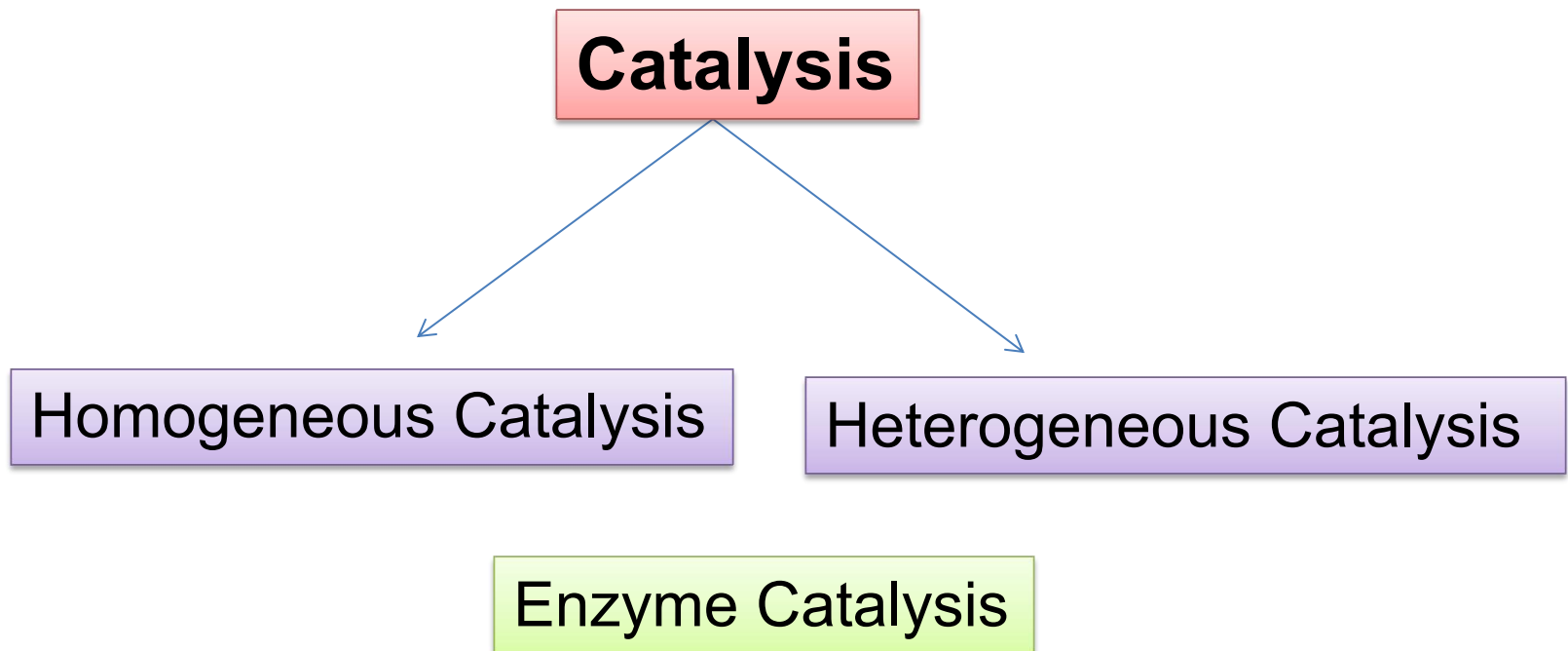
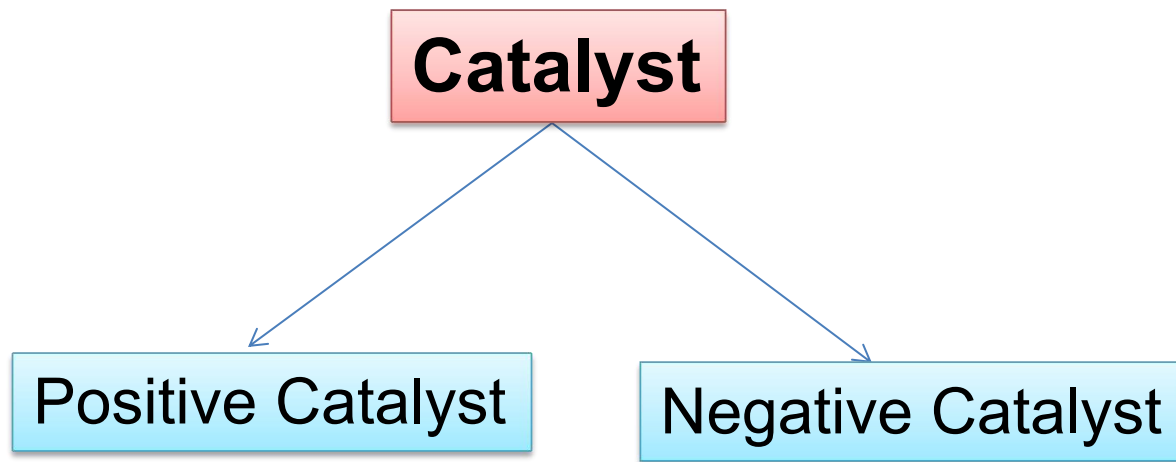
Chemical Kinetics & Catalysis



A catalyst is a substance which alters the rate of a chemical reaction, itself remaining chemically unchanged at the end of the reaction.

The process is called catalysis.

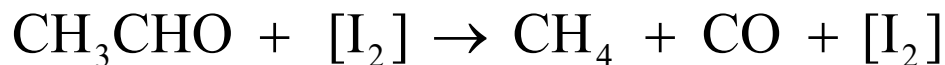
The term catalysis was introduced by J.J. Berzelius (1835).



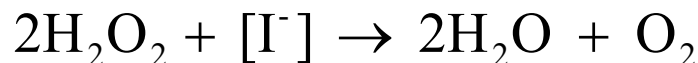
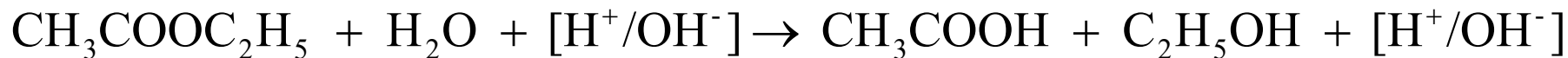
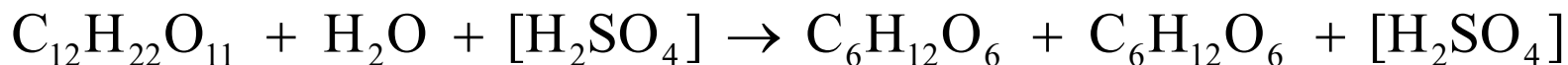
Homogeneous Catalysis

In homogeneous catalysis, the catalyst is in the same phase as the reactants and is evenly distributed throughout.

Catalysis in Gas Phase



Catalysis in Solution Phase



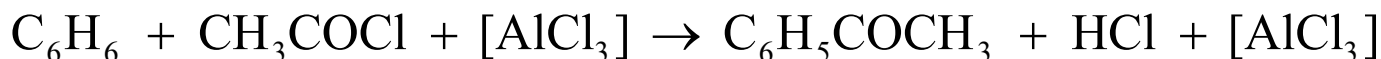
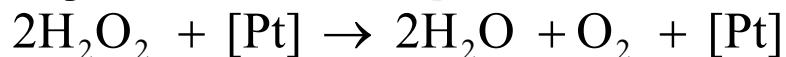
Heterogeneous Catalyst

*In heterogeneous catalysis, the catalyst is in different phase from the reactants. Also known as **Contact Catalysis**.*

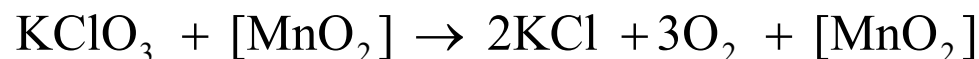
Catalysis with Gaseous Reactants



Catalysis with Liquid Reactants



Catalysis with Solid Reactants



Some Features:

Surface area

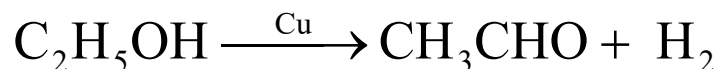
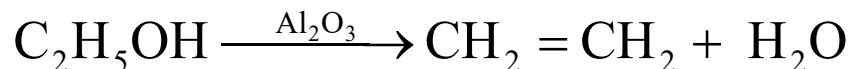
Activation energy

Promoter action

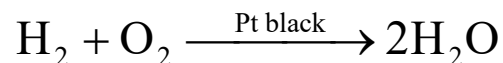
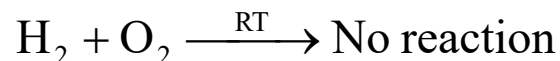
Catalytic poisons

Characteristic of Catalytic Reactions

- Remains unchanged in mass and chemical composition
- A small quantity is generally needed
- More effective when finely divided
- It is very specific



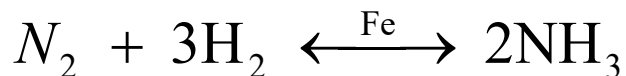
- In general, it cannot initiate a reaction



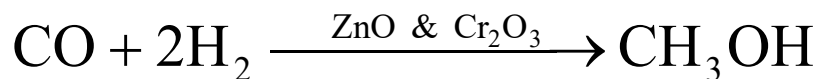
- It does not affect the equilibrium position
- Depends on temperature

Catalytic Promoter

A substance which, though itself not a catalyst, promotes the activity of a catalyst



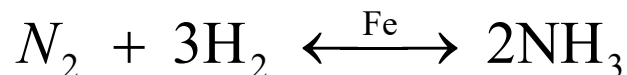
Promoter: Mo or Al_2O_3



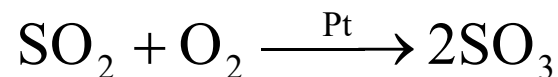
- Change of lattice spacing
- Increase of peaks and cracks

Catalytic Poison

A substance which, destroy the activity of a catalyst to accelerate a reaction



Poison: H_2S

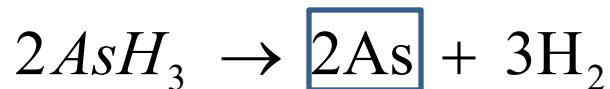


Poison: As_2O_3

- Preferential adsorption
- Chemical reaction

Autocatalyst

One of the product itself acts as a catalyst for the same reaction

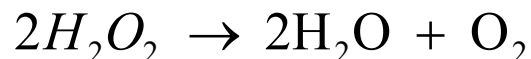


Negative Catalyst/Inhibitor

A substance, which reduces the rate of a reaction



Inhibitor: 2% ethanol

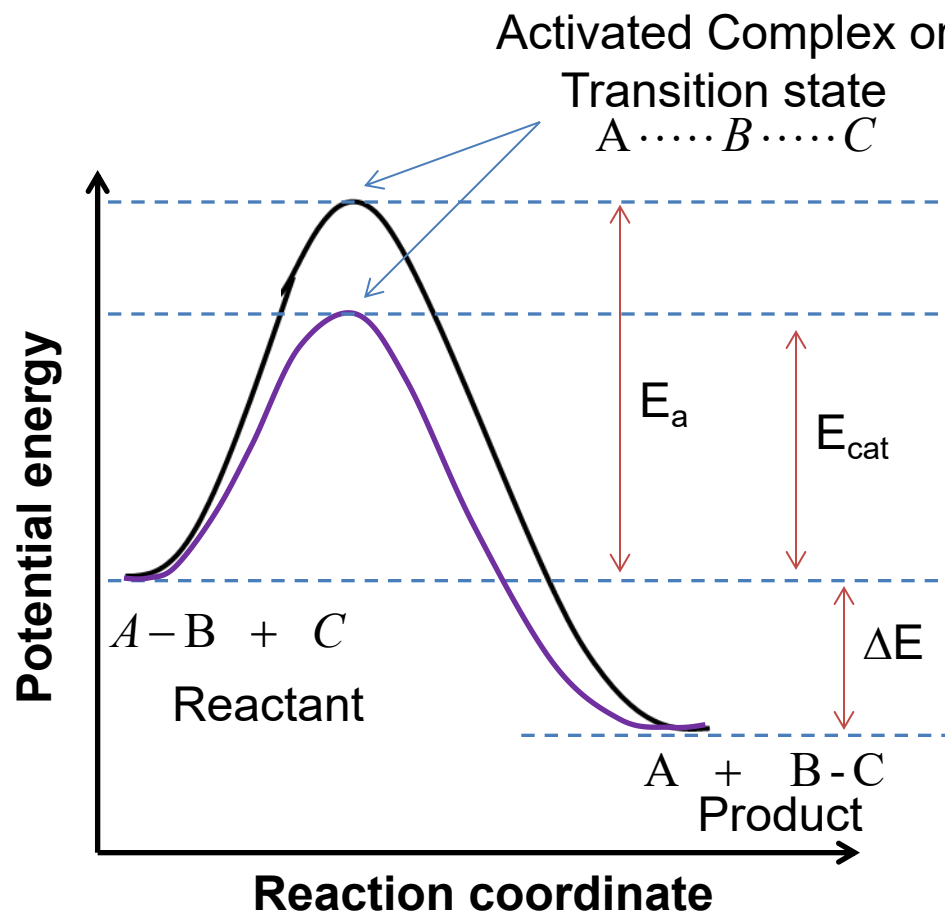


Inhibitor: Glycerol

Combustion of fuel

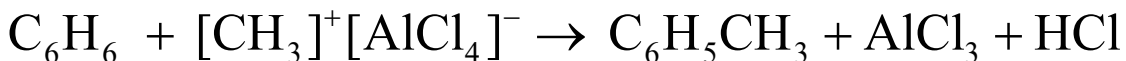
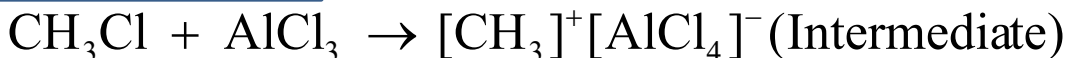
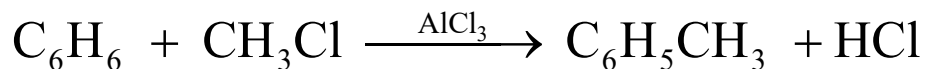
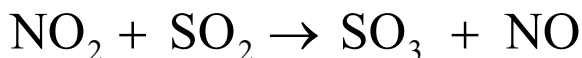
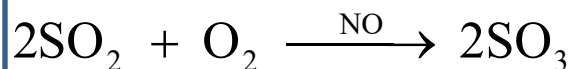
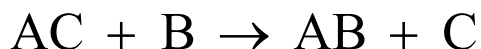
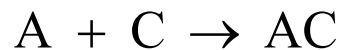
Inhibitor: $\text{Pb}(\text{C}_2\text{H}_5)_4$

Activation Energy and Catalysis



Theories of Catalysis

1. Intermediate Compound Formation Theory (For homogeneous catalysis)



Mechanism of homogeneous catalysis

Consider a homogeneous chemical reaction



The above reaction is catalysed by 'X'. According to the theory of homogeneous catalysis, the reaction proceeds as follows.

- (i) The catalyst first combines with the reactant to form an intermediate compound. This reactant with which the catalyst combines is generally termed as 'substrate'.



A is the substrate, X is the catalyst, AX is the intermediate compound and k_1 and k_2 are the velocity constants for the forward and backward reactions, respectively.

- (ii) The intermediate compound then reacts with the other reactant molecule B forming the product and the catalyst is regenerated.



The first step is fast and involves an equilibrium reaction, whereas the second step is slow. This step is the rate-determining step of the reaction.

$$\text{Rate of reaction} = k_3 [AX] [B] \quad (iii)$$

where k_3 is the velocity constant.

- (iii) The catalyst 'X' regenerated in the last step may further undergo steps (i) and (ii) to form more and more products. Thus, the rate of homogeneous catalytic reactions depends upon the concentration of the catalyst X and it is found that the rate of reaction increases with the increase in the concentration of the catalyst. This can be proved by studying the kinetics of the above reaction.

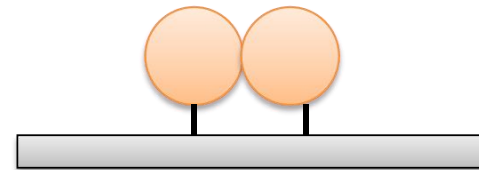
2. Adsorption Theory (For heterogeneous catalysis)

*This theory explains the mechanism of a reaction catalyzed by a solid catalyst.
The catalyst function by adsorption of the reacting molecules on its surface*

Step I: Adsorption of reactant molecules.



Step II: Formation of activated complex.

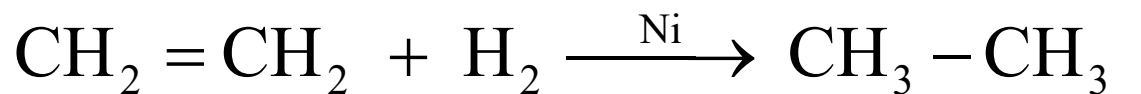


Step III: Decomposition of activated complex.

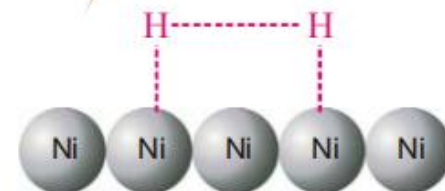


Step IV: Desorption of products.

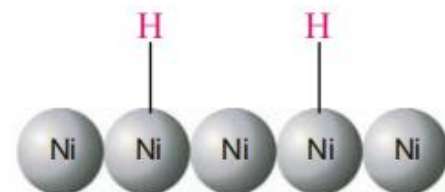




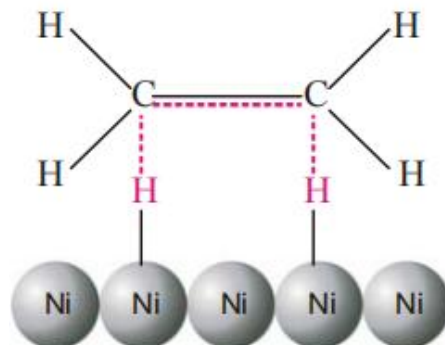
Step I: Adsorption of Hydrogen molecules.



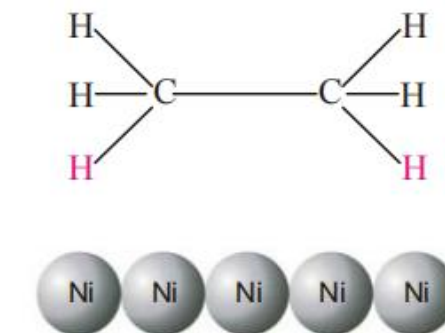
Step II: Broken of H-H bond.



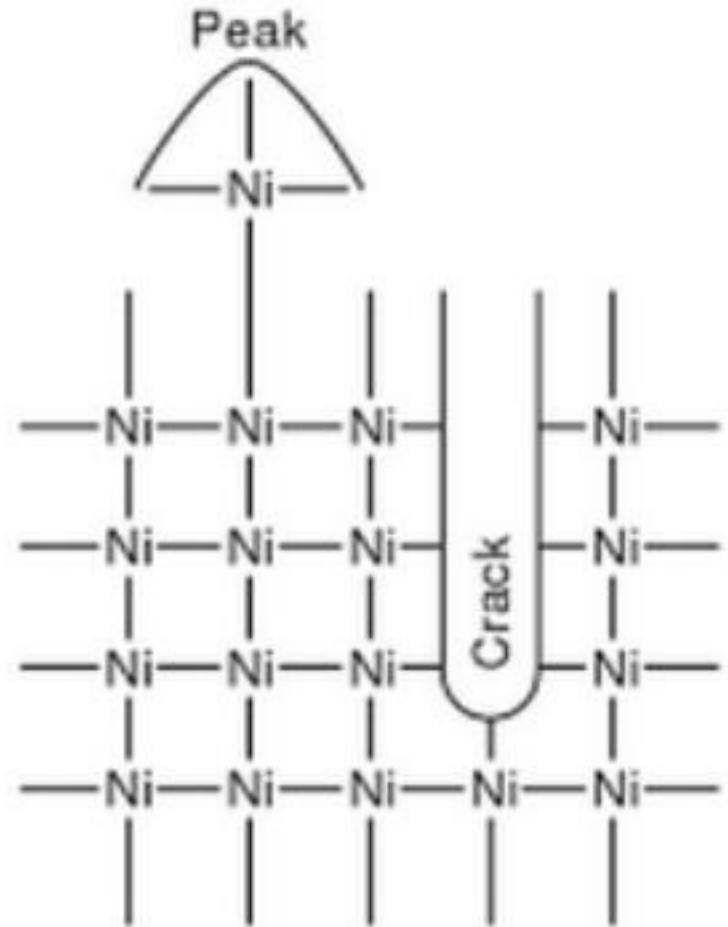
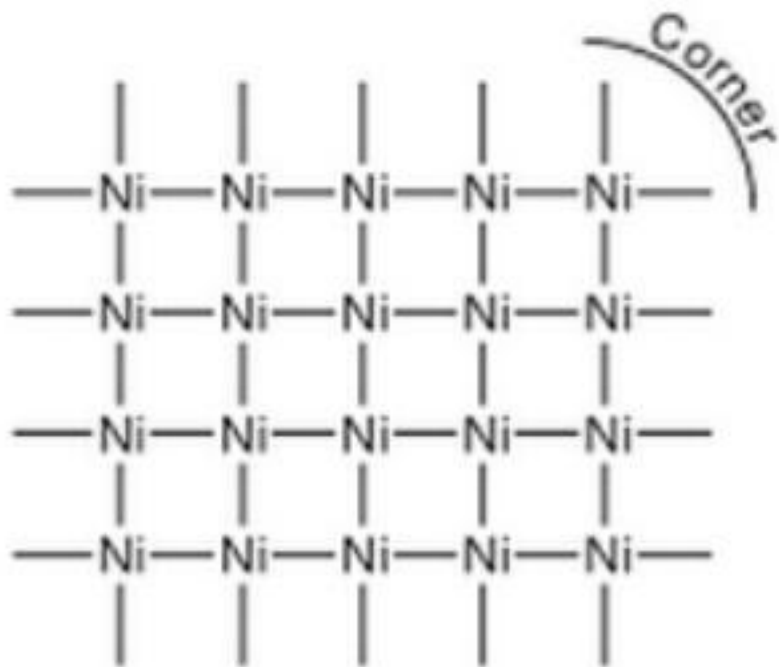
Step III: Formation of activated complex.



Step IV: Decomposition of the activated complex and Desorption of ethane molecules.



Active Centers on Catalyst surface



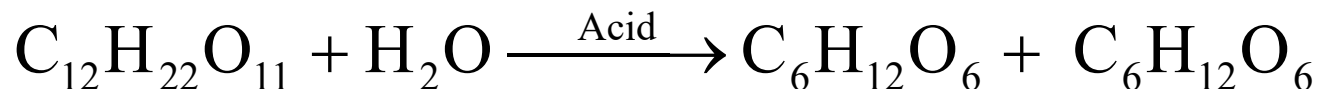
Adsorption Theory & Catalytic Activity

- Metals in a state of fine subdivision or colloidal form are rich in free valence bonds and hence they are more efficient catalysts than the metal in lumps
- Catalytic poisoning occurs because the so-called poison blocks the free valence bonds on its surface by preferential adsorption or by chemical combination.
- A promoter increases the valence bonds on the catalyst surface by changing the crystal lattice and thereby increasing the active centers.

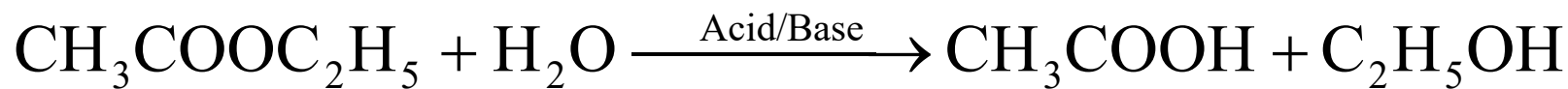
Acid-Base Catalysis

Homogeneous catalytic reaction catalyzed by acids or bases, or both acids and bases are known as acid-base catalysts.

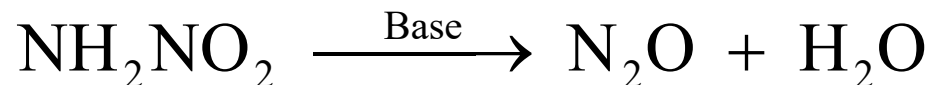
Inversion of Cane sugar



Hydrolysis of Ester



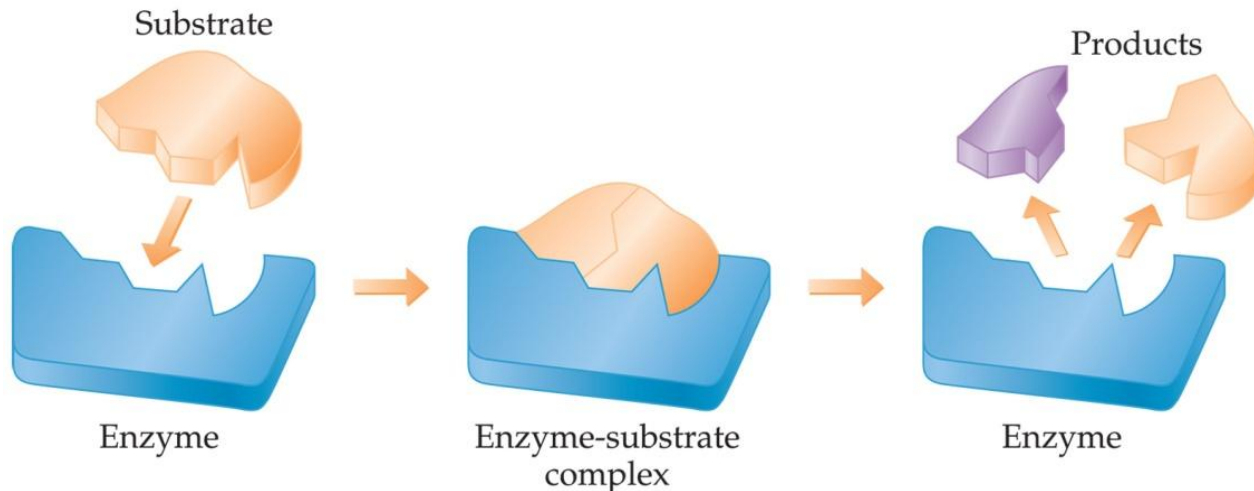
Decomposition of Nitramide



Enzyme Catalysis

The catalysis brought about by enzymes is known as enzyme catalysis

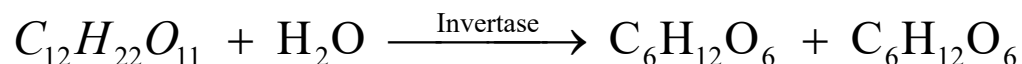
- Enzymes are catalysts in biological systems.
- The substrate fits into the active site of the enzyme much like a key fits into a lock.



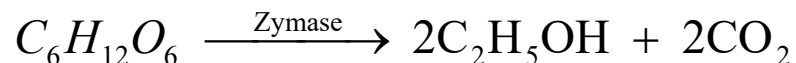
Characteristics of Enzyme Catalysis

- Most efficient catalysts known
- Marked by absolute selectivity and specificity
- Maximum at optimum temperature
- Maximum at optimum pH
- Greatly affected by inhibitors
- Greatly enhanced by Activator or Coenzyme

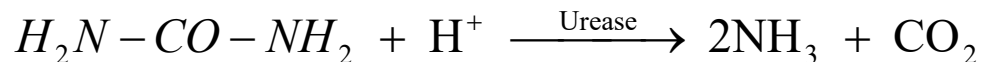
Inversion of cane sugar by Invertase present in yeast

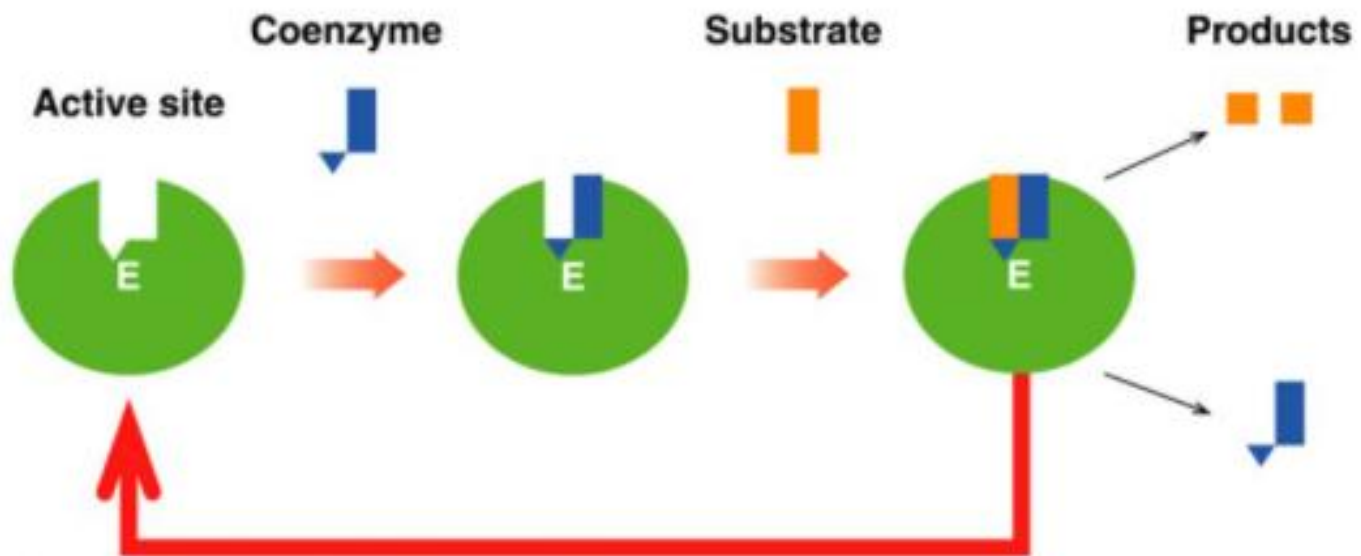
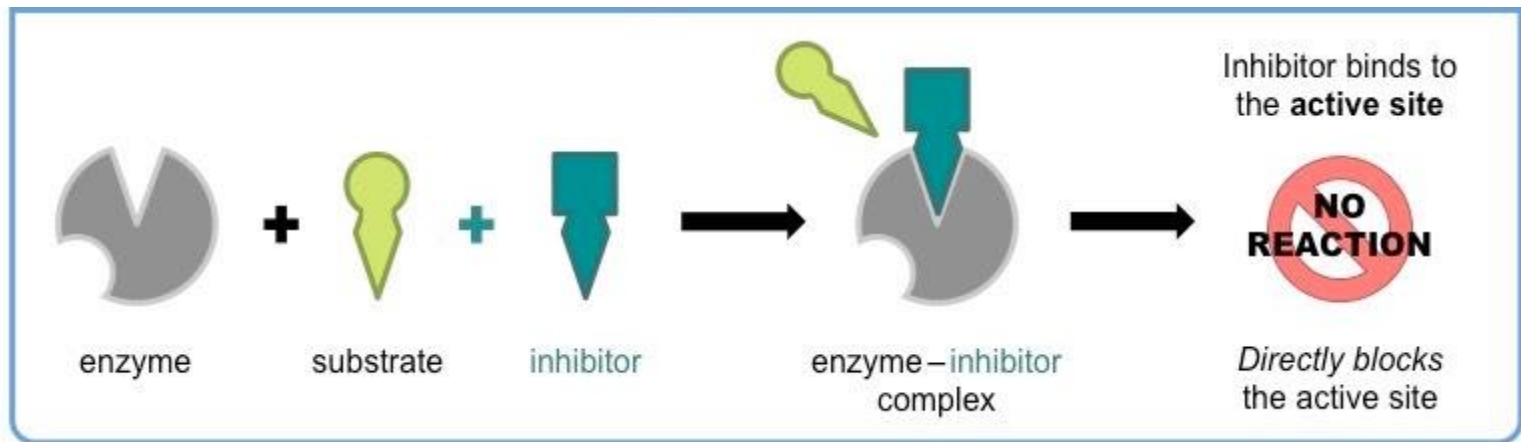


Conversion of glucose into ethanol by Zymase present in yeast



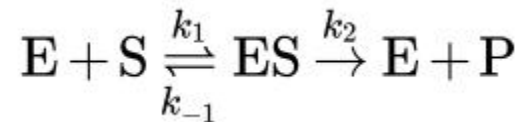
Hydrolysis of urea by Urease present in soya bean





The Michaelis-Menten Mechanism for Enzyme Catalysis

In 1913, L Michaelis and Mary Menten proposed a mechanism for the kinetics of enzyme-catalyzed reactions, which envisage the following steps:



Where, E is the enzyme, ES is the enzyme-substrate complex, and P is the product.

In the first step, the substrate binds to the active site of the enzyme.

In the second step, the substrate is converted into the product and released from the substrate.

For this mechanism, we can assume that the concentration of the enzyme-substrate complex, ES, is small and employ a steady-state approximation:

$$\frac{d[\text{ES}]}{dt} = k_1 [\text{E}] [\text{S}] - k_{-1} [\text{ES}]_{ss} - k_2 [\text{ES}]_{ss} \approx 0$$

Furthermore, because the enzyme is unchanged throughout the reaction, we express the total enzyme concentration as a sum of enzyme and enzyme-substrate complex:

$$[E]_0 = [ES] + [E]$$

Substituting for $[E]$ in the previous equation,

$$0 = k_1 ([E]_0 - [ES]_{ss}) [S] - k_{-1} [ES]_{ss} + k_2 [ES]_{ss}$$
$$[ES]_{ss} = \frac{k_1 [E]_0 [S]}{k_1 [S] + k_{-1} + k_2} = \frac{[E]_0 [S]}{[S] + \frac{k_{-1} + k_2}{k_1}}$$

We can then write the reaction rate of the product as

$$\frac{d[P]}{dt} = k_2 [ES]_{ss} = \frac{k_2 [E]_0 [S]}{[S] + \frac{k_{-1} + k_2}{k_1}} = \frac{k_2 [E]_0 [S]}{[S] + K_M}$$

where K_M is the Michaelis constant.

The above equation is known as the Michaelis-Menten equation.

When all the enzyme has reacted with the substrate at high concentration, the reaction will be going at maximum rate.

No free enzyme will remain so that

$$[E]_0 = [ES]$$

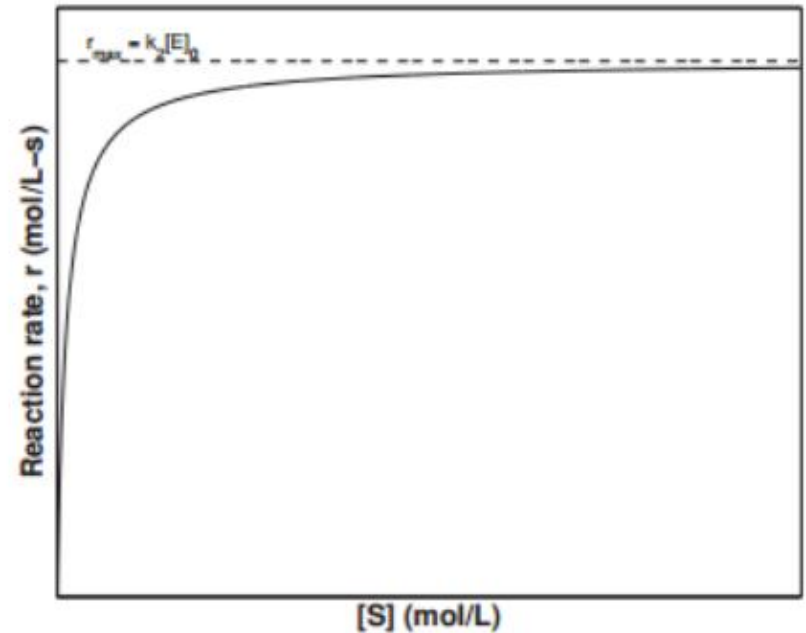
In this limit where there is a large amount of substrate present ($[S] \gg K_M$), the equation reduces to

$$\frac{d[P]}{dt} = r_{\max} = k_2[E]_0$$

where, r_{\max} is the maximum rate and k_2 is called the **turnover number** of the enzyme, which is the number of substrate molecules converted to product in a given time when all the active sites on the enzyme are occupied.

The plot for rate dependence on substrate concentration for an enzymatic reaction is known as the **Michaelis-Menten plot**.

Examining the figure, we can see that the reaction rate reaches a maximum value of $k_2[E]_0$ at large values of $[S]$.



Another commonly-used plot in examining enzyme kinetics is the **Lineweaver-Burk plot**, in which the inverse of the reaction rate, $1/r$, is plotted against the inverse of the substrate concentration $1/[S]$.

$$\frac{1}{r} = \frac{K_M + [S]}{k_2[E]_0 [S]} = \frac{K_M}{k_2[E]_0} \frac{1}{[S]} + \frac{1}{k_2[E]_0}$$

The Lineweaver-Burk plot results in a straight line with the slope equal to $K_M/k_2[E]_0$ and y-intercept equal to $1/k_2[E]_0$.

Good Luck

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