Physical Chemistry/ kinetics chemistry

(2025-2026)

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Lecture 6 31 / 12 / 2025

The kinetics of complex reactions

(Chain reactions , Consecutive reaction, Parallel reaction, Reversible reaction)

☒ Chain reactions

Chain reactions are examples of complex reactions, with complex rate expressions.

In a chain reaction, the intermediate produced in one step generates an intermediate in another step.This process goes on.

Intermediates are called chain carriers. Sometimes, the chain carriers are radicals; they can be ions as well. In nuclear fission they are neutrons.

There are several steps in a chain reaction.

1. **Chain initiation**

This can be by thermolysis (heating) or photolysis (absorption of light) leading to the breakage of a bond.

$$H_3C\text{-}CH_3 \rightarrow 2^{\cdot}CH_3$$

2. **Chain Propagation**

In this step the chain carrier makes another carrier.

$$^{\cdot}CH_3 + CH_3CH_3 \rightarrow CH_4 + {}^{\cdot}CH_2CH_3$$

3. Chain Inhibition

Chain carriers are removed by other processes, other than termination, say by foreign radicals.

$$CH_3CH_2^{\cdot} + {}^{\cdot}R \rightarrow CH_3CH_2R$$

4. Chain termination

Radicals combine and the chain carriers are lost.

$$CH_3CH_2^{\cdot} + CH_3CH_2^{\cdot} \rightarrow CH_3CH_2CH_2CH_3$$

Example;

$$2Br^- + H_2O_2 + 2H^+ \longrightarrow Br_2 + 2H_2O$$

Predicted Rate law;

$$\text{Rate} = d[Br_2]/dt = k\ [Br^-]\ [H_2O_2]\ [H^+]$$

Mechanism;

$$Br^- + H_2O_2 + H^+ \xrightarrow{k_1} HOBr + H_2O \qquad \text{slow step}$$

$$HOBr + Br^- + H^+ \xrightarrow{k_2} Br_2 + 2H_2O \qquad \text{fast step}$$

$$\text{Rate} = d[Br_2]/dt = k_2\ [HOBr]\ [H^+]\ [Br^-] \text{------ } 1$$

$$d[HOBr]/dt = \text{formation} - \text{disappearance}$$

According to the **steady-state approximation (SSA)**;

$$d[HOBr]/dt = 0$$

$$\text{Formation; } k_1\ [Br^-]\ [H_2O_2]\ [H^+]$$

$$\text{Disappearance; } k_2\ [HOBr]\ [H^+]\ [Br^-]$$

$$0 = k_1\ [Br^-]\ [H_2O_2]\ [H^+] - k_2\ [HOBr]\ [H^+]\ [Br^-]$$

$$[HOBr] = \frac{k_1\ \cancel{[Br^-]}\ [H_2O_2]\ \cancel{[H^+]}}{k_2\ \cancel{[H^+]}\ \cancel{[Br^-]}}$$

$$[HOBr] = \frac{k_1}{k_2}\ [H_2O_2] \text{ ------ } 2$$

Now substituting equation 2 in equation 1;

$$\text{Rate} = d[Br_2]/dt = \cancel{k_2}\ \frac{k_1}{\cancel{k_2}}\ [H_2O_2]\ [H^+]\ [Br^-]$$

$$\text{Rate} = d[Br_2]/dt = k_1\ [H_2O_2][H^+]\ [Br^-]$$

That means; predicted rate law = derived rate law

Minimum necessary are, **Initiation**, **propagation** and **termination**.

Now, how do we calculate for the rate of laws of chain reactions?

A chain reaction can have a simple rate law. As a first example, consider the pyrolysis, or thermal decomposition in the absence of air, of acetaldehyde (ethanal, CH_3CHO), which is found to be three- halves order in CH_3CHO:

Overall reaction,

$$CH_3CHO_{(g)} \rightarrow CH_{4(g)} + CO_{(g)} \qquad \mathbf{d[CH_4]/dt = k[CH_3CHO]^{3/2}}$$

The mechanism for this reaction known as Rice-Herzfeld mechanism is as follows.

1. Initiation: $CH_3CHO \rightarrow \boldsymbol{\cdot CH_3} + \boldsymbol{\cdot CHO}$

   $R = k_I\,[CH_3CHO]$

2. Propagation: $CH_3CHO + \boldsymbol{\cdot CH_3} \rightarrow \boldsymbol{CH_3CO\cdot} + CH_4$

   $R = k_P\,[CH_3CHO][\cdot CH_3]$

   Propagation: $\boldsymbol{CH_3CO\cdot} \rightarrow \boldsymbol{\cdot CH_3} + CO$ $\longleftarrow$ Product

   $R = K_{p-}[CH_3CO\cdot]$

3. Termination: $\boldsymbol{\cdot CH_3} + \boldsymbol{\cdot CH_3} \rightarrow CH_3CH_3$

   $R = k_T\,[\cdot CH_3]$

- The chain carriers $\boldsymbol{\cdot CH_3}$ and $\boldsymbol{\cdot CHO}$ are formed initially in the initiation step .
- To simplify the treatment, we shall **ignore** the subsequent reactions of $\boldsymbol{\cdot CHO}$.
- The chain carrier $\boldsymbol{\cdot CH_3}$ attacks other reactant molecules in the propagation steps, and each attack gives rise to a new carrier .
- Radicals combine and end the chain in the termination step .

To test the proposed mechanism we need to show that it leads to the observed rate law .

According to the **Steady-State Approximation (SSA)**, the net rate of change of the intermediates **($\cdot CH_3$** and **$CH_3CO\cdot$**) may be set equal to zero, That is, the change in its concentration over time is equal to zero.

$$d[^{\cdot}CH_3]/dt = 0$$

$$d[^{\cdot}CH_3]/dt = \text{formation} - \text{disappearance}$$

$$d[^{\cdot}CH_3]/dt = k_I[CH_3CHO] - k_P[^{\cdot}CH_3][CH_3CHO] + k_{P-}[CH_3CO^{\cdot}] - 2k_T[^{\cdot}CH_3]^2 = 0$$

$$d[CH_3CO^{\cdot}]/dt = k_P[^{\cdot}CH_3][CH_3CHO] - k_{P-}[CH_3CO^{\cdot}] = 0$$

The sum of the two equations ($d[^{\cdot}CH_3]/dt + d[CH_3CO^{\cdot}]/dt$) is

$$K_I[CH_3CHO] - k_P[^{\cdot}CH_3][CH_3CHO] + k_{P-}[CH_3CO^{\cdot}] - 2k_T[^{\cdot}CH_3]^2 = 0$$

$$+$$

$$K_P[^{\cdot}CH_3][CH_3CHO] - k_{P-}[CH_3CO^{\cdot}] = 0$$

We get:

$$K_I[CH_3CHO] - 2k_T[^{\cdot}CH_3]^2 = 0$$

Which shows that the steady-state approximation also implies that the rate of chain initiation is equal to the rate of chain termination.

The steady-state concentration of $^{\cdot}CH_3$ radicals is

$$[^{\cdot}CH_3] = (K_I/2k_T)^{1/2}\ [CH_3CHO]^{1/2} \text{-------------}(1)$$

If follows that the rate of formation of CH_4 from Propagation step above is;

$$CH_3CHO + \cdot CH_3 \rightarrow CH_3CO\cdot + CH_4$$

$$d[CH_4]/dt = k_p[CH_3CHO]\ [\cdot CH_3] \text{ ------ } (2)$$

Substituting Eq. (1) in Eq (2), we get:

$$d[CH_4]/dt = k_p[CH_3CHO]\ (K_I/2k_T)^{1/2}\ [CH_3CHO]^{1/2}$$

$$d[CH_4]/dt = k_p\ (K_I/2k_T)^{1/2}\ [CH_3CHO]^{3/2}$$

$$k_p\ (K_I/2k_T)^{1/2} = k$$

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

Thus the mechanism explains the observed rate expression. It is sure that the true rate law is more complicated than that observed experimentally.

What is Steady-State Approximation (SSA);

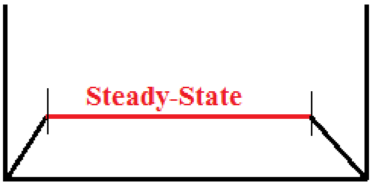
$A \longrightarrow P$ Simple reaction

$A \longrightarrow B$ Intermediate

$B \longrightarrow P$

The intermediate compound forms rapidly and reacts or disappears just as quickly; therefore:

Rate of formation of intermediate = Rate of disappearance of intermediate



Example;

$$A \xrightarrow{k_1} I \xrightarrow{k_2} P$$

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

Use SSA:

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

$$0 = k_1[A] - k_2[I]$$

$$k_1[A] = k_2[I]$$

$$\Rightarrow [I] = \frac{k_1}{k_2}[A]$$

$$\text{Rate} = \frac{d[\mathrm{P}]}{dt} = k_2[I] = k_1[A]$$

Example; $$\mathbf{A + B \longrightarrow P}$$

Mechanism;

$$\mathbf{A \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} C}$$

$$\mathbf{C + B \xrightarrow{k_2} P} \qquad \textbf{slow step}$$

$$\text{Rate} = -\,d[A]/dt = k_1\,[A]$$

$$\text{Rate} = -\,d[C]/dt = k_{-1}\,[C]$$

$$\text{Rate} = d[P]/dt = k_2\,[B]\,[C] \text{------ } 1$$

Using SSA;

Rate of formation of intermediate [C] = Rate of disappearance of intermediate [C]

$$K_1[A] = k_{-1}[C] + k_2[\,B]\,[C]$$

$$K_1[A] = [C]\ \{\,k_{-1}+ k_2[\,B]\}$$

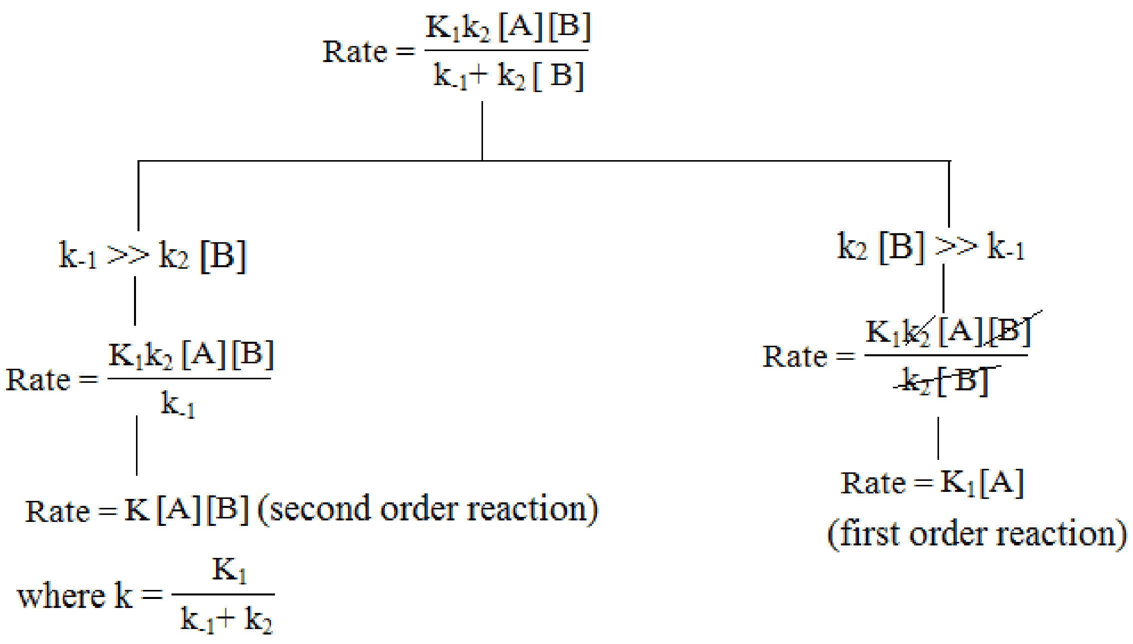
$$[C] = \frac{K_1[A]}{k_{-1}+ k_2[\,B]} \quad \text{------ } \mathbf{2}$$

Substituting equation 2 in equation 1;

$$\text{Rate} = k_2\,[B]\frac{K_1[A]}{k_{-1}+ k_2[\,B]} \Rightarrow \text{Rate} = \frac{K_1\,k_2\,[A][B]}{k_{-1}+ k_2[\,B]}$$

Case 1: if $k_{-1} >> k_2[B]$ (This means that removing the intermediate is slower compared to the reverse, the reaction is second order)

Case 2 : if $k_2[B] >> k_{-1}$ (This means converting the intermediate into product a very quickly, the reaction is first order)



$$\text{Rate} = \frac{K_1k_2[A][B]}{k_{-1} + k_2[B]}$$

$k_{-1} >> k_2[B]$

$$\text{Rate} = \frac{K_1k_2[A][B]}{k_{-1}}$$

$\text{Rate} = K[A][B]$ (second order reaction)

$$\text{where } k = \frac{K_1}{k_{-1} + k_2}$$

$k_2[B] >> k_{-1}$

$$\text{Rate} = \frac{K_1\cancel{k_2}[A]\cancel{[B]}}{\cancel{k_2[B]}}$$

$\text{Rate} = K_1[A]$

(first order reaction)

KINETICS OF CONSECUTIVE REACTIONS

Consider the following series of first-order irreversible reactions, where species A reacts to form an intermediate species, B, which then reacts to form the product, C:

$$\mathbf{A} \xrightarrow[\text{First order reaction}]{K_1} \underset{\textbf{(Intermediate)}}{\mathbf{B}} \xrightarrow[\text{First order reaction}]{k_2} \mathbf{C}$$

$$\begin{array}{l} A \xrightarrow{k_1} \cancel{B} \\ \cancel{B} \xrightarrow{k_2} C \\ \hline A \longrightarrow C \end{array}$$

Initial conditions:

$$\begin{aligned} [A\,(t=0)] &= [A]_0 \\ [B\,(t=0)] &= 0 \\ [C\,(t=0)] &= 0 \end{aligned}$$

$$\begin{array}{cccccc} & A & \xrightarrow{k_1} & B & \xrightarrow{k_2} & C \\ t=0 & [A]_0 & & 0 & & 0 \\ t=t & [A] & & [B] & & [C] \end{array}$$

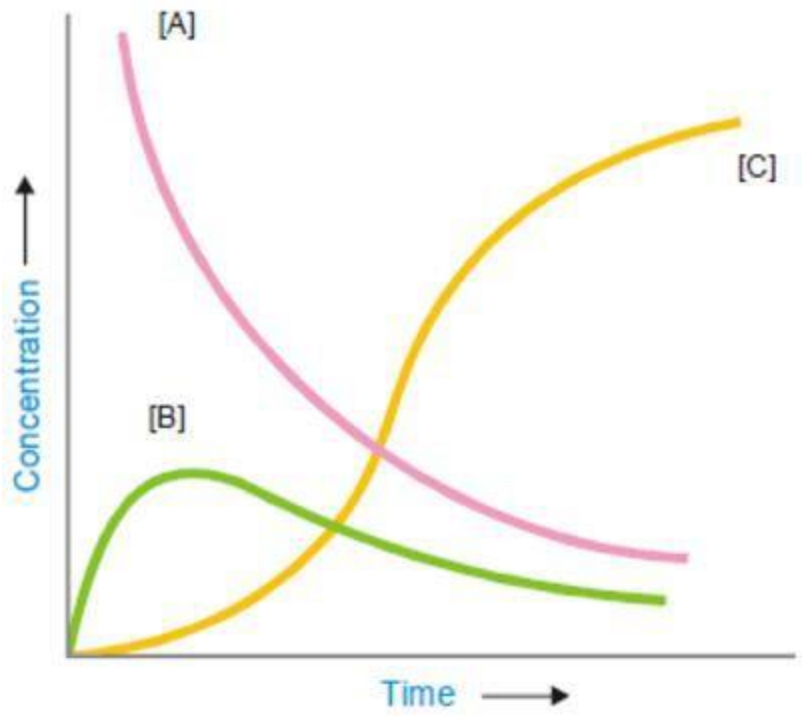
Mass balance equation is:

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

$$d[A]/dt = -k_1[A]$$

$$d[B]/dt = k_1[A] - k_2[B]$$

$$d[C]/dt = k_2[B]$$



First-order decay of [A]: $d[A]/dt = -k_1[A]$----- 1

$\ln A = -K_1\, t + I$ ------- 2

At t=0 , $[A] = [A]_0$ $\ln [A]_0 = -K_1 \times 0 + I$------ 3

$$I = \ln [A]_0$$

$\ln A = -K_1\, t + \ln [A]_0$------- 4

$\ln[A]/[A]_0 = -k_1\, t$----- 5

$[A] = [A]_0\, e^{-k1t}$------- 6

Substituting equation 6 in the equation 1, we get:

$d[A]/dt = -k_1[A]_0\, e^{-k1t}$-------- 7

Rate of formation of B:

$$d[B]/dt = k_1[A] – k_2[B] \text{------}8$$

Substituting equation 6 in the equation 8, we get:

$$d[B]/dt = k_1[A]_0\, e^{-k1t} – k_2[B] \text{----}\ 9$$

$$d[B]/dt + k_2[B] = k_1[A]_0\, e^{-k1t} \ \text{----}10 \quad \text{(multiply Eq. 10 in } e^{+k2t}\text{)}$$

$$\{d[B]/dt + k_2[B]\}\, e^{+k2t} = k_1[A]_0\, e^{-k1t} .\, e^{+k2t \text{--------}}\ 11$$

$$d[B]/dt .\, e^{+k2t} + k_2[B].\, e^{+k2t} = k_1[A]_0\, e^{-k1t} .\, e^{+k2t \text{------}}\ 12$$

For recall;

$$[A]/[A]_0 = e^{-k1t}\ \text{, and } [B]/[B]_0 = e^{-k2t} \Rightarrow [B]_0 /[B] = e^{+k2t}$$

$$[B]_0 = [B]\, e^{+k2t} \text{---}13$$

At t = 0 the initial concentration of $[B]_0 = 0$

$$0 = [B].\, e^{+k2t \text{--------}}\ 14$$

Substituting equation 14(it value 0) in the equation 12, we get:

$$d[B]/dt .\, e^{+k2t} = k_1[A]_0\, e^{-k1t} .\, e^{+k2t \text{------------------------}}\ 15$$

$$d[B]\, e^{+k2t} = k_1[A]_0\, e^{-(k1 - k2)\,t}\, dt\text{----------------}\ 16$$

$$e^{+k2t}\ {}_0\!\int^{[B]} d[B] = k_1[A]_0\ {}_0\!\int^{t} e^{-(k1 - k2)t}\, dt\ \text{-------}17$$

$$[B]e^{+k2t} = k_1[A]_0\ {}_0\!\int^{t} e^{-(k1 - k2)t}\, dt\ \text{-----}18$$

Now, solve the exponential integral (for $k_1 \neq k_2$), the right integral from eq. (18):

$$k_1[A]_0\ {}_0\!\int^{t} e^{-(k1-k2)\tau}\ dt = k_1[A]_0\, [–(k_1 –k_2)^{-1}].\, e^{-(k1 - k2)t}$$

Eq. 18 became;

$$[B]\, e^{+k2t} = k_1[A]_0\, [–(k_1 –k_2)^{-1}].\, e^{-(k1 - k2)t} + I\text{-----}\ 19$$

Now to find I integration constant;

At t = 0 ; [B] = 0 substituting in equation 19;

$$0 * e^{+k2 *0} = k_1\, [A]_0\, [–(k_1 –k_2)^{-1}].\, e^{-(k1 - k2)\, 0} + I$$

$$0 = k_1\, [A]_0\, [–(k_1 –k_2)^{-1}].\, e^{0} + I$$

$$I = – k_1\, [A]_0\, [–(k_1 – k_2)^{-1}].\, e^{0}$$

Where $e^0 = 1$;

$$I = -\, k_1\, [A]_0\, [-\, (k_1 - k_2)^{-1}] \text{-----}\ 20$$

Substituting equation 20 in equation 19;

$$[B]\, e^{+k2t} = k_1\, [A]_0\, [-\, (k_1 - k_2)^{-1}].\, e^{-(k1 - k2)t} - k_1 [A]_0\, [-\, (k_1 - k_2)^{-1}] \text{------}\ 21$$

$$[B]\, e^{+k2t} = k_1\, [A]_0 \left[\frac{e^{-(k1 - k2)t}}{-\,(k_1 - k_2)} - \frac{1}{-\,(k_1 - k_2)} \right]$$

$$[B]\, e^{+k2t} = \frac{k_1\, [A]_0}{k_2\text{-}k_1}\, [e^{-(k1 - k2)t} - 1]$$

Divide by e^{+k2t} we get;

$$[B] = \frac{k_1\, [A]_0}{k_2\text{-}k_1} \left[\frac{e^{-(k1 - k2)t}}{e^{+k2t}} - \frac{1}{e^{+k2t}} \right]$$

$$[B] = \frac{k_1\, [A]_0}{k_2\text{-}k_1}\, [\, e^{-k1t \cancel{+k2t}} . \cancel{e^{-k2t}} - e^{-k2t}\,]$$

$$[B] = \frac{k_1\, [A]_0}{k_2\text{-}k_1}\, [\, e^{-k1t} - e^{-k2t}\,]$$

The concentration of B at k_1 # k_2 can be written as:

$$[B] = \frac{k_1\, [A]_0}{k_2 - k_1}\, [\, e^{-k1t} - e^{-k2t}\,] \text{-----}\ 22$$

The concentration of B at $k_1 = k_2 = k$ can be written as:

$$[B] = k\, [A]_0\, e^{-k\,t \text{----------}} 23$$

Then, solving for [C], we find that mass balance equation is:

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

$$[A]_0 = [A]_0\, e^{-k1t} + k_1\, [A]_0 / k_2\text{-}k_1\, (e^{-k1t} - e^{-k2t}) + [C]_t$$

Where: $[A] = [A]_0\, e^{-k1t}$ from equation 6; and $[B]_t = k_1\, [A]_0 / k_2\text{-}k_1\, (e^{-k1t} - e^{-k2t})$

from equation 22 we get:

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

$$[C] = [A]_0 - [A]_0\, e^{-k1t} + k_1\, [A]_0 / k_2\text{-}k_1\, (e^{-k1t} - e^{-k2t})$$

$$[C] = [A]_0\, \{1 - e^{-k1t} + k_1 / k_2\text{-}k_1\, (e^{-k1t} - e^{-k2t})\}$$

$$[C] = [A]_0\, \{1 - \{e^{-k1t} + k_1 / k_2\text{-}k_1\, e^{-k1t} - k_1 / k_2\text{-}k_1\, e^{-k2t}\, \}\}$$

$$[C] = [A]_0 \{1 - \{\ e^{-k1t} + \frac{k_1 e^{-k1t}}{k_2 - k_1} - \frac{k_1 e^{-k2t}}{k_2 - k_1}\}\}$$

$$[C] = [A]_0 \{1 - \{\frac{(k_2 - k_1) e^{-k1t} + k_1 e^{-k1t} - k_1 e^{-k2t}}{(k_2 - k_1)}\}\}$$

$$[C] = [A]_0 \{1 - \{\frac{k_2 e^{-k1t} \cancel{- k_1 e^{-k1t}} \cancel{+ k_1 e^{-k1t}} - k_1 e^{-k2t}}{(k_2 - k_1)}\}\}$$

$$[C] = [A]_0 \{1 - \{\frac{k_2 e^{-k_1 t} - k_1 e^{-k_2 t}}{(k_2 - k_1)}\}\} \text{ --------23}$$

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

$$[A] = [A]_0 e^{-k1t} \text{---------6}$$

$$[B] = k_1 [A]_0 / k_2\text{-}k_1 (e^{-k1t} - e^{-k2t}) \text{----- 22}$$

$$[C] = [A]_0 \{1 - \{\frac{k_2 e^{-k_1 t} - k_1 e^{-k_2 t}}{(k_2 - k_1)}\}\} \text{ --------23}$$

$$[A]_0 = [A]_0 e^{-k1t} + k_1 [A]_0 / k_2\text{-}k_1 (e^{-k1t} - e^{-k2t}) +$$

$$[C] = [A]_0 \{1 - \{\frac{k_2 e^{-k_1 t} - k_1 e^{-k_2 t}}{(k_2 - k_1)}\}\}$$

$$\boxed{[A]_0 = [A]_0 [\ e^{-k1t} + k_1 / k_2\text{-}k_1 (e^{-k1t} - e^{-k2t}) + 1 - \{\frac{k_2 e^{-k1t} - k_1 e^{-k2t}}{(k_2 - k_1)}\}}$$

We can calculate the maximum B and maximum time by equation:

If $k_1 \neq k_2$

$$t_{max} = \frac{\ln \frac{k_2}{k_1}}{k_2 - k_1}$$

$$B_{max} = [A_0](\frac{k_2}{k_1})^{\frac{k_2}{k_1 - k_2}}$$

If $k_1 = k_2 = k$

$$t_{max} = 1 / k$$

$$[B]_{max} = [A]_0\, e^{-1}$$

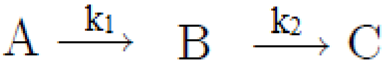
Because of at $t_{max} = 1 / k$;

$$[B]_{max} = [A]_0 e^{-k\, t_{max}} = [A]_0 e^{-k\, 1/k} = [A]_0\, e^{-1}$$

Notes:

- If $k_2 \gg k_1$(Meaning B quickly convert to C) B does not accumulate much and small $[B]_{max}$ and t_{max}.
- If $k_1 \gg k_2$ that meaning B accumulate at long period and increased $[B]_{max}$.

Example: how much time would be required for the B to reach maximum concentration for the reaction:



$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

$K_1 = 12$ and $k_2 = 2$ [t in min]

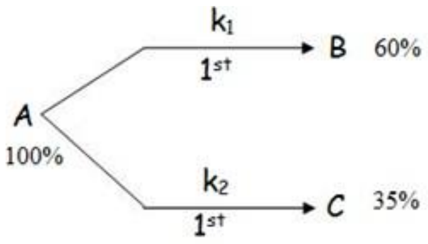
Answer:

$$t_{max} = (\ln k_1/k_2)^* (k_1 - k_2)^{-1}$$

$$= (\ln 12/2)^*(12-2) = 0.179 \text{ min}$$

☒ Kinetic of Parallel or Side Reactions

The reactions in which a substance reacts or decomposes in more than one way are called parallel or side reactions.



$K_1 > K_2$

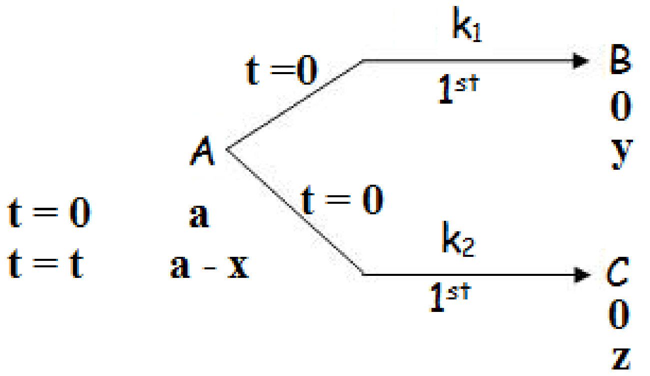
At t = 0

$[A] = [A]_0$

$[B] = 0$

$[C] = 0$

If we assume that both of them are first order, we get.



$$x = y + z$$

$$-\,d[A]/dt = k_1[A] + k_2[A]$$

$$-\,d[A]/dt = (k_1+k_2)\,[A]$$

Where $[A] = (a - x)$, $[A]_0 = a$, $[B] = y$, and $[C] = z$

$$-\frac{d}{dt}(a-x) = k_1\,(a-x) + k_2\,(a-x)$$

$$-\underbrace{\cancel{\frac{da}{dt}}}_{=0} + \frac{dx}{dt} = (\,k_1 + k_2\,)(a-x)$$

$$\frac{dx}{dt} = (\,k_1 + k_2\,)(a-x)$$

$$\int_0^x \frac{dx}{(a-x)} = \int_0^t (\,k_1 + k_2\,)\,dt$$

$$\left[\,\ln\frac{1}{a-x}\,\right]_0^x = k_1 + k_2\left[\,t\,\right]_0^t$$

$$\ln\frac{1}{a-x} - \ln\frac{1}{a-0} = (\,k_1 + k_2\,)(t-0\,)$$

$$\ln\frac{1}{a-x} - \ln\frac{1}{a} = (\,k_1 + k_2\,)\,t$$

$$\ln\frac{a}{a-x} = (k_1 + k_2)\,t$$

$$-\ln\frac{a-x}{a} = (k_1 + k_2)\,t$$

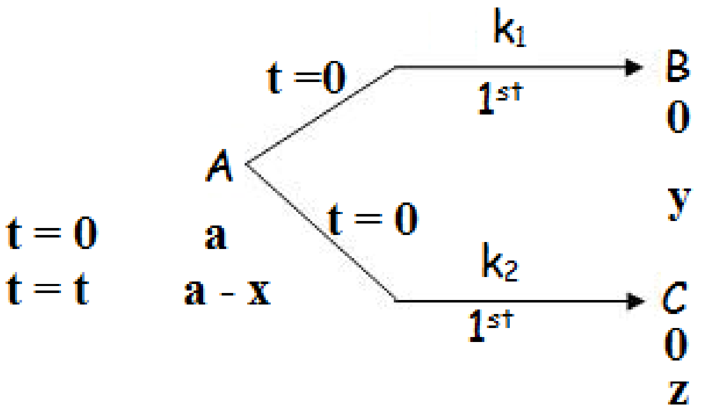
$$\ln\frac{a-x}{a} = -(k_1 + k_2)\,t$$

$$\frac{a-x}{a} = e^{-(k_1 + k_2)\,t}$$

Where $[A]_0 = a$, $[A] = (a\text{-}x)$

$$\frac{[A]}{[A]_0} = e^{-(k_1 + k_2)\,t}$$

$$\boxed{[A] = [A]_0\, e^{-(k_1 + k_2)\,t}}$$



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

$$\frac{d[B]}{dt} = k_1\,[A]_0\, e^{-(k_1 + k_2)t}$$

$$\int_0^y d[B] = \int_0^t k_1\,[A]_0\, e^{-(k_1 + k_2)t}\,dt$$

$$\int_0^y d[B] = k_1\,[A]_0 \int_0^t e^{-(k_1 + k_2)t}\,dt$$

$$[B]_0^y = k_1 [A]_0 \int_0^t e^{-(k_1+k_2)t}\, dt$$

Mathematically $\int e^{x}\, dx = \frac{e^{-x}}{-1}$

$$[B] = k_1 [A]_0 \left[\frac{e^{-(k_1+k_2)t}}{-(k_1+k_2)} \right]_0^t$$

$$[B] = \frac{k_1 [A]_0}{-(k_1+k_2)} \left[e^{-(k_1+k_2)t} - e^0 \right]$$

$$[B] = \frac{k_1 [A]_0}{-(k_1+k_2)} \left[e^{-(k_1+k_2)t} - 1 \right]$$

$$[B] = \frac{k_1}{(k_1+k_2)} [A]_0 \left[1 - e^{-(k_1+k_2)t} \right]$$

$$\boxed{[B] = y = \frac{k_1}{(k_1+k_2)} [A]_0 \left[1 - e^{-(k_1+k_2)t} \right]}$$

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

$$\boxed{[C] = z = \frac{k_2}{(k_1+k_2)} [A]_0 \left[1 - e^{-(k_1+k_2)t} \right]}$$

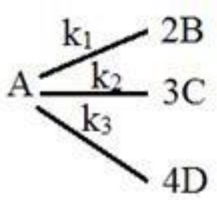
$$\frac{[B]}{[C]} = \frac{y}{z} = \frac{k_1}{k_2}$$

Ratio of concentration of B and C is constant for all time.

If $k_1 > k_2$ then;

$A \longrightarrow B$ is main reaction

$A \longrightarrow C$ is side reaction



1. $A = A_0\, e^{-(k1+k2+k3)\,t}$

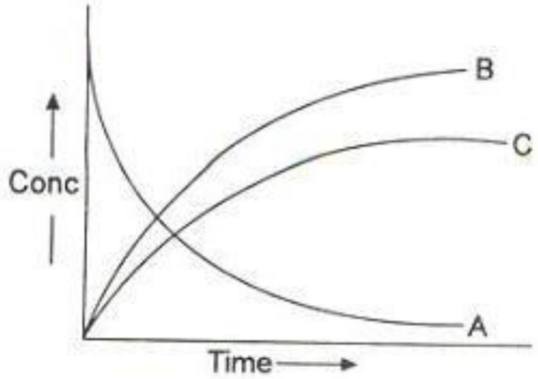
2. $B = \dfrac{2k_1}{k_1+k_2+k_3}[A_0 - A\ ]$

$$B = \frac{2k_1}{k_1+k_2+k_3}[A_0 - e^{-(k1+k2+k3)t}]$$

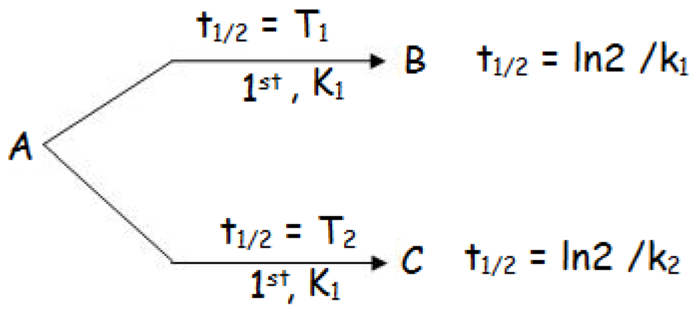
3. $D = \dfrac{4\,k_1}{k_1+k_2+k_3}[A_0 - A_0\, e^{-(k1+k2+k3)t}]$

4. $\dfrac{B}{D} = \dfrac{k_B}{k_D} = \dfrac{2k_1}{4k_3}$

5. $\%B = \dfrac{2k_1}{2k_1+3k_2+4k_3}$ x 100



Effective half-life:



Two independent cases with half-lives; we have two processes or mechanisms that occur together:

$T_1 = \ln 2/k_1 \quad \Rightarrow \quad k_1 = \ln 2/\,T_1$

And $T_2 = \ln 2/\,k_2 \quad \Rightarrow \quad k_2 = \ln 2/T_2$

Where T is Half-life , k is decay constant

When both processes occur together (active decomposition), the resulting decomposition has a total decomposition constant:

$$K_f = k_1 + k_2$$

Effective half-life is T_f;

$$T_f = \ln 2/k_f \Rightarrow k_f = \ln 2/T_f$$

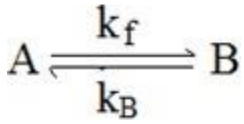
$$K_f = k_1+k_2$$

$$\ln 2/T_f = \ln 2/T_1 + \ln 2/T_2$$

$$1/T_f = 1/T_1 + 1/T_2$$

According to this equation, when there are two independent decomposition processes, the effective half-life is smaller than each one separately because the combined influence of the two processes causes decomposition to happen more quickly.

☒ The kinetics of reversible reaction



$$A \underset{k_B}{\overset{k_f}{\rightleftharpoons}} B$$

$t = 0$	A_0	0
$t = t$	$A_0 - x$	x
$t = t_{eq}$	$A_0 - xe$	xe
	$[A]_{eq}$	$[B]_{eq}$

Rate of forward reaction = $k_f\,[A]$

Rate of backward reaction = $k_B\,[B]$

At equilibrium;

Rate of forward reaction = Rate of backward reaction

$$k_f\,[A]_{eq} = k_B\,[B]_{eq}$$

$$k_f\,(A_0 - xe) = k_B\,xe$$

$$k_f\,A_0 - k_f\,xe = k_B\,xe$$

$$k_f A_0 = k_B xe + k_f xe$$

$$k_f A_0 = (k_B + k_f) xe$$

$$\boxed{\frac{k_f}{k_f + k_B} A_0 = xe = [B]_{eq}}$$

$$[A]_{eq} = A_0 - xe$$

$$[A]_{eq} = A_0 - [\ \frac{k_f}{k_f + k_B}\ A_0\ ]$$

$$[A]_{eq} = A_0\ [\ 1 - \frac{k_f}{k_f + k_B}\ ]$$

$$[A]_{eq} = A_0\ [\ \frac{\cancel{k_f} + k_B - \cancel{k_f}}{k_f + k_B}\ ]$$

$$\boxed{[A]_{eq} = A_0\ [\frac{k_B}{k_f + k_B}]}$$

Conclusion:

① $[A]_{eq} = A_0\ [\frac{k_B}{k_f + k_B}]$

② $[B]_{eq} = \frac{k_f}{k_f + k_B} A_0$

$kt = \ln \frac{A_0}{[A]} \Rightarrow kt = \ln \frac{A_0}{A_0 - xe}$, where $[A] = A_0 - xe$

③ $(k_f + k_B)t = \ln \frac{xe}{xe - x}$

Expression for $t_{1/2}$

$$t = t_{1/2}\ ,\ x = xe/2$$

$$(k_f + k_b)t_{1/2} = \ln \frac{xe}{xe - xe/2}$$

$$(k_f + k_b)\,t_{1/2} = \ln \frac{\cancel{xe}}{\cancel{xe}/2}$$

$$(k_f + k_b)t_{1/2} = \ln 2 \Rightarrow t_{1/2} = \frac{\ln 2}{k_f + k_b}$$

④ $t_{1/2} = \dfrac{0.693}{k_f + k_b}$

⑤ $[B] = x$

$$(k_f + k_b)t = \ln \frac{xe}{xe - x}$$

$$e^{(kf + kb)t} = \frac{xe}{xe - x}$$

$$xe - x = xe\, e^{-(kf + kb)t}$$

$$x = xe - xe\, e^{-(kf + kb)t}$$

$$[B] = x = xe - xe\, e^{-(kf + kb)t}$$

⑥ $[A] = A_0 - x$

$$[A] = A_0 - xe - xe\, e^{-(kf + kb)t}$$

$$[A] = A_0 - xe\, [- e^{-(kf + kb)t}]$$

Physical chemistry / Kinetic chemistry
(2025-2026)

2nd week 08/10/2025

Lecturer Prof. Dr. Abdulqadier Hussien Al Khazraji

What is Molecularity of reaction and how it different from order of reaction?

Molecularity of the reaction can be defined as the total number of reacting species in a rate-determining step. While, the order of reaction is the summation of powers of concentration of the reactant molecules in the rate equation of the reaction.

Molecularity	**Order**
The number of ions or molecules that take part in the rate-determining step is known as molecularity.	The sum of powers to which the reactant concentrations are raised in the rate law equation is known as the order of the reaction.
It is always a whole number	It can either be a whole number or a fraction
The molecularity of the reaction is determined by looking at the reaction mechanism	The order of the reaction is determined by the experimental methods
The molecularity of the reaction is obtained by the rate-determining step	The order of the reaction is obtained by the sum of the powers to which the reactant concentrations are raised in the rate law equation.

Rate Laws and the Rate-Determining Step

Take the following example of a gas phase reaction:

$$CO + NO_2 \rightarrow CO_2 + NO$$

If this reaction occurred in a single step, its rate law would be:

$$\text{Rate} = k\,[NO_2]\,[CO]$$

However, experiments show that the rate equation is:

$$\text{Rate} = k[NO_2]^2$$

The fact that the experimentally-determined rate law does not match the rate law derived from the overall reaction equation suggests that the reaction occurs over multiple steps. Further, the experimental rate law is second-order, suggesting that the reaction rate is determined by a step in which two NO_2 molecules react, and therefore the CO molecule must enter at another, faster step. A possible mechanism that explains the rate equation is:

$$\begin{array}{lll}
\cancel{2}\mathrm{NO_2}(g) & \xrightarrow{slow} \mathrm{NO}(g) + \cancel{\mathrm{NO_3}}(g) & \text{Elementary step 1} \\
\cancel{\mathrm{NO_3}}(g) + \mathrm{CO}(g) & \xrightarrow{fast} \cancel{\mathrm{NO_2}}(g) + \mathrm{CO_2}(g) & \text{Elementary step 2} \\
\hline
\mathrm{NO_2}(g) + \mathrm{CO}(g) & \longrightarrow \mathrm{NO}(g) + \mathrm{CO_2}(g) & \text{Overall reaction}
\end{array}$$

The rate reaction law was taken from slow step:

$$\text{Rate} = k[NO_2]^2$$

Since the first step is the slowest, and the entire reaction must wait for it, it is the rate-determining step, that determines how quickly reactants can become products.

If the first step in a mechanism is rate-determining, it is easy to find the rate law for the overall expression from the mechanism. If the second or a later step is rate-determining, determining the rate law is slightly more complicated. We will explore how to write that rate law later.

Slow Step Followed by a Fast Step

As discussed in the previous concept, if the first step in a reaction mechanism is the slow, rate-determining step, then the overall rate law for the reaction is easy to write, and simply follows the stoichiometry of the initial step. For example, consider the following reaction:

$$H_{2(g)} + 2ICl_{(g)} \rightarrow I_{2(g)} + 2HCl_{(g)}$$

The proposed reaction mechanism is given as follows:

(1) slow reaction : $H_2 + ICl \rightarrow \cancel{HI} + HCl$ rate$_1$ = $k_1[H_2][ICl]$

(2) fast reaction : $\cancel{HI} + ICl \rightarrow I_2 + HCl$ rate$_2$ = $k_2[HI][ICl]$

Overall reaction; $H_{2(g)} + 2ICl_{(g)} \rightarrow I_{2(g)} + 2HCl_{(g)}$

Since the first step is the rate-determining step, the overall reaction rate for this reaction is given by this step:

$$\text{rate} = k\,[H_2][ICl]$$

As it turns out, this rate law has been verified with experimental evidence.

Fast Step Followed by a Slow Step

If the rate-determining step is not the first step in the reaction mechanism, the derivation of the rate law becomes slightly more complex. Consider the following reaction:

$$2NO_{(g)} + O_{2(g)} \rightarrow 2NO_{2(g)}$$

The proposed mechanism is given by:

$$\text{(1)Step1, fast:}\quad NO_{(g)} + NO_{(g)} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \cancel{N_2O_{2(g)}} \qquad \text{rate}_1=k_1[NO]^2 \ \text{equilibrium}$$

$$\text{(2)Step2, slow:}\quad \cancel{N_2O_{2(g)}} + O_{2(g)} \xrightarrow{k_2} 2NO_{2(g)} \qquad \text{rate}_2=k_2[N_2O_2][O_2]$$

Overall reaction; $2NO_{(g)} + O_{2(g)} \rightarrow 2NO_{2(g)}$

Step two is the slow, rate-determining step, so it might seem reasonable to assume that the rate law for this step should be the overall rate law for the reaction. However, this rate law contains N_2O_2, which is a reaction intermediate, and not a final product.

$$\text{rate}_2 = k_2[N_2O_2][O_2]$$

The rate law cannot contain any intermediates, because the rate law is determined by experiment only, and such intermediates are not observable. To get around this, we need to go back and consider the first step, which involves an equilibrium between NO and N_2O_2. At equilibrium, the rate of the forward reaction will equal the rate of the reverse reaction. We can write this as follows:

$$\text{rate} = k_1[\text{NO}]^2$$

$$\text{rate} = k_{-1}[\text{N}_2\text{O}_2]$$

at equilibrium;

$$k_1[\text{NO}]^2 = k_{-1}[\text{N}_2\text{O}_2]$$

Rearranging for $[N_2O_2]$, we have:

$$[\text{N}_2\text{O}_2] = k_1 [\text{NO}]^2 / k_{-1}$$

We can now substitute this expression into the rate law for the second, rate-determining step. This yields the following:

$$\text{Rate} = k_2(k_1/k_{-1})[\text{NO}]^2[\text{O}_2] = k [\text{NO}]^2[\text{O}_2]$$

$$\text{Where } k = k_2(k_1/k_{-1})$$

This overall rate law, which is second-order in NO and first-order in O_2, has been confirmed experimentally.

❖ How do we determine the slow or fast step?

There are multiple ways to find which step is the slow/fast step without it being given to you.

1) Look at **k**. The smaller **k** is probably the slower step.

2) Look at the activation energy **(E_a)** for each step. The step with larger activation energy is the slower step (as the fraction of collisions with enough energy to react will be smaller - activation energy requirement is higher) this derives from the Arrhenius equation:

$$k = A * e^{\wedge(-Ea/RT)}$$

Where A and R are constants, T = temp, and E_a = activation energy. As you can see, as Ea increases, k decreases. Thus, the higher the E_a, the slower the reaction rate.

حساب قانون سرعة التفاعل

تعيين قيم رتب التفاعل لكل مادة متفاعلة في قانون سرعة التفاعل.

1. التفاعل من **الرتبة الأولى:** معدل الزيادة في السرعة يساوي معدل الزيادة في التركيز

2. التفاعل من **الرتبة الثانية** : إذا كانت مضاعفة التركيز مرة واحدة يصاحبها مضاعفة معدل السرعة أربع مرات (2^2) ومرتين ثمان مرات (2^3)

3. لتفاعل من **الرتبة الصفرية :** الزيادة في التركيز لا تؤثر على قيمة معدل سرعة التفاعل

4. التفاعل من الدرجة السالبة أو الكسرية: يصاحبها دائماً انخفاض في قيمة السرعة مع الزيادة في التركيز.

تفاعل الرتبة الصفرية

Zero-Order Reactions (n=0)

Zero order reaction means that the rate of the reaction is proportional to zero power of the concentration of reactants.

يكون التفاعل من الرتبة الصفرية إذا كانت الزيادة في التركيز لا تؤثر على قيمة معدل سرعة التفاعل.

$$A \rightarrow \text{products}$$

التفاعل اعلاه اذا كان من المرتبة الصفرية هذا يعني ان المتفاعلات على اليسار لاتتفاعل لتكون الناتج على يمين المعادلة الا اذا كان هناك مؤثر خارجي كالعوامل المساعدة او الضوء او التفريغ الكهربائي.

Rate does not change with concentration.

For a zero order process, the rate law can be written:

	R	$\longrightarrow$	**P**
at t = 0	$[R]_0$		0
at t = t	[R]		x

R: reactant and P: Products

Where; $[R]_0$ is initial concentration of reactant.

التركيز الابتدائي للمادة المتفاعلة.

x is concentration of products.

تركيز المادة الناتجة، اي يمثل تركيز المستهلك من المادة المتفاعلة.

[R] is the remaining of the concentration of the reactants

ماتبقى من تركيز المادة المتفاعلة.

Now consider the reaction:

$$R \rightarrow P$$

$$\text{Rate} = -\frac{d[R]}{dt} = k[R]_0$$

As any quantity rose to power zero is unity

$$\text{Rate} = -\frac{d[R]}{dt} = k \times 1$$

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

Integrating both sides

$$[R] = -k\,t + I$$

Where , I is the constant of integration.

At (t = 0), the concentration of the reactant R = $[R]_0$, where $[R]_0$ is initial concentration of the reactant.

Substituting in equation

$$[R] = -k\,t + I$$

$$[R]_0 = -k * 0 + I$$

$$[R]_0 = I$$

Substituting the value of I in the equation

$$[R] = -k\,t + I$$

we get

$$[R] = -k\,t + [R]_0$$

$$[R] = [R]_0 - Kt$$

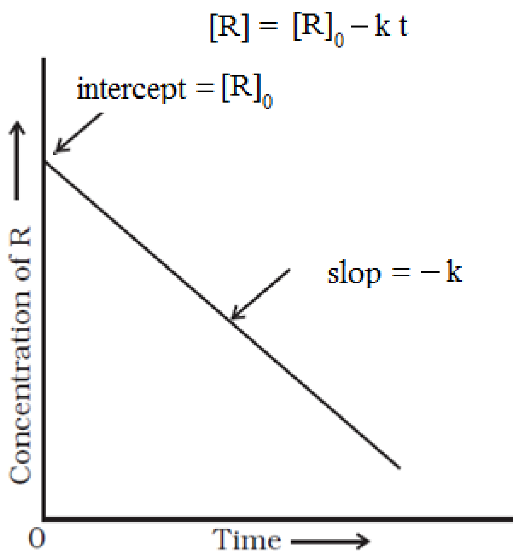
Comparing with equation of a straight line‘ y = mx + c, if we plot **[R]** against **t**, we get a straight line (Fig. below) with **slope = –k** and **intercept = $[R]_0$**.

Further simplifying equation:

$$[R] = [R]_0 - Kt$$

We get the rate constant, **k** as

$$K = [R]_0 - [R] / t$$



Zero order reactions are relatively uncommon but they occur under special conditions. Some enzyme catalyzed reactions and reactions which occur on metal surfaces are a few examples of zero order reactions. The decomposition of gaseous ammonia on a hot platinum surface is a zero order reaction at high pressure.

$$2NH_3\ g \xrightarrow[\text{Pt catalyst}]{1130K} N_2\ g + 3H_2\ g$$

$$\text{Rate} = k\,[NH_3]^0 = k$$

In this reaction, platinum metal acts as a catalyst. At high pressure, the metal surface gets saturated with gas molecules. So, a further change in reaction conditions is unable to alter the amount of ammonia on the surface of the catalyst making rate of the reaction independent of its concentration. The thermal decomposition of HI on gold surface is another example of zero order reaction.

First Order Reactions

In this class of reactions, the rate of the reaction is proportional to the first power of the concentration of the reactant R. For example,

$$R \rightarrow P$$

$$\text{Rate} = \frac{d\,R}{dt} = k\,R$$

$$\text{or}\quad \frac{d\,R}{R} = -k\,dt$$

Integrating this equation, we get

$$\ln [R] = -Kt + I$$

Again, I is the constant of integration and its value can be determined easily.

When t = 0, R = $[R]_0$, where $[R]_0$ is the initial concentration of the reactant.

Therefore, equation

$$\ln [R] = -Kt + I$$

We can be written as

$$\ln [R]_0 = -k \times 0 + I$$

$$\ln [R]_0 = I$$

Substituting the value of I in equation

$$\ln [R] = -Kt + I$$

we get

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

Rearranging this equation

$$\ln \frac{[R]}{[R]_0} = kt$$

or

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

At time t_1 from equation $\ln[R] = -kt + \ln[R]_0$

$$\ln [R]_1 = -Kt_1 + \ln [R]_0$$

And time t_2

$$\ln [R]_2 = -Kt_2 + \ln [R]_0$$

where, $[R]_1$ and $[R]_2$ are the concentrations of the reactants at time t_1 and t_2 respectively.

Subtracting $\ln [R]_2 = - Kt_2 + \ln [R]_0$ from $\ln [R]_1 = - Kt_1 + \ln [R]_0$

We get

$$\ln[R]_1 - \ln[R]_2 = - kt_1 - (-kt_2)$$

$$\ln [R]_1/[R]_2 = K(t_2-t_1)$$

$$K = 1/ (t_2-t_1) \ \ln [R]_1/[R]_2$$

Equation $\ln[R] = -kt + \ln[R]^0$ can also be written as

$$\ln [R] / [R]_0 = -k\,t$$

Taking antilog of both sides

$$[R] / [R]_0 = e\ -^{k\,t}$$

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

Comparing equation $\ln[R] = -kt + \ln[R]^0$ with $y = mx + c$, if we plot ln [R] against (**t**) (Fig. below) we get a straight line with slope = –k and intercept equal to ln [R]0 The first order rate equation (10) can also be written in the form

$$K = 2.303/ t \ \log [R]_0 / [R]$$

$$\log [R]_0 / [R] = (K\,t) / 2.303$$

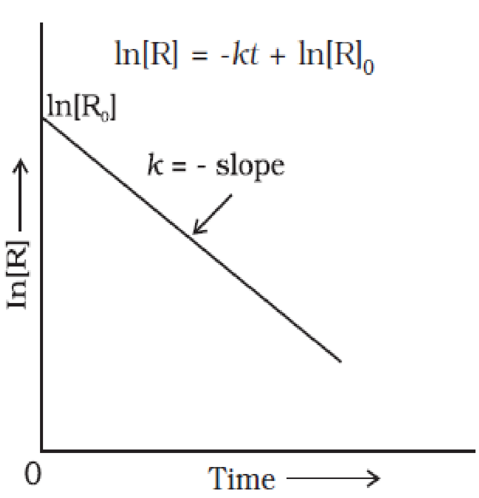
If we plot a graph between $\log [R]^0/[R]$ vs t, (Fig.below) ‹the slope = k/2.303

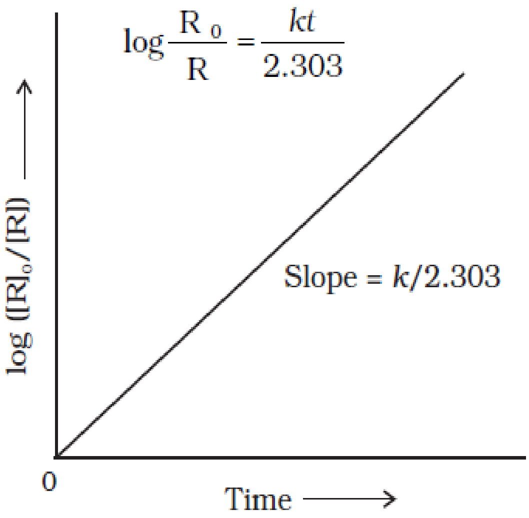
Hydrogenation of ethene is an example of first order reaction.

$$C_2H_4(g) + H_2\ (g) \rightarrow C_2H_6(g($$

$$Rate = k\ [C_2H_4[$$

All natural and artificial radioactive decay of unstable nuclei take place by first order kinetics.





Example

The initial concentration of N_2O_5 in the following first order reaction

$$N_2O_{5(g)} \rightarrow 2\,NO_{2(g)} + 1/2O_{2\,(g)}$$

was 1.24×10^{-2} mol L^{-1} at 318 K. The concentration of N_2O_5 after 60 minutes was 0.20×10^{-2} mol L^{-1}.Calculate the rate constant of the reaction at 318 K.

Solution: For a first order reaction

$$\log\frac{[R]_1}{[R]_2} = \frac{k(t_2 - t_1)}{2.303}$$

$$k = \frac{2.303}{(t_2 - t_1)}\log\frac{[R]_1}{[R]_2}$$

$$= \frac{2.303}{(60\,\text{min} - 0\,\text{min})}\log\frac{1.24\times10^{-2}\,\text{mol}\,L^{-1}}{0.20\times10^{-2}\,\text{mol}\,L^{-1}}$$

$$= \frac{2.303}{60}\log 6.2\,\text{min}^{-1}$$

$$k = 0.0304\ \text{min}^{-1}$$

Let us consider a typical first order gas phase reaction

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

Let p_i be the initial pressure of A and p_t the total pressure at time ‘t’. Integrated rate equation for such a reaction can be derived as Total pressure

$$p_t = p_A + p_B + p_C \text{ (pressure units)}$$

p_A, p_B and p_C are the partial pressures of A, B and C, respectively. If x atm be the decrease in pressure of A at time t and one mole each of B and C is being formed, the increase in pressure of B and C will also be x atm each.

	A(g)	$\rightarrow$	B(g)	+	C(g)
At $t = 0$	p_i atm		0 atm		0 atm
At time t	$(p_i - x)$ atm		x atm		x atm

where, p_i is the initial pressure at time $t = 0$.

$$p_t = (p_i - x) + x + x = p_i + x$$

$$x = (p_t - p_i)$$

where, $p_A = p_i - x = p_i - (p_t - p_i)$

$$= 2p_i - p_t$$

$$k = \left(\frac{2.303}{t}\right)\left(\log\frac{p_i}{p_A}\right) \quad \text{..........................16}$$

$$= \frac{2.303}{t}\log\frac{p_i}{(2p_i - p_t)}$$

Example

The following data were obtained during the first order thermal decomposition of N_2O_5 (g) at constant volume:

$$2N_2O_5\ g \rightarrow 2N_2O_4\ g + O_2\ g$$

S.No.	Time/s	Total Pressure/(atm)
1.	0	0.5
2.	100	0.512

Calculate the rate constant.

Solution: Let the pressure of N_2O_5(g) decrease by 2x atm. As two moles of N_2O_5 decompose to give two moles of N_2O_4(g) and one mole of O_2 (g), the pressure of N_2O_4 (g) increases by 2x atm and that of O_2 (g) increases by x atm.

	$2N_2O_5$ g	$2N_2O_4$ g	O_2 g
Start $t = 0$	0.5 atm	0 atm	0 atm
At time t	(0.5 – 2x) atm	2x atm	x atm

$$p_t = p_{N_2O_5} + p_{N_2O_4} + p_{O_2}$$

$$= (0.5 - 2x) + 2x + x = 0.5 + x$$

$$x \quad p_t \quad 0.5$$

$$p_{N_2O_5} = 0.5 - 2x$$

$$= 0.5 - 2\ (p_t - 0.5) = 1.5 - 2p_t$$

$$\text{At} \quad t = 100\text{ s};\ p_t = 0.512\text{ atm}$$

$$p_{N_2O_5} = 1.5 - 2 \times 0.512 = 0.476\text{ atm}$$

Using equation (16)

$$k = \frac{2.303}{t}\log\frac{p_1}{p_A} = \frac{2.303}{100\,\text{s}}\log\frac{0.5\,\text{atm}}{0.476\,\text{atm}}$$

$$= \frac{2.303}{100\,\text{s}} \times 0.0216 = 4.98 \times 10^{-4}\text{s}^{-1}$$

Half-Life of a Reaction

The half-life of a reaction is the time in which the concentration of a reactant is reduced to one half of its initial concentration. It is represented as $t_{1/2}$.

For a **zero order** reaction, rate constant is given by equation:

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

$$\text{At } t = t_{1/2}, \quad [R] = \frac{1}{2}[R]_0$$

The rate constant at $t_{1/2}$ becomes

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

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

It is clear that $t_{1/2}$ for a zero order reaction is directly proportional to the initial concentration of the reactants and inversely proportional to the rate constant.

For the **first order** reaction

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

$$\text{at} \quad t = t_{1/2} \qquad [\mathrm{R}] = \frac{[\mathrm{R}]_0}{2}$$

So, the above equation becomes

$$k = \frac{2.303}{t_{1/2}} \log \frac{\cancel{\mathrm{R}}_0}{\cancel{\mathrm{R}}_0/2}$$

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

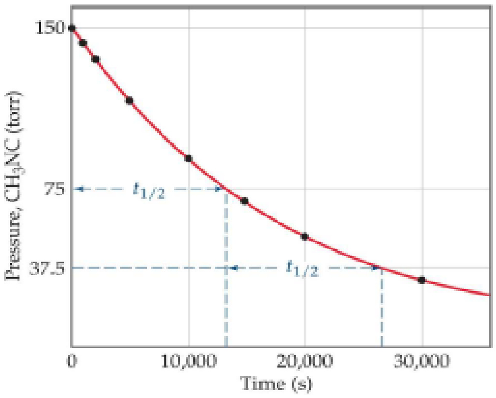
$$t_{1/2} = \frac{2.303}{k} \quad 0.301$$

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

Or

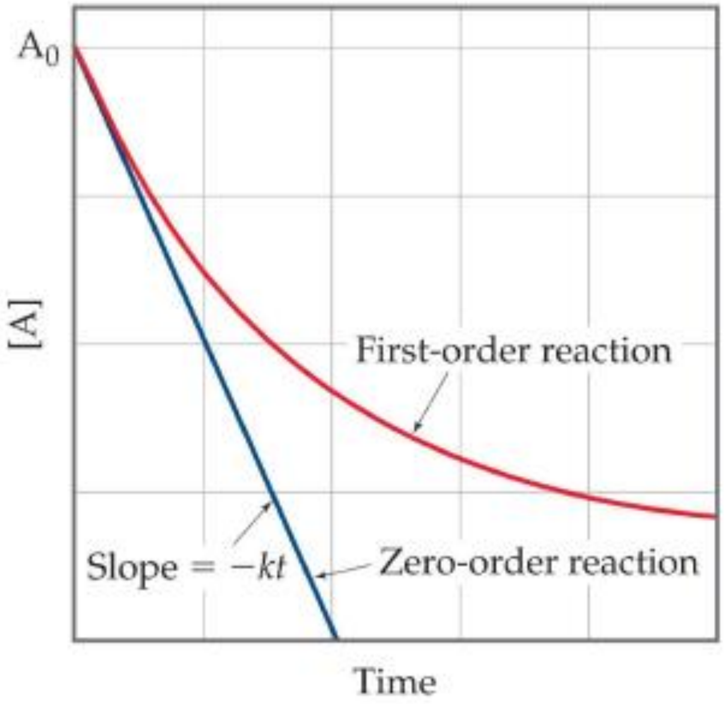
$[A]_{t1/2} = ½[A]_0$

For a 1st order $\ln \frac{[A]_t}{[A]_0} = -kt$



$$t_{1/2} = -\frac{\ln \frac{[A]_t}{[A]_0}}{k} = -\frac{\ln \frac{½[A]_0}{[A]_0}}{k} = -\frac{\ln \frac{1}{2}}{k} = \frac{\ln 2}{k} = \frac{0.693}{k}$$

It can be seen that for a first order reaction, half-life period is constant, i.e., it is independent of initial concentration of the reacting species. The half-life of a first order equation is readily calculated from the rate constant and vice versa.



For **zero order** reaction $t_{1/2} \propto [R]_0$. For **first order** reaction $t_{1/2}$ is independent of $[R]_0$.

Example

A first order reaction is found to have a rate constant, $k = 5.5 \times 10^{-14}\ s^{-1}$. Find the half-life of the reaction.

Solution: Half-life for a first order reaction is

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

$$t_{1/2} = \frac{0.693}{5.5\times10^{-14} s^{-1}} = 1.26 \times 10^{13} s$$

Example

Show that in a first order reaction, time required for completion of 99.9% is 10 times of half-life ($t_{1/2}$) of the reaction.

Solution: When reaction is completed 99.9%, $[R]_n = [R]_0 - 0.999[R]_0$

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

$$= \frac{2.303}{t} \log \frac{[R]_0}{[R]_0 - 0.999[R]_0} = \frac{2.303}{t} \log 10^3$$

$$t = 6.909/k$$

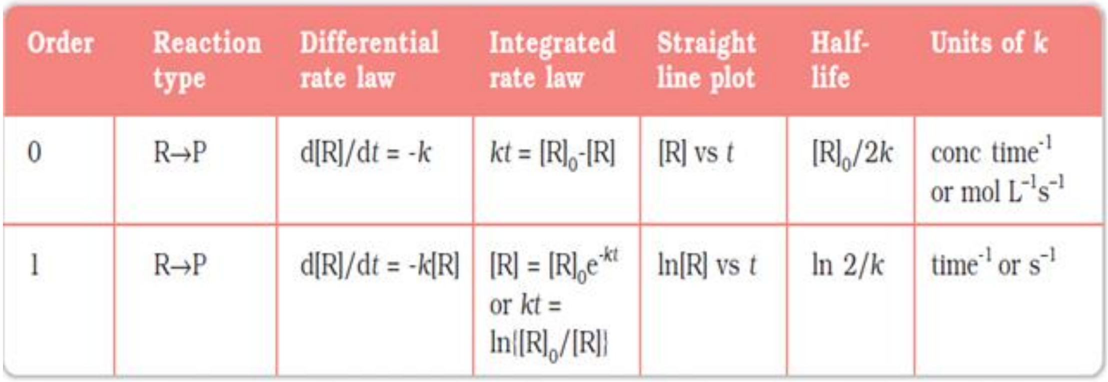
For half-life of the reaction

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

$$\frac{t}{t_{1/2}} = \frac{6.909}{k} \times \frac{k}{0.693} = 10$$

Table below summarizes the mathematical features of integrated laws of zero and first order reactions

Table : Integrated Rate Laws for the Reactions of Zero and First Order



Order	Reaction type	Differential rate law	Integrated rate law	Straight line plot	Half-life	Units of k
0	R→P	$d[R]/dt = -k$	$kt = [R]_0 - [R]$	[R] vs t	$[R]_0/2k$	conc time^{-1} or mol L^{-1}s^{-1}
1	R→P	$d[R]/dt = -k[R]$	$[R] = [R]_0 e^{-kt}$ or $kt = \ln\{[R]_0/[R]\}$	ln[R] vs t	$\ln 2/k$	time^{-1} or s^{-1}

Example for order reaction calculated:

Consider the table of initial rates for the reaction: $2ClO_2 + 2OH^{1-} \rightarrow ClO_3^{1-} + ClO_2^{1-} + H_2O$.

Experiment	$[ClO_2]_o$, mol/L	$[OH^{1-}]_o$, mol/L	Initial Rate, mol/(L · s)
1	0.050	0.100	5.75×10^{-2}
2	0.100	0.100	2.30×10^{-1}
3	0.100	0. 050	1.15×10^{-1}

a . Order with respect to ClO_2: ____________________

b. Order with respect to OH^{1-}: ____________________

c. Rate law for this reaction: ____________________________________

d. Value and units for the rate constant: ____________________________________

Answer:

$$\frac{rate_2}{rate_1} = \frac{k[ClO_2]_2^m[OH^-]_2^n}{k[ClO_2]_1^m[OH^-]_1^n}$$

$$\frac{0.230}{0.0575} = \frac{0.100^m}{0.0500^m}$$

$$4 = 2^m$$

2 = m, so order is 2

$$\frac{rate_2}{rate_3} = \frac{k[ClO_2]_2^m[OH^-]_2^n}{k[ClO_2]_3^m[OH^-]_3^n}$$

$$\frac{0.230}{0.115} = \frac{0.100^m}{0.0500^m}$$

$$2 = 2^n$$

1 = n, so order is 1

a. Order with respect to ClO_2: 2

b. Order with respect to OH^{1-}: 1

c. Rate law for this reaction: so, rate = $k[ClO_2]^2[OH^{1-}]^1$

d. Value and units for the rate constant: $k = 230 \frac{L^2}{mol^2 \cdot s}$

Consider the table of initial rate for the reaction between hemoglobin (Hb) and carbon monoxide.

Experiment	[HB]$_o$, μmol/L	[CO] $_o$, μmol/L	Initial Rate, μmol/(L · s)
1	2.21	1.00	0.619
2	4.42	1.00	1.24
3	3.36	2.40	2.26

a . Order with respect to HB: ________________

b. Order with respect to CO: ________________

c. Rate law for this reaction: ____________________________

d. Value and units for the rate constant: ____________________________

Answer:

$$\frac{rate_2}{rate_1} = \frac{k[HB]_2^m[CO]_2^n}{k[HB]_1^m[CO]_1^n}$$

$$\frac{1.24}{0.619} = \frac{4.42^m}{2.21^m} \text{ s}$$

$$2 = 2^m$$

1 = m, so the order is 1

$$\frac{rate_3}{rate_1} = \frac{k[HB]_3^m[CO]_3^n}{k[HB]_1^m[CO]_1^n}$$

$$\frac{2.26}{0.619} = \frac{3.36^{\ 1}}{2.21^{\ 1}} \frac{2.41^{\ n}}{1.00^{\ n}}$$

$$2.4 = 2.4^n$$

1 = n, so the order is 1

a. Order with respect to HB: 1

b. Order with respect to CO: 1

c. Rate law for this reaction: so, rate = $k[HB]^1[CO]^1$

d. Value and units for the rate constant: $k = 0.28 \ \frac{L}{mol \cdot s}$

Physical chemistry / Kinetic chemistry
(2025-2026)

4th week 19/11/2025

Prof. Dr. Abdulqadier Hussien Alkhazraji

Lecture 4

Third order reaction 3nd

In general, a third order reaction can be represented as:

بشكل عام ، يمكن تمثيل تفاعل من المرتبة الثالثة كالاتي:

- $3A \rightarrow$ Products (when a reaction involves only one reactant)
- $2A + B \rightarrow$ Products (when a reaction involves only two reactants)
- $A + B + C \rightarrow$ Products (when a reaction involves three different reactants)

Case (I) : When a reaction involves only one reactant or when all the reactants have same initial concentration ([A] =[B]=[C]:

Consider a general third order reaction:

الحالة (I): عندما يتضمن التفاعل مادة تفاعل واحدة فقط أو عندما يكون لجميع المتفاعلات نفس التركيز الأولي ([A] = [B] = [C]):

ضع في اعتبارك التفاعل العام من الرتبة الثالثة:

$$A + B + C \rightarrow \text{Products}$$

$$3A \rightarrow \text{Products}$$

$$\begin{array}{lcc} t = 0 & a & 0 \\ t = t & a-x & x \end{array}$$

The rate law applicable for a third order reaction at time (t) is given by

يتم إعطاء قانون معدل سرعة التفاعل المطبق على تفاعل المرتبة الثالثة في الوقت (t) :

$$\frac{dx}{dt} = K\,(a-x)^3$$

Rearranging the equation, we get;

$$\frac{dx}{(a-x)^3} = K\,dt$$

Integrating the equation between proper limits, we get;

$$\int_0^x \frac{dx}{(a-x)^3} = \int_0^t K\,dt$$

$$\frac{1}{2(a-x)^2} = Kt + I$$

When (t = 0), (x = 0), where x is the initial concentration of the reactant. Therefore, equation can be written as

$$\frac{1}{2(a-0)^2} = K * 0 + I$$

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

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

$$K = \frac{1}{2t}\left[\frac{1}{(a-x)^2} - \frac{1}{2a^2}\right]$$

This is the expression for the rate constant for third order reaction with equal initial concentration of reactants.

Units of rate constant (k):

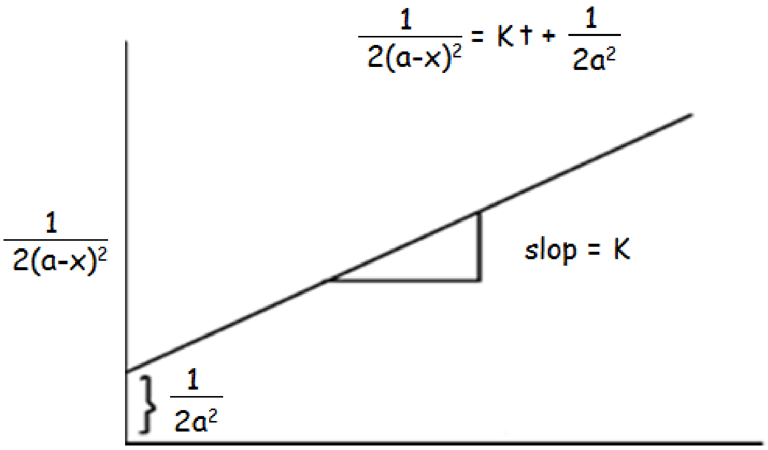
lit^{2}.mole^{-2}sec^{-1}, lit2.mole^{-2}min^{-1}, lit^{2}.mole^{-2} hour^{-1}, lit^{2}.mole^{-2}day$^{-1,}$ lit^{2}.mole^{-2}year^{-1}

The value of rate constant (k) is depends on the units of concentration used. This is because the rate equation involves the term of concentration.

قيمة ثابت معدل سرعة التفاعل (k) تعتمد على وحدات التركيز المستخدمة لأن معادلة معدل سرعة التفاعل تتضمن مصطلح التركيز.

For a third order reaction (with equal initial conc.), a graph of 1/2(a-x)^{2} vs. t is a straight line, the slope = k and intercept =1/2a^{2}

تفاعل المرتبة الثالثة (بتركيز أولي متساوٍ) ، يمثل بالرسم البياني بين 1/2(a-x)^{2} على محور (y) و قيمة الوقت (t) على محور (x).



Half-Life of a 3rd order reaction, where [A] = [B] = [C]

نصف العمر لتفاعل الرتبة الثالثة ، حيث [A] = [B] = [C]

Concentrations from the equation,

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

At $t = t_{1/2}$ *and* $x = a/2$

$$Kt_{1/2} = \frac{1}{2(a-\frac{a}{2})^2} - \frac{1}{2a^2}$$

$$t_{1/2} = \frac{1}{k}\left[\frac{1}{2(\frac{a}{2})^2} - \frac{1}{2a^2}\right] \Rightarrow t_{1/2} = \frac{1}{k}\left[\frac{1}{\frac{2a^2}{4}} - \frac{1}{2a^2}\right]$$

$$t_{1/2} = \frac{1}{k}\left[\frac{4}{2a^2} - \frac{1}{2a^2}\right] \Rightarrow t_{1/2} = \frac{3}{2ka^2}$$

- *Case (II) , where [A] ≠ [B] ≠ [C]*

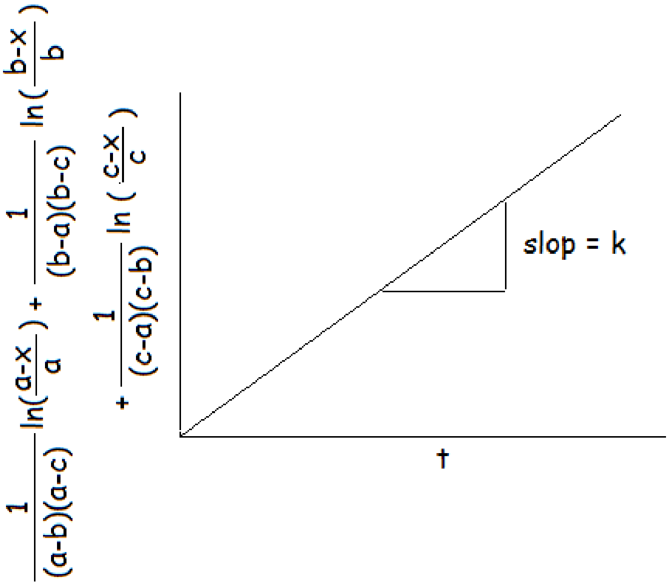
	A	+	B	+	C	→	Products
t = 0	*a*		*b*		*c*	→	*0*
t =t	*(a-x)*		*(b-x)*		*(c-x)*	→	*x*

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

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

$$\int_0^x \frac{dx}{(a-x)(b-x)(c-x)} = k\int_0^t dt$$

$$\frac{1}{(a-b)(a-c)}\ln\left(\frac{a-x}{a}\right) + \frac{1}{(b-a)(b-c)}\ln\left(\frac{b-x}{b}\right) + \frac{1}{(c-a)(c-b)}\ln\left(\frac{c-x}{c}\right) = kt$$



- *Case (III) , where* $[A]=[B] \neq [C]$

$$A + B + C \rightarrow \text{Products}$$

$$2A + B \rightarrow \text{Products}$$

$$A + 2B \rightarrow \text{Products}$$

$$dx/dt = k\,(a-x)(b-x)(c-x)$$

Where a = b; (a-x) = (b-x)

$$(a-x)\,(b-x) = (a-x)^2$$

$$dx/dt = K\,(a-x)^2\,(c-x)$$

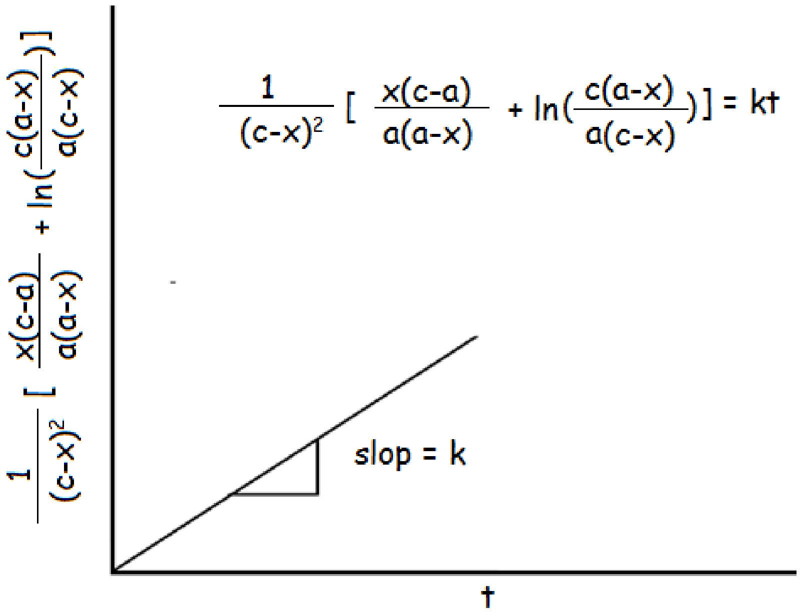
Rearrange the following equation above we get:

$$dx/(a-x)^2\,(c-x) = kt$$

Integrating both sides

$$\int_0^x \frac{dx}{(a-x)^2(c-x)} = k\int_0^t dt$$

$$\frac{1}{(c-x)^2}\left[\frac{x(c-a)}{a(a-x)} + \ln\left(\frac{c(a-x)}{a(c-x)}\right)\right] = kt$$



- Methods for finding the reaction constant and reaction order for simple reaction

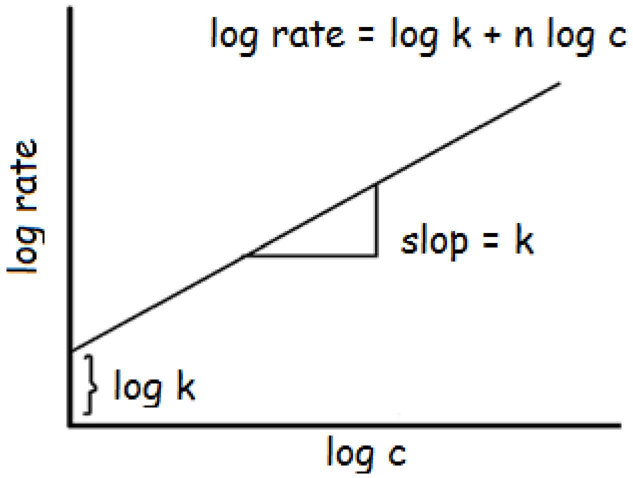
1. Differential Method

$$dx/dt = kc^n$$

Where c is reactant concentration, n is order reaction

$$Log(dx/dt) = \log (kc^n)$$

$$\log rate = \log k + n \log c$$

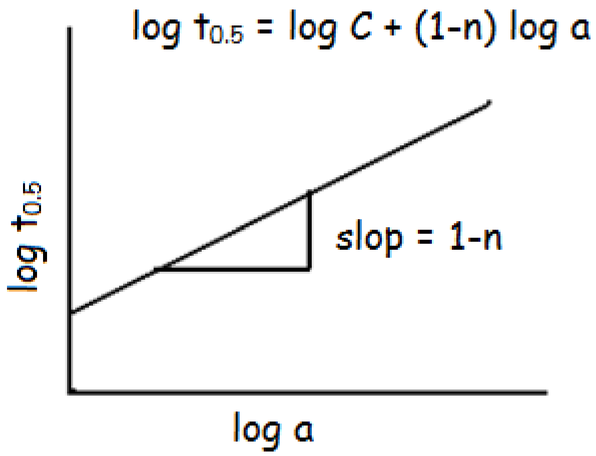


2. Half-Life Method

$$t_{0.5} \propto a^{1-n}$$

$$t_{0.5} = C\, a^{1-n}$$

$$\log t_{0.5} = \log C + (1-n) \log a$$



Physical chemistry / Kinetic chemistry
(2025-2026)

1st week 01/10/2025
Lecturer Prof. Dr. Abdulqadier Hussien Al Khazraji

مفاهيم عامة للحركية الكيميائية

GENERAL IDEAS OF CHEMICAL KINETICS

يبيّن الثرموديناميك أنّه عند حدوث تحوّل كيميائي يمكن بسهولة معرفة الطاقات المرافقة للتحوّل مثل انثالبية التحوّل والطاقة الحرة للتفاعل ...الخ وعندما تكون في تفاعل كيميائي طاقة النواتج أخفض من طاقة المواد المتفاعلة فإنّ التحوّل يمكن أن يحدث بصورة تلقائية، وبمعنى أخر فإنّ تغيّرات الطاقة الحرة المرافقة لتفاعل معين يمكن أن تعطي دليلاً عن إمكانية حدوث التفاعل بصورة تلقائية ($\Delta G < 0$) أو أن يكون متوازناً (معكوس)($\Delta G = 0$) أو عدم إمكانية حدوثه ($\Delta G > 0$) ، جميع تغيّرات الدوال الثرموديناميكية تتعلق فقط بالحالة البدائية (طاقة المواد المتفاعلة) والحالة النهائية (طاقة المواد الناتجة) للتفاعل الإجمالي وليس له علاقة بالطريق المسلوك أو الزمن الذي يستغرقه التفاعل حتى يتم نحو التمام، فمثلاً التفاعل التالي:

$$H_{2(g)} + 1/2O_{2(g)} = H_2O_{(l)} \; ; \; \Delta H^o = -285 \text{ kJ/mol} \; , \; \Delta G^o = -237 \text{ kJ/mol}$$

من المفروض أن يحدث بصورة تلقائية، غير أنّ التفاعل عند الشروط العادية من درجة الحرارة والضغط لا يحدث ولو بعد عدة سنوات، أي أنّ التفاعل بطيء للغاية، إلا أنّه يحدث بصورة سريعة عند حدوث شرارة كهربائية أو وجود وسيط وهذا يدل على أنّ التفاعل مُمكن ثرموديناميكياً إلا أنّه غير مُمكن حركيّاً وذلك لأنّ الطريق الذي ينقل المواد المتفاعلة إلى نواتج يحتاج إلى طاقة عالية غير متوفرة، حيث أنّ طاقة الروابط للهيدروجين والأوكسجين 435 and 490 kJ/mol على التوالي لذلك يدخل الزمن كمتغيّر لوصف الحالة في الحركيّة الكيميائية. إنّ العملية الكيميائية التي يتم بموجبها تحوّل المواد المتفاعلة إلى نواتج التفاعل هي موضوع دراسة الحركيّة الكيميائية، والتي تهتم بتحديد سرعة التفاعل والشروط التي تؤثّر في هذه السرعة لذا نجد مما تقدم أنّ موضوع الحركيّة الكيميائية هو دراسة مستفيضة للتفاعل الكيميائي: كيف يحدث مع الزمن، وتأثير الشروط، ووضع آلية التفاعل، وإيجاد العلاقة بين المُميزات الحركيّة مع تركيب المواد المتفاعلة، وطاقة العملية وفيزيائية تنشيط الجسيمات.

جزيئية التفاعل Molecularity of a reaction

الجزيئية في الكيمياء هي الإشارة إلى عدد الجزيئات التي تتقارب من بعضها من أجل إجراء تفاعل أولي، وهو يوافق مجموع المعاملات الستوكيومترية للمتفاعلات في التفاعل الأولي، أي أنها إشارة إلى عدد الجزيئات التي تكون مسؤولة عن تحديد المرحلة المحددة لسرعة التفاعل واعتماداً على عدد الجزيئات المشتركة في العملية يمكن أن يكون التفاعل أحادي الجزيء أو ثنائي الجزيء أو ثلاثي الجزيء.

التفاعل أحادي الجزيء هو تفاعل يشارك فيه جزيء واحد فقط في التفاعل، يتصادم جزيئين متفاعلين مع بعضهما البعض في تفاعل ثنائي الجزيء ويتضمن التفاعل الجزيئي الثلاثي لثلاثة جزيئات متفاعلة في خطوة أولية واحدة وهذه التفاعلات الجزيئية نادرة نسبيًا لأنها تنطوي على الاصطدام المتزامن لثلاثة جزيئات في الاتجاه الصحيح ، وهو حدث نادر.

Molecularity	Chemical Reaction
Unimolecular	$PCl_5 \rightarrow PCl_3 + Cl_2$
Bimolecular	$2HI \rightarrow H_2 + I_2$
Trimolecular	$2SO_2 + O_2 \rightarrow 2SO_3$
Bimolecular	$NO + O_3 \rightarrow NO_2 + O_2$
Trimolecular	$2CO + O_2 \rightarrow 2CO_2$
Trimolecular	$2FeCl_3 + SnCl_2 \rightarrow SnCl_2 + 2FeCl_2$

اذن التفاعل الكيميائي الذي يحدث في خطوة واحدة فقط ، أي أن كل ما يحدث في خطوة واحدة يسمى تفاعل أولي.

$$PCl_5 \rightarrow PCl_3 + Cl_2$$

بينما يسمى التفاعل الكيميائي الذي يحدث في تسلسل من خطوتين أو أكثر تفاعلًا معقدًا.

$$2NO_{(g)} + O_{2(g)} \rightarrow 2NO_{2(g)}$$

يسمى تسلسل الخطوات التي يحدث من خلالها تفاعل معقد آلية او ميكانيكية التفاعل وكل خطوة في الآلية هي تفاعل أولي،

على سبيل المثال ، يتم تحلل H_2O_2 في الخطوتين التاليتين:

Overall Reaction: $H_2O_2 \rightarrow H_2O + 1/2O_2$

Step 1: $H_2O_2 \rightarrow H_2O + [O]$ Slow

Step 2: $[O] + [O] \rightarrow O_2$ Fast

الخطوة البطيئة (slow step) هي من تحدد معدل سرعة التفاعل وهذا يعني في المثال اعلاه ان الخطوة الاولى هي من تحدد جزيئية التفاعل وبالتالي التفاعل هو أحادي الجزيء.

Notes:

- Molecularity is a theoretical concept.
- Molecularity cannot be zero, -ve, fractional, infinite and imaginary.
- Molecularity cannot be greater than three because more than three molecules may not mutually collide with each other.

ملاحظات:

- الجزيئية مفهوم نظري.
- لا يمكن أن تكون الجزيئية صفراً ، أو قيمة سالبة ، أو كسرية ، أو قيمة غير محددة ، أو خيالية.
- لا يمكن أن تكون الجزيئية أكبر من ثلاثة لأن أكثر من ثلاثة جزيئات قد لا تصطدم بعضها ببعض.

There are some chemical reactions whose molecularity appears to be more than three from stoichiometric equations, e.g.

هناك بعض التفاعلات الكيميائية التي يبدو أن جزيئاتها أكثر من ثلاثة من المعاملات الستكيومترية ، على سبيل المثال

$$2NO_2 + F_2 \rightarrow 2NO_2F$$

The proposed mechanism is:

Over all reaction: $2NO_2 + F_2 \rightarrow 2NO_2F$

Step 1: $NO_2 + F_2 \rightarrow NO_2 + F$ Slow

Step 1: $NO_2 + F \rightarrow NO_2F$ Fast

The reaction is bimolecular.

GENERAL IDEAS OF CHEMICAL KINETICS

Outline: Kinetics

Reaction Rates	How we measure rates.
Rate Laws	How the rate depends on amounts of reactants.
Integrated Rate Laws	How to calculate amount left or time to reach a given amount.
Order of Reactions	How we measure order.
Half-life	How long it takes to react 50% of reactants.
Arrhenius Equation	How rate constant changes with temperature.
Mechanisms	Link between rate and molecular scale processes.

Rules of logarithms

$$\log(1) = 0 \qquad \ln(1) = 0$$

$$\log(10) = 1 \qquad \ln(e) = 1$$

$$\log(100) = 2 \qquad \ln(e^x) = x$$

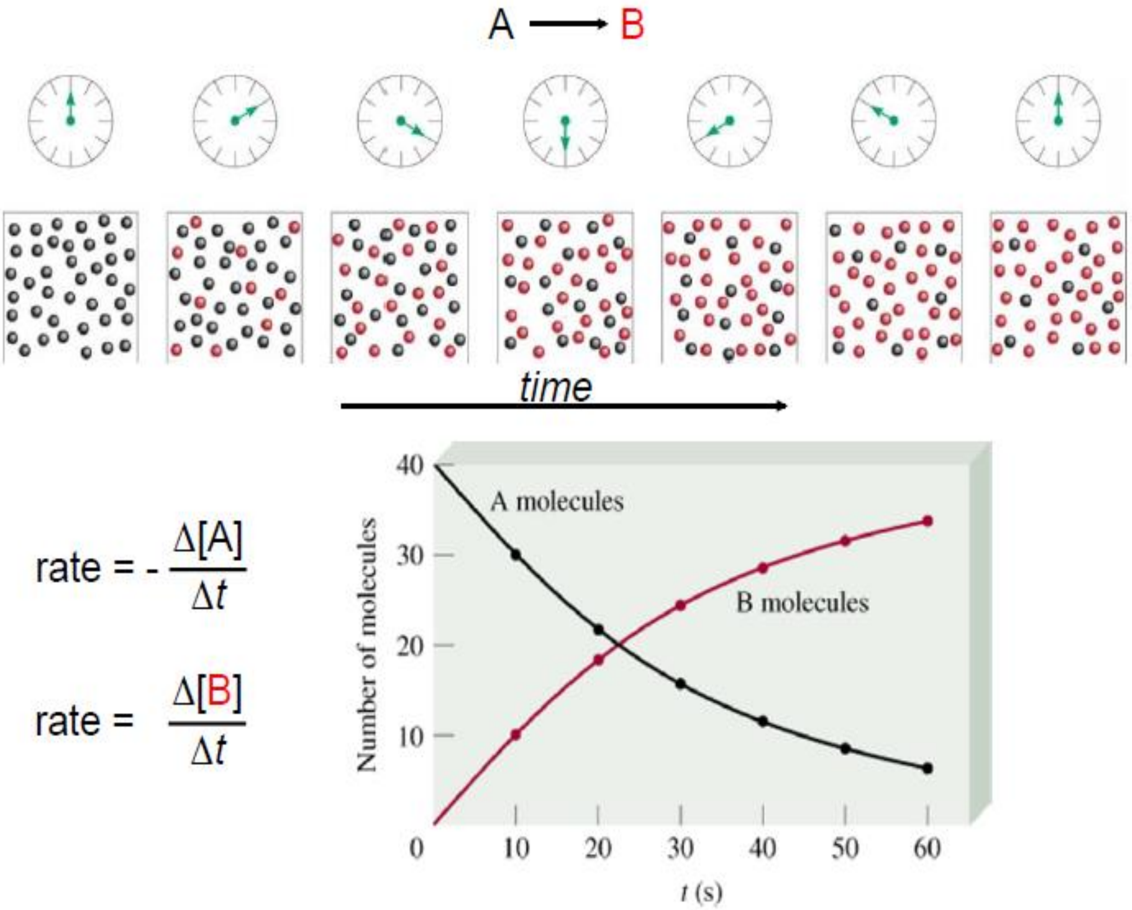
$$\text{Log}(10^x) = x$$

$$\log A^x = x\log A \qquad \ln A^x = x\ln A$$

$$\log\left(\frac{A^x}{B^x}\right) = \log\left(\frac{A}{B}\right)^x = x\log\left(\frac{A}{B}\right)$$

$$\log(AB) = \log A + \log B \qquad \log\left(\frac{A}{B}\right) = \log A - \log B$$

- Typically a plot of [A] or [B] *vs*. time will not yield a straight line, but instead a curve; concentration vs. time curve.
  Consider the difference in shape of concentration *vs*. time curve for reactants & products.



$$\text{rate} = -\frac{\Delta[A]}{\Delta t}$$

$$\text{rate} = \frac{\Delta[B]}{\Delta t}$$

تبيّن العلاقة اعلاه أنّ ميل المنحني عند أي زمن يكون مساوياً لسرعة التفاعل عند ذلك الزمن. ويلاحظ أنّ ميل المنحني الممثّل لتغيّرات تركيز A أو B مع الزمن يكون في البداية كبيرًا ويتناقص بالتدريج مع الزمن.

معدل سرعة التفاعل Reaction rate:

لأجل دراسة حركية تفاعل معين فلابد من الاهتمام بثلاث متغيرات رئيسية وهي **الزمن والتركيز ودرجة الحرارة** اضافة الى متغيرات اخرى قد تكون مهمة لبعض التفاعلات مثل العوامل المساعدة والمذيبات وتغير الضغط الخ ....

ويمكن تعريف معدل سرعة التفاعل (**r**) على انه معدل التغير في تركيز المواد المتفاعلة او الناتجة عند زمن معين حيث تنخفض تراكيز المواد المتفاعلة بمرور الزمن بينما تزداد تراكيز المواد الناتجة.

نلاحظ مماسبق ان العلاقة بين معدل سرعة التفاعل والتركيزعلاقة طردية فيعبرعن سرعة التفاعل الكيميائي بمعدل اختفاءالمتفاعل أو معدل تكوين أوظهورالنواتج.

Reaction Rate: The change in the concentration of a reactant or a product with time (M/s).

$$\text{Reactant} \rightarrow \text{Products}$$

$$A \rightarrow B$$

Reactant

$$\text{Average rate} = -\frac{\text{change in number of moles of A}}{\text{change in time}}$$

$$\text{Rate} = \frac{\Delta(\text{moles of A})}{\Delta t} = -\frac{\Delta[A]}{\Delta t} = -\frac{[A]_2 - [A]_1}{t_2 - t_1}$$

$$\text{Average rate} = \frac{\text{change in number of moles of B}}{\text{change in time}}$$

$$\text{Rate} = \frac{\Delta(\text{moles of B})}{\Delta t} = \frac{\Delta[B]}{\Delta t} = \frac{[B]_2 - [B]_1}{t_2 - t_1}$$

Products

[A] = molar concentration of reactant

$[A]_2 < [A]_1$

rate of *consumption* of reactant

[B] = molar concentration of product

$[B]_2 > [B]_1$

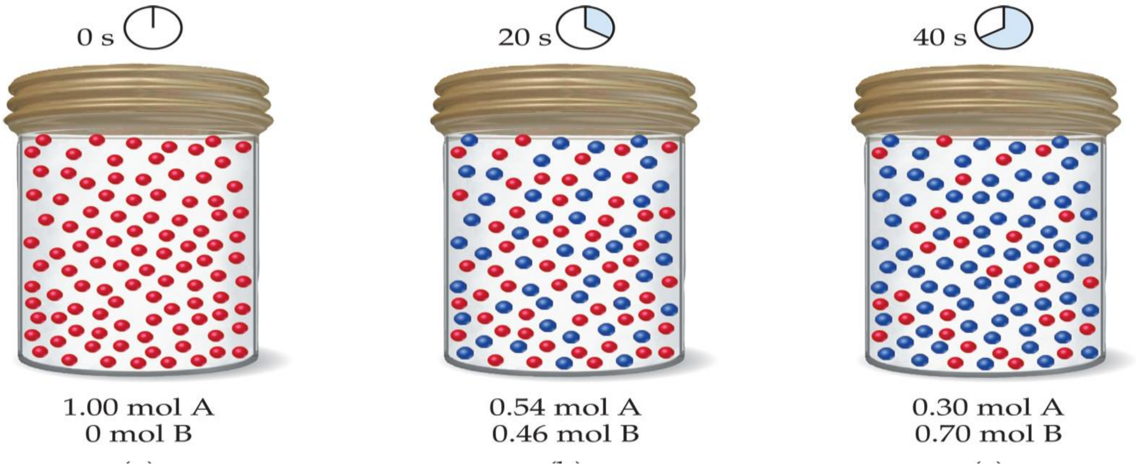
rate of *formation* of product

Rates of reactions can be determined by monitoring the change in concentration of either reactants or products as a function of time **t**.

يمكن تحديد معدلات التفاعلات من خلال مراقبة التغير في تركيز المواد المتفاعلة أو الناتجة كدالة للزمن t.

[A] = concentration of reactant A

[B] = concentration of product B



- ✓ Reactions are reversible, so as products accumulate them can begin to turn back into reactants.
- ✓ Early on the rate will depend on only the amount of reactants present.
- ✓ We want to measure the reactants as soon as they are mixed.
- ✓ The most useful (and general) way of measuring the rate of the reaction is in terms of change in concentration per unit time…

$$\textbf{Rate} = -\Delta[A]/\Delta t$$

$$\textbf{Rate} = \Delta[B]/\Delta t$$

Most Common Units… Rate = M/s = $mol.L^{-1}.s^{-1}$

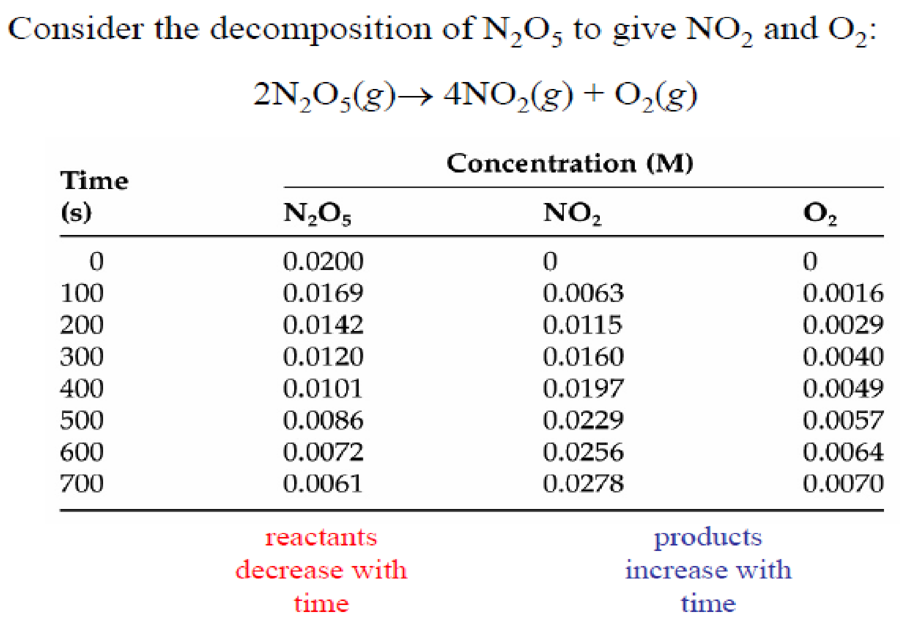
Where Molarity (M) = moles/Liter.

*الاشارة السالبة دليل نقصان تركيز المواد المتفاعلة بمرور الزمن.

*تعتمد سرعة التفاعل الكيميائي على الكتل الفعالة للمواد المتفاعلة او بعضها وكذلك على درجة الحرارة ووجود بعض المواد مثل العوامل المساعدة ، ويقصد بالكتل الفعالة **التراكيز** في حالة المحاليل **والضغط** في حالة الغازات **ومساحة السطح** في حالة المواد الصلبة.

* لاتمام اي تفاعل كيميائي لابد من اصطدام (Collision) جزيئات المواد المتفاعلة وعندما يكون الاصطدام فعال فأنه يؤدي الى حدوث التفاعل وهذا يفسر لماذا تزيد سرعة التفاعل بزيادة تركيز المواد المتفاعلة حيث ان الاصطدامات تزداد.

المثال ادناه يوضح قيم تحلل N_2O_5 مع الزمن



Consider the decomposition of N_2O_5 to give NO_2 and O_2:

$$2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$$

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

Factors Affecting Reaction Rate Constants:

Factors that Affect the Reaction Rate Constant

1. Temperature: At higher temperatures, reactant molecules have more Kinetic energy, move faster, and collide more often and with greater energy

- Collision Theory: When two chemicals react, their molecules have to collide with each other with sufficient energy for the reaction to take place.
- Kinetic Theory: Increasing temperature means the molecules move faster.
- Generally, as temperature increases, so does the reaction rate, this is because rate constant (k) is temperature dependent.

درجة الحرارة: في درجات الحرارة المرتفعة ، تحتوي الجزيئات المتفاعلة على المزيد من الطاقة الحركية ، تتحرك بشكل أسرع ، وتتصادم في كثير من الأحيان وبطاقة أكبر

- نظرية التصادم: عندما تتفاعل مادتان كيميائيتان يجب أن تتصادم جزيئاتهما مع بعضها البعض بطاقة كافية لحدوث التفاعل.
- النظرية الحركية: زيادة درجة الحرارة تعني أن الجزيئات تتحرك بشكل أسرع.
- بشكل عام ، كلما زادت درجة الحرارة ، يزداد معدل سرعة التفاعل أيضًا ، وذلك لأن معدل ثابت سرعة التفاعل (k) يعتمد على درجة الحرارة.

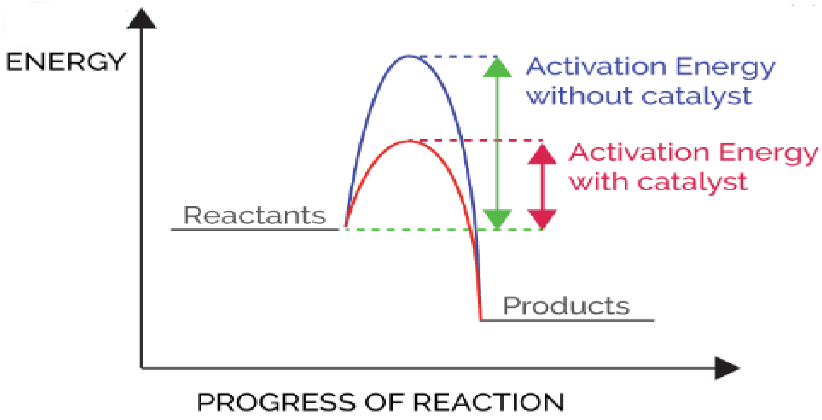
2. Concentrations of reactants

- As the concentration of reactants increases, so does the likelihood that reactant molecules will collide, in other hand, concentration affects reaction rate constant.

مع زيادة تركيز المواد المتفاعلة ، يزداد احتمال تصادم جزيئات المادة المتفاعلة ، ومن ناحية أخرى ، يؤثر التركيز على ثابت معدل التفاعل.

3. Catalysts

Speed up reactions by lowering activation energy.



4. Surface area of a solid reactant

More area for reactants to be in contact

مساحة أكبر للمواد المتفاعلة لتكون على اتصال

5. Pressure of gaseous reactants or products

Increased number of collisions

بزيادة الضغط تزداد عدد الاصطدامات

Here’s another way of looking at reaction rates…

For same reaction above:

$$2N_2O_{5(g)} \rightarrow 4NO_{2(g)} + O_{2(g)}$$

Notice that for every 1 mole of O_2 that appears, 4 moles of NO_2 will also appear. In the meantime, twice as many moles of N_2O_5 will be disappearing as moles of O_2 forming. Changes in concentrations of the reactants and /or products are inversely proportional to their stoichiometric proportions. This means that the rate of the reaction could be written like this:

$$\text{Rate} = -\tfrac{1}{2}\ \Delta\ [N_2O_5]/\Delta t \quad = \quad \tfrac{1}{4}\ \Delta[NO_2]/\Delta t \quad = \quad \Delta[O_2]/\Delta t$$

* (Notice the negative sign on the rate of $[N_2O_5]$ reminds us that it is disappearing.)

إليك طريقة أخرى للنظر في معدلات التفاعل ...

للتفاعل:

$$2N_2O_{5(g)} \rightarrow 4NO_{2(g)} + O_{2(g)}$$

لاحظ أنه مقابل كل ١ مول من غاز O_2 يظهر ، ستظهر أيضًا ٤ مولات من غاز NO_2. في غضون ذلك ، سيختفي ضعف عدد مولات غاز N_2O_5 مثل عدد مولات O_2 المتكونة. التغييرات في تركيزات المواد المتفاعلة و / أو الناتجة تتناسب عكسياً مع نسبها المتكافئة. هذا يعني أنه يمكن كتابة معدل سرعة التفاعل على النحو التالي:

$$\text{Rate} = -\tfrac{1}{2}\ \Delta\ [N_2O_5]/\Delta t \quad = \quad \tfrac{1}{4}\ \Delta[NO_2]/\Delta t \quad = \quad \Delta[O_2]/\Delta t$$

* (لاحظ الإشارة السالبة على معدل $[N_2O_5]$ تذكرنا أنها تختفي)

- **Reaction Rate and Stoichiometry:**

  In general for the reaction:

$$aA + bB \rightarrow cC + dD$$

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

Reaction Rate Laws:

Rate law – equation that shows the dependence of a reaction's rate on concentration.

قانون معدل سرعة التفاعل - المعادلة التي توضح اعتماد معدل سرعة التفاعل على التركيز.

For the general reaction:

$$aA + bB \rightarrow cC + dD$$

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

m and n – order of reaction with respect to A & B, determined from experiment. Typically small, positive, whole numbers. Negative numbers and fractions are possible.

Note: for a reaction, the rate law must be determined experimentally.

- The proportionality constant k is called the rate constant.

if m = 1, the reaction is 1st order in A

if n = 2, the reaction is 2nd order in B

overall order of the reaction = m + n

m و n - مرتبة التفاعل فيما يتعلق بـ A & B ، تحدد من التجربة وتأخذ أعداد صحيحة وموجبة وصغيرة عادةً اضافة الأعداد والكسور السالبة ممكنة.

ملاحظة: للتفاعل يجب تحديد قانون معدل سرعة التفاعل تجريبيًا.

- ثابت التناسب k يسمى ثابت معدل سرعة التفاعل.

إذا كانت m = 1 ، يكون التفاعل من الدرجة الأولى بالنسبة للمادة A

إذا كانت n = 2 ، يكون التفاعل من الدرجة الثانية النسبة للمادة B

رتبة التفاعل العام = n+m

➢ Reactions of the same overall order will have similar characteristics.

التفاعلات التي تمتلك نفس المرتبة العامة سيكون لها خصائص متشابهة.

Specifically we will discuss 0, 1st, 2nd and 3rd order overall reactions.

سنناقش على وجه التحديد تفاعلات الرتب العامة ٠ و ١ و ٢ و ٣.

- To generalize, for the reaction

Type	**Elementary Reaction**	**Rate law**
Unimolecular	A = products	Rate = $\mathbf{k[A]}$
Bimolecular	A + B = products	Rate = $\mathbf{k[A][B]}$
Bimolecular	2A = products	Rate = $\mathbf{k[A]^2}$
Termolecular	A + B + C = products	Rate = $\mathbf{k[A][B][C]}$
Termolecular	2A + B = products	Rate = $\mathbf{k[A]^2[B]}$
Termolecular	3A = product	Rate = $\mathbf{k[A]^3}$

A **rate law** describes the dependence of the (forward) rate on the concentrations of reactants.

يصف قانون معدل سرعة التفاعل اعتماد المعدل على تراكيز المواد المتفاعلة.

1. For an elementary reaction **(and <u>ONLY</u> for an elementary reaction)**, the rate law can be determined by simply looking at the balanced equation and using common sense. Below is a table of every possible elementary reaction.

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

بالنسبة للتفاعل الأولي (والتفاعل الأولي فقط) ، يمكن تحديد قانون المعدل بمجرد النظر إلى المعادلة المتوازنة واستخدام الفطرة السليمة. يوجد أدناه جدول بكل تفاعل أولي محتمل.

2. For a reaction with two reactants (A and B), the rate law is:

٢. بالنسبة للتفاعل المتكون من متفاعلين (**A** و **B**) ، يكون قانون المعدل هو:

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

Complete the table for the elementary reactions above:

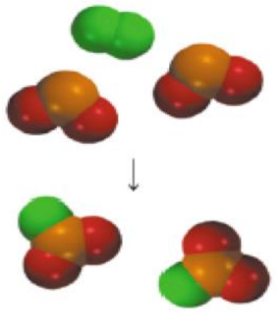
Elementary Reaction	**Order with respect to . . .**			Overall Order
	A	**B**	**C**	
A = products	First	-	-	First
A + B = products	First	First	-	Second
2A = products	Second	-	-	Second
A + B + C = products	First	First	First	Third
2A + B = products	Second	First	-	Third
3A = product	Third	-	-	Third

Concentration and Rate

❖ Rate laws are always determined experimentally.

➢ Reaction order is always defined in terms of reactant (**not product**) concentrations.

➢ The order of a reactant is not related to the stoichiometric coefficient of the reactant in the balanced chemical equation.



$$F_2\,(g) + \enclose{circle}{2}ClO_2\,(g) \longrightarrow 2FClO_2\,(g)$$

$$\text{rate} = k\,[F_2][ClO_2]^{\enclose{circle}{1}}$$

➢ In general, rates of reactions increase as concentrations increase since there are more collisions occurring between reactants.

➢ The overall concentration dependence of reaction rate is given in a rate law or rate expression.

رتبة التفاعل Order of Reactions:

لقد وجد ان معدل سرعة التفاعل تعتمد اعتمادا رئيسيا على تراكيز المواد المتفاعلة لكثير من التفاعلات.

بالنسبة للتفاعل التالي :

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

نجد ان معدل سرعة التفاعل ينخفض بأنخفاض تركيز المادة المتفاعلة (A) وفق العلاقة الاتية:

$$r \ \alpha \ [\ A\ ]^{n}$$

حيث (n) هي كمية ثابتة بالنسبة للتفاعل وتدعى رتبة التفاعل وهي الاس التي يرفع اليه التركيز لكي تتغير السرعة وفقا له، وهو كمية تجريبية اي يمكن ايجاده بالتجربة وهو كمية ثابتة بالنسبة لمادة متفاعلة معينة ولكنه قد يتغير.

اذا كانت $n = 0$ يدعى التفاعل من الرتبة الصفرية اي ان تراكيز المواد المتفاعلة ليس لها تأثير على معدل سرعة التفاعل وذلك يعني ان المواد المتفاعلة لاتعطي ناتج الا بوجود عامل مؤثر خارجي.

اذا كانت $n = 1$ يدعى التفاعل من الرتبة الاولى اي ان معدل السرعة يتناسب طرديا مع التركيز.

اذا كانت $n = 2$ يدعى التفاعل من الرتبة الثانية اي ان معدل السرعة يتناسب مع مربع التركيز المتبقي من المادة المتفاعلة عند زمن معين وقد تكون الرتبة كمية كسرية.

أما اذا كان التفاعل يشمل على أكثر من مادة متفاعلة واحدة وكما يأتي:

$$A + B + C + \cdots\cdots \rightarrow \text{Product}$$

فأن معدل السرعة في هذه الحالة سوف يتناسب مع المتبقي من تراكيز كل من المواد المتفاعلة مرفوعة لرتبة معينة وعند زمن معين، اي ان :

$$r \ \alpha \ [A]^{n1}[B]^{n2}[C]^{n3}$$

وسوف يكون التفاعل في هذه الحالة من الرتبة $n1$ بالنسبة للمادة A ومن الرتبة $n2$ بالنسبة للمادة B ومن الرتبة الثالثة بالنسبة للمادة C وهكذا.

ان الرتبة الكلية للتفاعل سوف تساوي مجموع الرتب الفردية للمواد المتفاعلة:

$$n = n_1 + n_2 + n_3 + \dots$$

ومن الجدير بالملاحظة فأن معادلة السرعة توضح كيفية تغير تراكيز المواد المتفاعلة في خطوات التفاعل الرئيسية دون اشتراك تراكيز المواد الناتجة في المعادلة الا نادرا. ومن جهة اخرى اذا تفحصنا العلاقة بين معدل السرعة والتركيز بصورة جيدة فأننا نجدها علاقة تناسب طرديه وعليه يمكن كتابة المعادلة اعلاه بالشكل التالي:

$$r \; \alpha \; [\, A \,]^n$$

لتصبح:

$$r = K\,[A]^n$$

حيث ان K ثابت معدل سرعة التفاعل وهو كمية ثابتة لتفاعل معين عند درجة حرارة معينة ولايتأثر بتغير التركيز او تغير الزمن الا انه يتأثر كثيرا عند تغير درجة الحرارة ويمكن الاعتماد على قيمة ثابت سرعة التفاعل لمقارنة تفاعل ما مع تفاعل اخر ، ويعد التفاعل سريعا اذا كانت قيمة K عالية مقارنة بتفاعل اخر اما وحداته فتعتمد على رتبة التفاعل.

ملاحظة مهمة : إذاضاعفنا التركيزالبدائي للمادة A ونتج عن ذلك تضاعف في معدل سرعة التفاعل فإنّ التفاعل يكون من المرتبة الأولى بالنسبة إلى A ، أما إذا أصبحت السرعة أربع أمثال فإنّ التفاعل يكون من المرتبة الثانية بالنسبة إلى A .

- A reaction is zero order in a reactant if the change in concentration of that reactant produces no effect.

$$r = k\,[A]^0$$

- A reaction is 1st order if doubling the concentration causes the rate to double.

$$r = k\,[A]^1$$

- A reaction is 2nd order if doubling the concentration causes a quadruple increase in rate.

$$r = k\,[A]^2$$

- 3rd order…doubling concentration leads to 2^3 (or 8 times) the rate.
- Note: The rate constant, k, does not depend on concentration.
- Once we have determined the rate law and the rate constant, we can use them to calculate initial reaction rates under any set of initial concentrations.

بصوره اخرى وبتوضيح اكثر:

Reaction Order & Rate Change with Concentrationconsider the reaction:

$$A \rightarrow B + C$$

☒ if 1st order overall:

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

if [A] increases by factor of 2, rate will increase by factor of 2^1 *OR* rate will double.

$$\text{Rate} = k[2]^1 = k[2]$$

☒ if 2nd order overall:

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

if [A] increases by factor of 2, rate will increase by factor of 2^2 *OR* rate will quadruple.

$$\text{Rate} = k\,[2]^2 = k\,[4]$$

☒ if 3nd order overall:

$$\text{Rate} = k\,[A]^3$$

☒ if [A] increases by factor of 2, rate will increase by factor of 2^2 *OR* rate will eight times.

$$\text{Rate} = k[2]^3 = k[8]$$

☒ if –1 order overall:

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

if [A] increases by factor of 2, rate will change by factor of 2^{-1} OR rate will decrease by half

$$\text{Rate} = k[2]^{-1} = k\,[\,0.5]$$

- ☒ if 0 order overall:

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

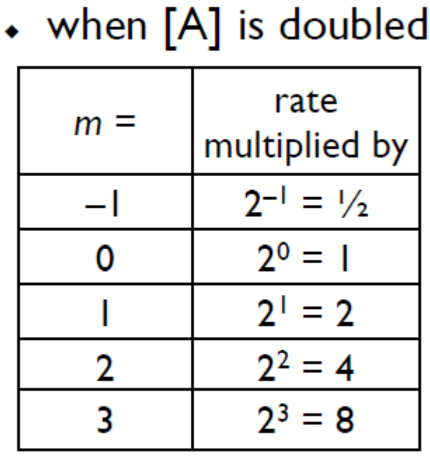
rate is constant; changes in [A] have no effect on the rate as long as some A is Present.

- ☒ in general, for the reaction:

$$A \rightarrow B + C$$

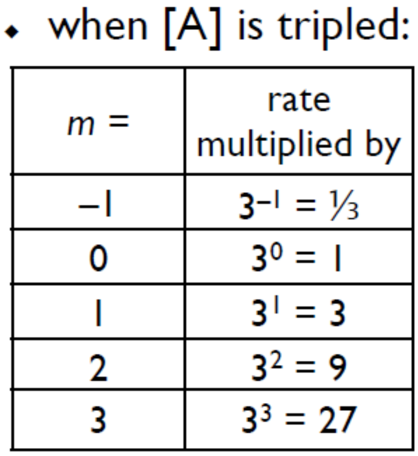
$$\text{Rate} = k[A]^m$$

If [A] changes by a factor of x, the rate will change by a factor of x^m



- when [A] is doubled:

m =	rate multiplied by
–1	$2^{-1} = ½$
0	$2^0 = 1$
1	$2^1 = 2$
2	$2^2 = 4$
3	$2^3 = 8$



- when [A] is tripled:

m =	rate multiplied by
–1	$3^{-1} = ⅓$
0	$3^0 = 1$
1	$3^1 = 3$
2	$3^2 = 9$
3	$3^3 = 27$

Units for the rate constant:

- ☒ The units of a rate constant will change depending upon the overall order.
- ☒ The units of rate are always M/s
- ☒ To find the units of a rate constant for a particular rate law, simply divide the units of rate by the units of molarity in the concentration term of the rate law.

$$\text{Rate (Ms}^{-1}) = \text{k[A]} \qquad 1^{\text{st}} \text{ order}$$

$$\text{k(units)} = \frac{\text{Ms}^{-1}}{\text{M}} = \text{s}^{-1}$$

Reaction Order & Units of *k*

order	rate law	$k =$	k units
1st	Rate = $k[A]$	k = Rate/[A]	s^{-1}
2nd	Rate = $k[A]^2$	k = Rate/$[A]^2$	$M^{-1}\bullet s^{-1}$
3rd	Rate = $k[A]^3$	k = Rate/$[A]^3$	$M^{-2}\bullet s^{-1}$
0	Rate = k	k = Rate	$M\bullet s^{-1}$

Physical chemistry / Kinetic chemistry

(2025-2026)

3^{rd} week 22/10/2025

Lecturer Prof. Dr. Abdulqadier Hussien Al Khazraji

Lecture 3

Second-Order Reactions

The two most common forms of second-order reactions will be discussed in detail in this section.

1. $A + A \rightarrow P$ rate = $k [A]^2$ second order

Or $2A \rightarrow P$

2. $A + B \rightarrow P$ rate = $k [A]^1[B]^1$ second order

<u>Case 1: Identical Reactants</u>

When materials A and B are present with the same initial concentration as $b = a$, or when A, B are the same substance as in the general equation.

Two of the same reactant (A) combine in a single elementary step.

$$A + A \rightarrow P$$

$$2A \rightarrow P$$

The reaction rate for this step can be written as;

$$\text{Rate} = -\frac{1}{2}\frac{d[A]}{dt} = +\frac{d[P]}{dt}$$

and the rate of loss of reactant A

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

Where k is a second order rate constant with units of M^{-1} min^{-1} or M^{-1} s^{-1}. Therefore, doubling the concentration of reactant A will quadruple the rate of the reaction.

$$2R \rightarrow P$$

At	t =0	R_0	0
At	t =t	R	x

The reaction rate for this step can be written as:

$$\text{Rate} = -\,dR/dt = K\,R^2$$

(Integrate dR from R_0 to R and dt from 0 to t)

$$dR/\,R^2 = -\,K\,dt$$

$$\int_{R_0}^{R} \frac{dR}{R^2} = -K\int_0^t dt$$

Mathematically;

$$\int \frac{dx}{x^2} = -\,\frac{1}{x} + I$$

$$-1/R + I = -\,Kt$$

$$-1/R = -\,Kt - I$$

$$1/R = Kt + I$$

Factor I is the constant of integration and its value can be determined easily.

When ($t = 0$), ($R = R_0$). Therefore, equation can be written as;

Therefore, equation ($1/R = Kt + I$) can be written as

$$1/R_0 = K^* 0 + I$$

$$I = 1/R_0$$

Substituting the value of I in equation ($1/R = Kt + I$);

$$1/R = Kt + 1/R_0$$

Equation above can also be written as;

$$1/R - 1/R_0 = Kt$$

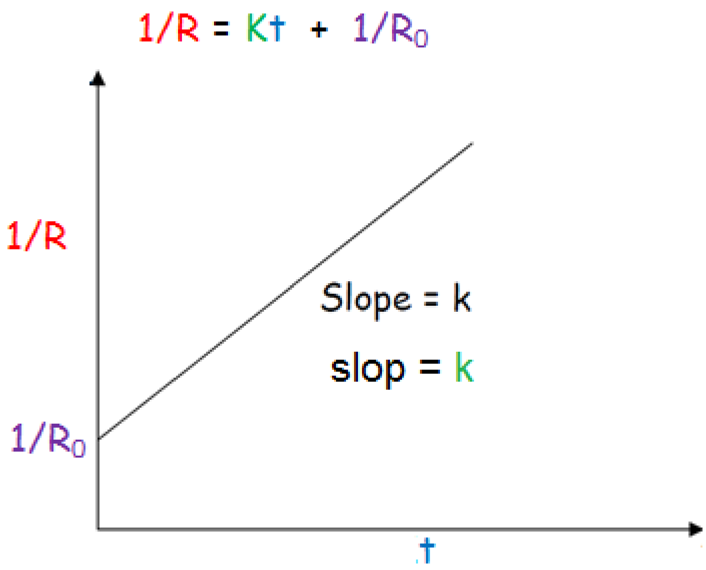
$$K = 1/R - 1/R_0 / t$$

Now for rate constant calculate by diagram:

$$1/R = Kt + 1/R_0$$

$$Y = mx + c$$

Plotting a straight line ($y = mx + c$) corresponding to this equation ($y = 1/[R]$, $x = t$, $m = k$, $c = 1/[R]_0$)



It can be observed that the slope of the straight line is equal to the value of the rate constant, k.

Half-Life of Second-Order Reactions (2R → P)

The half-life of a chemical reaction is the time taken for half of the initial amount of reactant to undergo the reaction.

Therefore, while attempting to calculate the half life of a reaction, the following substitutions must be made:

For a second order reaction, by equation:

$$1/R - 1/R_0 = Kt$$

At $t = t_{1/2}$ and $R = R_0/2$

$$\frac{1}{R_0/2} - \frac{1}{R_0} = K\,t_{1/2}$$

$$K\,t_{1/2} = \frac{2}{R_0} - \frac{1}{R_0}$$

$$K\,t_{1/2} = \frac{1}{R_0} \Rightarrow t_{1/2} = \frac{1}{R_0 K}$$

This equation for the half life implies that the half life is inversely proportional to the concentration of the reactants.

When the initial concentration of the reactant decreases to a quarter ([R] = [R]$_0$/4) we get:

$$\frac{1}{R_0/4} - \frac{1}{R_0} = K\,t_{3/4}$$

$$K\,t_{3/4} = \frac{4}{R_0} - \frac{1}{R_0} \Rightarrow K\,t_{3/4} = \frac{3}{R_0}$$

$$t_{3/4} = \frac{3}{R_0 K}$$

$$t_{3/4} - t_{1/2} = \frac{3}{R_0 K} - \frac{1}{R_0 K} = \frac{2}{R_0 K} = 2\,t_{1/2}$$

If R = R$_0$/8, obtain to:

$$\frac{1}{R_0/8} - \frac{1}{R_0} = K\,t_{7/8}$$

$$K\,t_{7/8} = \frac{8}{R_0} - \frac{1}{R_0} \Rightarrow t_{7/8} = \frac{7}{R_0 K}$$

$$t_{7/8} - t_{3/4} = \frac{7}{R_0 K} - \frac{3}{R_0 K} = \frac{4}{R_0 K} = 4\,t_{1/2}$$

We find that in the case of the second order reaction, and when there is only one reactant, the subsequent decrease in the initial concentration in half leads to the doubling of the differences between the corresponding times.

Case 2: Different Reactants(First order in each of two components ([A] ≠ [B])

Case 2: Different Reactants (First order in each of two components ([A] ≠ [B] , [A] = a and [B] = b)

	A	+	B	→	P
At t=0	a		b		0
t= t	a-x		b-x		x

$$\text{Rate} = -\,d[A]/dt = K\,[A][B] \qquad (1)$$

Two different reactants (A and B) combine in a single elementary step (Second order reaction with multiple reactants). As before, the rate at which (A) decreases can be expressed using the differential rate equation:

$$[A] = (a-x) \text{ and } B = (b-x) \qquad (2)$$

$$d[A] = d(a-x)/dt; \qquad (3)$$

$$d[A] = da/dt - dx/dt; \quad a = \text{constant}$$

$$d[A] = 0 - dx/dt = -\,dx/dt$$

$$\text{Rate} = -\,d[A]/dt = -\,(-\,dx/dt) = dx/dt$$

$$-\,d[A]/dt = dx/dt \qquad (4)$$

Substituting Eq. 4 in the Eq. 1, get:

$$dx/dt = K\,(a-x)(b-x) \qquad (5)$$

$$dx/(a-x)(b-x) = K\,dt \qquad (6)$$

$$\text{At} \quad t = 0 \quad ; \quad x = 0$$

$$\text{At} \quad t = t \quad ; \quad x = x$$

$$\int_0^x \frac{dx}{(a-x)\,(b-x)} = k\int_0^t dt$$

$$\int_0^x \frac{1}{(a-x)\,(b-x)}\,dx = k\int_0^t dt \qquad (1)$$

Method of partial fraction;

$$\frac{1}{(a-x)\,(b-x)} = \frac{A}{(a-x)} + \frac{B}{(b-x)}$$

$$\frac{1}{\cancel{(a-x)\,(b-x)}} = \frac{A(b-x) + B(a-x)}{\cancel{(a-x)\,(b-x)}}$$

$$1 = Ab - Ax + Ba - Bx$$

$$1 = Ab + Ba - Ax - Bx$$

$$1 = x\,(-A-B) + Ab + Ba$$

The left side is a constant (1) and without ***x*** coefficient, so ***x*** coefficient on the right side must be zero:

$$0x + 1 = -x\,(A+B) + Ab + Ba$$

After that, we match the coefficients to obtain

$$Ab + Ba = 1 \qquad (2)$$

$$A + B = 0 \qquad (3)$$

From equation 2 we get;

$$A = -B \qquad (4)$$

Substitute the value of A (from equation 3) in equation 1;

$$-Bb + Ba = 1$$
$$B(a - b) = 1$$
$$B = 1/(a - b)$$

From equation 4; $A = -B$
Hence; $A = -1/(a - b)$

$$\frac{1}{(a-x)(b-x)} = \frac{A}{(a-x)} + \frac{B}{(b-x)}$$

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

$$= \frac{1}{(a-b)}\left\{-\frac{1}{(a-x)} + \frac{1}{(b-x)}\right\} \qquad (5)$$

As a reminder, substitute equation (5) into equation (1).

$$\int_0^x \frac{1}{(a-x)(b-x)}\,dx = k\int_0^x dt \qquad (1)$$

$$= \frac{1}{(a-b)}\left\{-\int_0^x \frac{1}{(a-x)}\,dx + \int_0^x \frac{1}{(b-x)}\,dx\right\} = k\int_0^t dt$$

$$= \frac{1}{(a-b)}\left\{-\int_0^x \frac{1}{(a-x)}\,dx + \int_0^x \frac{1}{(b-x)}\,dx\right\} = kt$$

where: $\int_0^x \frac{dx}{a-x} = -\ln(a-x)$; and $\int_0^x \frac{dx}{b-x} = -\ln(b-x)$

$$= \frac{1}{(a-b)}\left\{\ln(a-x) - \ln(b-x)\right\} + I = kt$$

$$\frac{\ln(a-x) - \ln(b-x)}{(a-b)} + I = kt$$

Factor I is the constant of integration, At t = 0 , x =0

$$\frac{1}{a-b}\ln\frac{a-0}{b-0}+I=K*0$$

$$I=-\frac{1}{a-b}\ln\frac{a-0}{b-0}$$

$$I=-\frac{1}{a-b}\ln\frac{a}{b}$$

$$I=\frac{\ln\frac{b}{a}}{a-b}$$

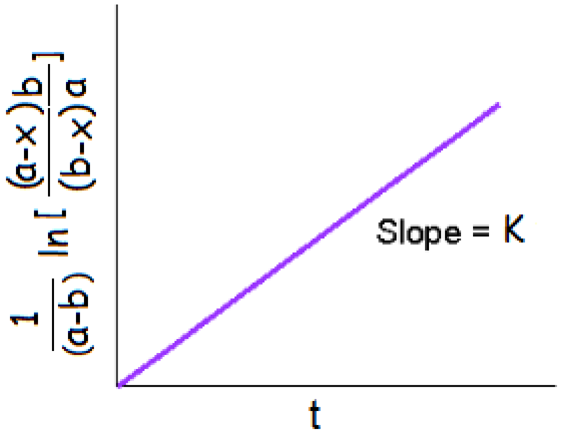
Substituting the value of I in equation $\left(\frac{1}{a-b}\ln\frac{a-x}{b-x}+I=Kt\right)$

$$\frac{1}{a-b}\ln\frac{a-x}{b-x}+\frac{\ln b/a}{a-b}=Kt$$

$$\frac{1}{a-b}\ln\frac{a-x}{b-x}+\ln\frac{b}{a}\,\frac{1}{a-b}=Kt$$

$$\frac{1}{a-b}\left[\ln\frac{a-x}{b-x}+\ln\frac{b}{a}\right]=Kt$$

$$\frac{1}{(a-b)}\ln\left[\frac{(a-x)b}{(b-x)a}\right]=Kt$$



We can found "K" value by equation

$$K = \frac{1}{t(a-b)} \ln \frac{(a-x)b}{(b-x)a}$$

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

It can be prove that the reaction is of the second order by finding the value of the reaction rate constant at different times of the relationship:

If reaction 1 mole of A with 3 mole of B:

$$A + 3B \rightarrow P$$

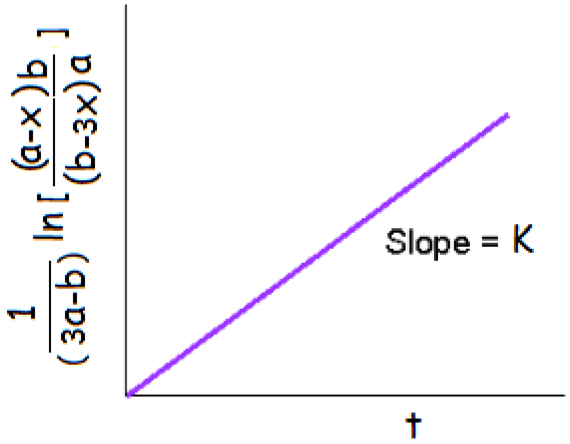
$$-dA/dt = -1/3\ dB/dt = K\,[A][B]$$

Since if x disappears from A, 3x disappears from B:

$$dx/dt = K\,(a-x)(b-3x)$$

$$\int_0^x \frac{dx}{(a-x)\,(b-3x)} = k \int_0^t dt$$

$$\frac{1}{(3a-b)} \ln\left[\frac{(a-x)b}{(b-3x)a}\right] = K\,t$$



Physical Chemistry/ kinetics chemistry (part I)

(2025-2026)

Prof. Dr. Abdulqadier Hussien Alkhazraji

Lecture 5 03 / 12/ 2025

Temperature dependence of the rate of a chemical reaction

The rate of reaction depends on temperature via the rate constant. In a simple reaction, both the rate constant and the rate of reaction increase with temperature. The rate of parallel and consecutive reactions also increases with temperature. In reactions proceeding by more complex mechanisms, the rate may decrease with temperature.

Van’t Hoff rule

With the temperature raised by 10 ^{o}C, the rate of a chemical reaction increases 1.5 to 3 times. This qualitative rule often allows for distinguishing chemical reactions from physical processes and from biochemical reactions proceeding in living organisms. If the rate of reaction obeys the van’t Hoff rule, it is highly probable that the reaction in question is chemical. If, on the contrary, the rate of reaction increases substantially less, the studied process is most likely of a physical nature, this may be, e.g., gas diffusion or adsorption on a solid surface.

Differential equation of Van’t Hoff :

$$d(\ln K)/dT = \Delta H / (R\ T^2)$$

Where:

K is Equilibrium constant

T is Absolute temperature (K)

ΔH is Enthalpy change

R is Universal gas constant (8.314 J/mol K)

Assuming ΔH is constant, the integration between two temperatures gives:

$$\ln\frac{K_2}{K_1}=\frac{\Delta H^0}{R}\left[\frac{1}{T_1}-\frac{1}{T_2}\right]$$

From thermodynamics:

$$\Delta G^o = \Delta H^o - T\Delta S^o$$

Where S is the entropy of the system, and the Gibbs free energy equation:

$$\Delta G^o = - RT\ln K$$

$$\Delta G^o = \Delta G^o$$

$$\Delta H^o - T\Delta S^o = - RT\ln K$$

$$\ln K = - \Delta H^o / RT + \Delta S^o / R$$

Differentiation of this expression with respect to the variable T yields the van't Hoff equation.

Provided that ΔH^o and ΔS^o are constant, the preceding equation gives ln K as a linear function of 1/T, and hence is known as the linear form of the van't Hoff equation. Therefore, when the range in temperature is small enough that the standard reaction enthalpy and reaction entropy are essentially constant, a plot of the natural logarithm of the equilibrium constant versus the reciprocal temperature gives a straight line. The slope of the line may be multiplied by the gas constant R to obtain the standard enthalpy change of the reaction, and the intercept may be multiplied by R to obtain the standard entropy change.

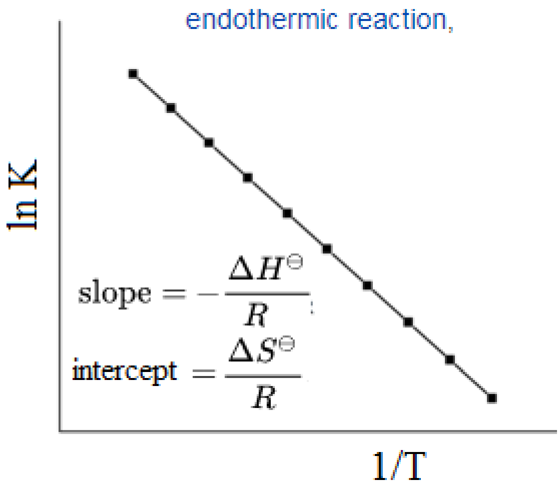
For an **endothermic reaction ($\Delta H > 0$)**, heat is absorbed, making the net enthalpy change positive. Thus, according to the definition of the slope:

$$\text{Slope} = -\Delta H^o / R$$

For an endothermic reaction, $\Delta H > 0$ (and the gas constant $R > 0$), so

$$\text{Slope} = -\Delta H^o / R < 0$$

Thus, for an endothermic reaction, the van't Hoff plot should always have a negative slope.



If the reaction is endothermic ($\Delta H > 0$): Increasing the temperature increases K → the reaction shifts toward the products.

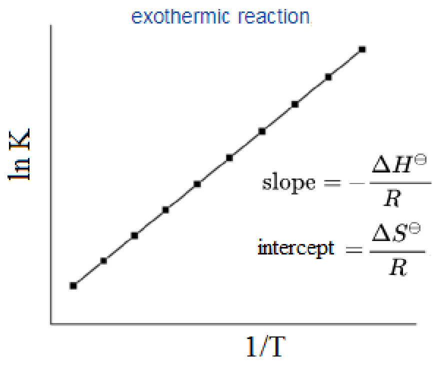
For an **exothermic reaction ($\Delta H<0$),** heat is released, making the net enthalpy change negative ($-\Delta H^o$). Thus, according to the definition of the slope:

$$\text{Slope} = -\Delta H^o / R$$

From an exothermic reaction, $\Delta H < 0$, so

$$\text{Slope} = -\Delta H^o / R > 0$$

Thus, for an **exothermic** reaction, the van't Hoff plot should always have a positive slope.



If the reaction is exothermic ($\Delta H < 0$): Increasing the temperature decreases K → the reaction shifts toward the reactants.

A positive value of ΔH indicates an endothermic reaction, and a negative value indicates an exothermic reaction.

For tow temperature:

$$\ln K_1 = -\Delta H^o / RT_1 + \Delta S^o / R \text{ ----1}$$

$$\ln K_2 = -\Delta H^o / RT_2 + \Delta S^o / R\text{-----2}$$

Now , equation 2 – equation 1

$$\ln K_2 - \ln K_1 = (-\Delta H^o / RT_2 + \Delta S^o / R) - (-\Delta H^o / RT_1 + \Delta S^o / R)$$

$$\ln K_2/K_1 = (-\Delta H^o / RT_2) - (-\Delta H^o / RT_1)$$

$$\ln\frac{K_2}{K_1} = -\frac{\Delta H^0}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right]$$

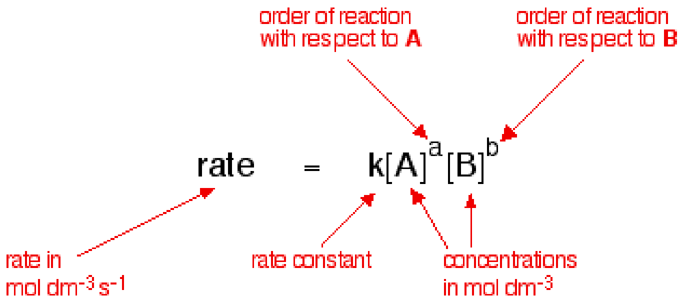
$$\ln\frac{K_2}{K_1} = \frac{\Delta H^0}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

In this equation K_1 is the equilibrium constant at absolute temperature T_1, and K_2 is the equilibrium constant at absolute temperature T_2.

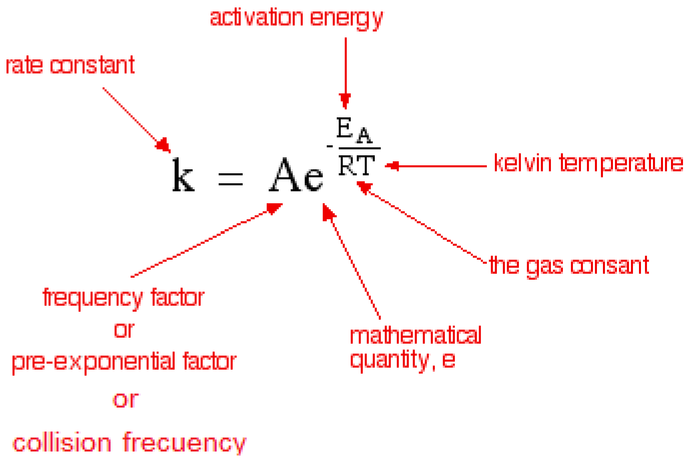
Theories explaining the kinetics of reactions

1. Arrhenius equation

The rate equation for a reaction between two substances, A and B, is the following:



The rate equation shows the effect of changing the reactant concentrations on the rate of the reaction. All other factors affecting the rate—temperature and catalyst presence, for example—are included in the rate constant, which is only constant if the only change is in the concentration of the reactants. If the temperature is changed or a catalyst is added, for example, the rate constant changes. This is shown mathematically in the Arrhenius equation:



We well know collision theory،

1. The molecules must collision to react;
2. The collision must have correct orientation in space to be effective collisions;

3. Finally those collision must have enough energy for the reaction to occur.

All these ideas of collision theory are contained in the Arrhenius equation;

$$K = Ae^{-(Ea/RT)}$$

Where:

K is Rate constant, so **k** is the rate constant the one we talk about in our rate laws.

A is called the frequency factor. Also called the pre – exponential factor and includes things like the **frequency of our collisions**, and also the **orientation of those collisions**.

$e^{-(Ea/RT)}$ is talking about the fraction of collisions with enough energy for a reaction to occur. So we symbolize this by lowercase f, so the fraction of collisions f depended on the activation energy Ea, which needs to be in Joules /mole. R is gas constant (8.314 J/ mol. K) and T is temperature in K.

How changing the activation energy or changing the temperature for a reaction? Then;

How that affects the fraction of collisions with enough energy for our reaction to occur?

We start with activation energy (E_a) of 40000 J/mol, and the temperature is 373 K.

$$K = A\underbrace{e^{-(Ea/RT)}}_{f}$$

f value equal to:

$$\mathbf{f} = e^{-Ea/RT}$$

and we have gas constant **R** and then this is going to be multiplied by the temperature, which is 373K.

See what we get:

$$f = e^{\text{-40000 J/mol / 8.314 J.mol-1k-1 . 373 k}}$$

$$= 2.5 * 10^{-6}$$

So what does this mean?

If we had one million collisions (1000000 collisions):

$$\frac{x}{1000000} = 2.5 * 10^{-6}$$

X is number of collisions have enough energy to occur the reaction (x = 2.5), that mean for every one million collisions in our reaction, only 2.5 collisions have enough energy to react.

Now we change the value of activation energy from 40 kJ /mol to 10 kJ/mol, that mean decrease the activation energy and we are keeping the temperature the same.

f is equal:

$$f = e^{\text{-10000 J/mol / 8.314 J.mol/k . 373 k}}$$

$$= 0.04$$

If we had one million collisions (1000000 collisions):

$$x / 1000000 = 0.04$$

$$x = 40000$$

We have increase f value, i.e, We've gone from f equal $2.5*10^{-6}$ to 0.04. So every one million collisions that we have in our reaction this found about 40000 collisions have enough energy to react, hence, lead to if decrease activation energy increase the value for f, i.e it increase the number of effective collisions.

This time we're gonna change the temperature. The same activation energy 10 KJ/mol with changing the temperature from 373 k to 437, how that affects the value for f .

$$f = e^{-10000\ \text{J/mol} / 8.314\ \text{J.mol-1k-1} . 473\ \text{k}}$$

we get, 0.08, so here we've increased the value for **f**. i.e, we went from 0.04 to 0.08 and keep our idea of one million collisions.

$$x/1000000 = 0.08$$

$$x = 80000$$

so every million collisions that we have in our reaction, now we have 80000 collisions with enough energy to react. So we've increased the temperatures. Gone from 373 to 473 k. We increased the number of collisions with enough energy to react. We increased the value for **f**.

Finally, what these things (change of Ea and T)do to the rate constant. we go back up here to our equation;

$$K = Ae^{-(Ea/RT)}$$

To increase **f**, we could either decrease the activation energy, or we could increase the temperature. And if we increase **f** increase the rate constant **k**.

- Decrease **Ea** lead to increase fraction of collisions **f,** that means increase rate constant **K**, which lead to increase rate of reaction.

- Increase **T** lead to increase fraction of collisions **f,** that means increase rate constant **K**, which lead to increase rate of reaction.

$$\text{Rate of reaction} = k\,[\text{conc.}]$$

In other word, if we decrease the activation energy, or if we increase the temperature, we increase the fraction collisions with enough energy to occur, therefore we increase the rate constant k, and since k directly proportional to the rate of our reaction rate, we increase the rate of reaction, so the ideas of collision theory are contained in the Arrhenius equation, and so we'll go more into this equation.

We already seen one form of the Arrhenius equation, there are other forms of the Arrhenius equation which you might want to use, depending on the problem. So let's go the Arrhenius equation and find other forms:

$$K = Ae^{-(Ea/RT)}$$

$$\ln k = \ln (Ae^{-(Ea/RT)})$$

$$\ln k = \ln A + \ln e^{-(Ea/RT)}$$

$$\ln k = \ln A - (Ea/RT)$$

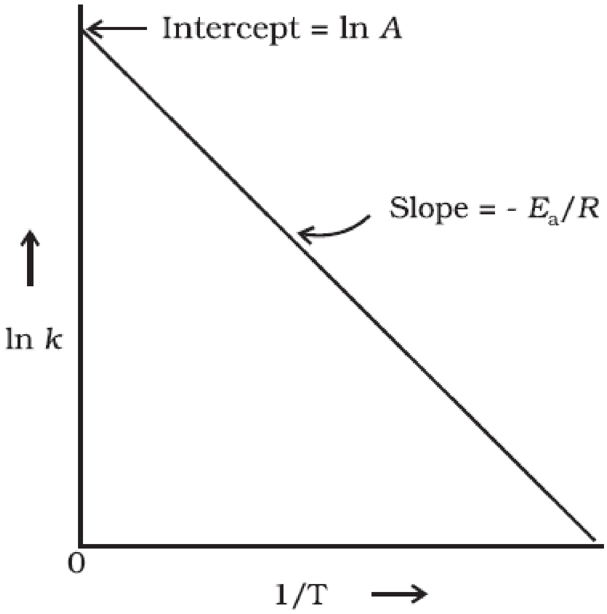
$$\ln k = -\frac{Ea}{R}\left(\frac{1}{T}\right) + \ln A$$

And the reason I wrote it this way, is its easier to see the form **y** is equal to **mx** plus **b**

$$y = mx + b$$

$$\underset{y}{\ln k} = \underset{m}{-\frac{Ea}{R}}\,\underset{x}{\left(\frac{1}{T}\right)} + \underset{b}{\ln A}$$

So if we graph the natural log of k on the y-axis and one over T on the x-axis, we're going to get a straight line, and the slope of that line, which of course is m. So we can find the activation energy from the slope of the line. And if we wanted to find the frequency factor we know that the y intercept is equal to the natural log of A. So we could find the frequency factor if we wanted to. So this is another for of the Arrhenius equation



$$2.303 \log_{10} K = 2.303 \log_{10} A - Ea / RT$$

$$\mathbf{\log_{10} K = \log_{10} A - Ea / 2.303RT}$$

Now, if we have different temperatures, we're going to have different rate constants K_1 and K_2.

K_1------- T_1 $T_1 < T_2$

K_2-------- T_2 $K_1 < K_2$

So now we have two different equations here for two different temperatures with two different rates constant.

$$\ln k_1 = \ln A - (Ea/RT_1) \ldots\ldots\ldots\ldots\ldots..(1)$$

$$\ln k_2 = \ln A - (Ea/RT_2) \ldots\ldots\ldots\ldots\ldots\ldots.(2)$$

equation 2 – equation 1

$$\ln k_2 - \ln k_1 = - Ea/RT_2 - (-Ea/RT_1)$$

we get:

$$\ln k_2 / k_1 = -Ea/RT_2 + Ea/RT_1$$

$$\ln k_2 / k_1 = Ea/RT_1 - Ea/RT_2$$

$$\ln k_2 / k_1 = Ea/R \ (1/T_1 - 1/T_2)$$

$$\ln k_2 / k_1 = Ea/R \ (T_2 - T_1 / T_1T_2)$$

$$\log k_2/k_1 = Ea/ 2.303R \ (T_2 - T_1 / T_1T_2)$$

Now we get graph:

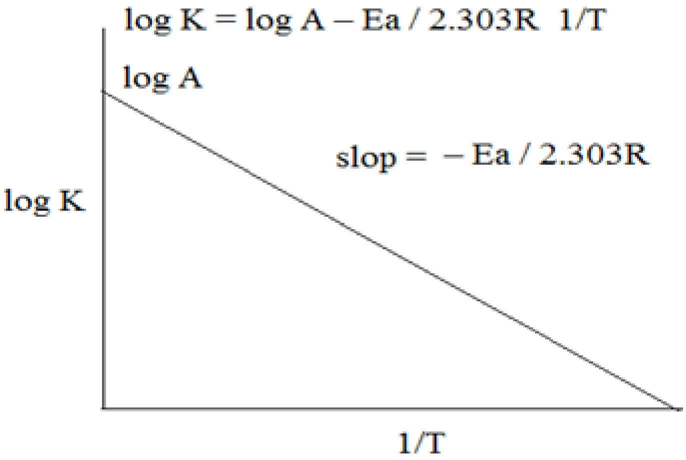
$$K = Ae^{-(Ea/RT)}$$

$$\ln k = - Ea/R \ \ 1/T + \ln A$$

$$\log K = - Ea / 2.303R \ \ 1/T + \log A$$

$$\mathbf{y = m\ x + b}$$

y = ln k or log k , b = ln A or log A , m=Slop = – Ea/RT or – Ea / 2.303RT



It has been found that **for a chemical reaction with rise in temperature by 10°, the rate constant is nearly doubled.**

$$T_1 = 25^oC \qquad T_1 = T \qquad = K_1$$

$$T_2 = 35^oC \qquad T_2 = T \qquad = K_2$$

$$K_2 = 2\ K_1$$

Looking at the Arrhenius equation, the denominator of the exponential function contains the gas constant **R**, and the temperature **T**. This is only the case when dealing with **moles of a substance**, because **R** has the units of J/mol.K. When dealing with **molecules of a substance**, the gas constant in the dominator of the exponential function of the Arrhenius equation is replaced by the Boltzmann constant $\mathbf{k_B}$. The Boltzmann constant has the units J/k.

Recall again Arrhenius equation per mole:

$$K = Ae^{-(Ea/RT)}$$

Arrhenius Equation per molecule:

$$K = Ae^{-(Ea/KBT)}$$

It is important to note that the decision to use the gas constant or the Boltzmann constant in the Arrhenius equation depends primarily on the canceling of the units. To take the inverse log of a number, the number must be unit less. Therefore all the units in the exponential factor must cancel out. If the activation energy is in terms of joules per moles, then the gas constant **R** should be used in the dominator. However, if the activation energy is in unit of joules per molecule, then the constant $\mathbf{K_B}$ should be used.

2. Collision theory

The collision theory explains the rate of chemical reactions in terms of collisions between reacting molecules. A reaction occurs only when molecules collide with sufficient energy and proper orientation to overcome the activation energy barrier.

The rate of the reaction depends on the number of effective collisions between molecules of A and B that have energy ≥ activation energy (E_a).

Following three rules are supposed in the collision theory.

- Molecules must collide react
- Collisions must have the correct orientation in space.
- Collisions must have enough energy.

Not all collisions produce a reaction, only those that have energy ≥ Ea

The collision frequency per unit volume between A and B is:

$$Z_{AB} = \sigma_{AB} * \sqrt{(8kT/\pi\mu)} * N_A * N_B$$

Where:

Z_{AB} is collision frequency (number of collision)

σ_{AB} is collision cross-section

μ is reduced mass = $(m_A * m_B)/(m_A + m_B)$

k is Boltzmann constant

T is absolute temperature

N_A, N_B = number densities of A and B

Only a fraction f of the total collisions have sufficient energy to react. According to the Maxwell–Boltzmann distribution:

$$f = e^{-E_a/RT}$$

Hence, the rate constant can be written as:

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

Where P is the steric factor that accounts for molecular orientation during collision.

The Rate of Reaction for the bimolecular gaseous reaction is:

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

Substitute for k:

$$\text{Rate} = P * Z_{AB} * e^{-E_a/RT} * [A][B]$$

As temperature increases, the fraction of molecules with energy ≥ E_a increases. Thus, the rate constant k increases exponentially with temperature, following the Arrhenius law.

Note:

- Collision theory provides a molecular-level explanation for reaction kinetics.

- The reaction rate depends on collision frequency, activation energy, and molecular orientation.

- The derived rate expression aligns with the Arrhenius equation:

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

Where;

$$A = P * Z_{AB}$$

Derivation of the rate equation according to collision theory

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

$$n_A \quad n_B$$

$$-\,d[A] / dt = -\,d[B]/dt = k\,[A]\,[B] \text{ ---- } 1$$

$$-\,dn_A / dt = -\,dn_B/dt = k\, n_A n_B \text{ ----- } 2$$

$$-\,dn_A/dt = Z_{AB}\, .\, e^{(-Ea/RT)} \text{ ---- } 3$$

$$\text{Rate} = Z_{AB}\, .\, e^{(-Ea/RT)} \text{ ---}4$$

$e^{(-Ea/RT)}$ is Boltzmann factor which represented how many molecules are colliding.

Z_{AB} is frequency or number collisions that occur per unit volume per unit time. It is also referred to as Collision density.

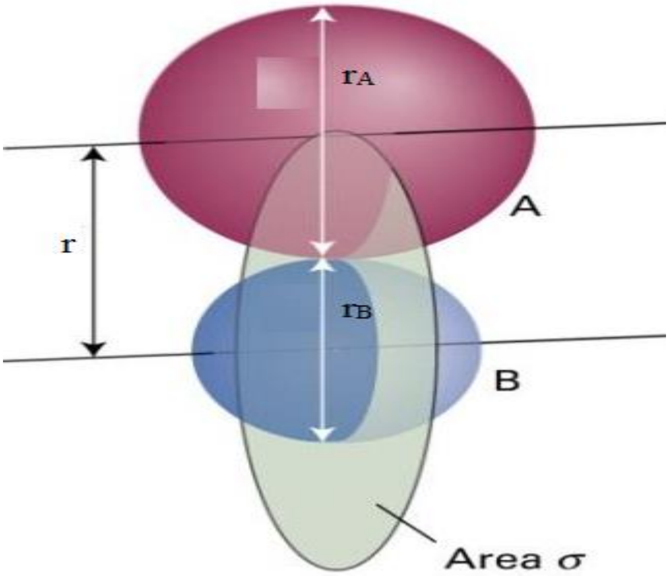
$\mathbf{n_A}$ and $\mathbf{n_B}$ are is the number density of A and B molecules in the gas in units of L^{-1};

$$n_A = [A]\ N_A,\ \text{and}\ n_B = [B]\ N_A \text{ ----- } 5$$

$\mathbf{N_A}$ is Avogadro number (6.02×10^{23} mol^{-1}).

[A] and [B] are the concentration of A and B molecules in the gas in units of mol/L^{-1}.

In collision theory it is considered that two particles A and B will collide if their nuclei get closer than a certain distance. The area around a molecule A in which it can collide with an approaching B molecule is called the **cross section (σ_{AB}) of the reaction** and is, in simplified terms, the area corresponding to a **circle whose radius (r_{AB})** is the sum of the radii of both reacting molecules, which are supposed to be spherical.



A moving molecule will therefore sweep a **volume ($\pi r^2_{AB}u_A$)** per second as it moves, where u_A is the average velocity of the particle. From kinetic theory it is known that a molecule of A has an average velocity is:

$$u_A=(8K_BT/\pi m_A)^{1/2}$$

Where m_A is the mass of the molecule.

The solution of the two-body problem states that two different moving bodies can be treated as one body which has the reduced mass of both and moves with the velocity of the center of mass, so, in this system μ_{AB} must be used instead of m_A, the relative velocity can be calculated using the reduced mass of A and B:

$$u_{AB} = (8K_BT/\pi\ \mu_{AB})^{1/2}.$$

For a reaction between A and B, the collision frequency calculated with the hard-sphere model is:

$$Z_{AB} = \pi\ (r_A + r_B)^2\ (8k_BT/\pi\mu_{AB})^{1/2}\ n_A.\ n_B \text{ ---- } 6$$

We know from equation 5:

$$n_A = [A]\ N_A, \text{ and } n_B = [B]\ N_A \text{ ----- } 5$$

Substitution of equation 5 in equation 6 we get;

$$Z_{AB}= \sigma_{AB}\ (8k_BT/\pi\ \mu_{AB})^{1/2}\ N_A^2\ [A][B] \text{----- } 7$$

σ_{AB} is the reaction cross section (m^2), the area when two molecules collide with each other, simplified to ;

$$\sigma_{AB} = \pi\ (r_A + r_B)^2$$

k_B is the Boltzmann's constant unit J K^{-1}.(1.38×10^{-23} J K^{-1})

T is the absolute temperature (unit K).

μ_{AB} is the reduced mass of the reactants A and B, $\mu_{AB}=(m_A\ m_B/\ m_A + m_B)$ (kg).

$(8k_BT/\pi\mu_{AB})^{1/2}$ is root mean speed of molecules (is velocity)

Substitution of equation 7 in equation 3;

$$-\ dn_A/dt = Z_{AB}\ .\ e^{(-Ea/RT)} \text{ ---- } 3$$

We get;

$$-dn_A/dt = \pi\,(r_A + r_B)^2\,(8k_BT/\pi\mu_{AB})^{1/2}\,n_A.\,n_B\,.e^{(-Ea/RT)} \quad \textbf{----8}$$

Derivation of rate constant;

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

$$\text{where;}\quad [A] = \frac{n_A}{N_A}\ ,\ \text{and}\ \ [B] = \frac{n_B}{N_A}$$

$$-\frac{dn_A}{dt\,N_A} = k\left(\frac{n_A}{N_A}\right)\left(\frac{n_B}{N_A}\right)$$

$$-\frac{dn_A}{dt\,\cancel{N_A}} = \frac{k\,n_A\,n_B}{N_A^{\cancel{2}}}$$

$$-\frac{dn_A}{dt} = \frac{k\,n_A\,n_B}{N_A} \Rightarrow k = \frac{-\frac{dn_A}{dt}\quad N_A}{n_A\,n_B} \quad \text{-----9}$$

Substitution of equation 8 in equation 9 we get;

$$k = \left(\frac{N_A}{\cancel{n_A\,n_B}}\right)\pi\,(r_A + r_B)^2\left(\frac{8k_BT}{\pi\mu_{AB}}\right)^{1/2}\cancel{n_A.\,n_B}\,.\,e^{(-Ea/RT)}$$

$$K = N_A\,\pi\,(r_A + r_B)^2\,(8k_BT/\pi\mu_{AB})^{1/2}\,.\,e^{(-Ea/RT)} \quad \text{--- 10}$$

$$\text{where;}\quad Z = N_A\,\pi\,(r_A + r_B)^2\,(8k_BT/\pi\mu_{AB})^{1/2} \quad \text{---- 11}$$

The factor ½ is due to avoid double counting of collision for A-B molecules.

Substitution of equation 11 in equation 10 we get;

$K = Z\,.\,e^{(-Ea/kT)}$ ------------Collision theory (if molecules)

$K = Z\,.\,e^{(-Ea/RT)}$ ------------Collision theory (if moles)

$K = A\,.\,e^{(-Ea/RT)}$ ------- Arrhenius equation

$$A \neq Z$$

$A \neq Z$ because the collision theory is applicable on a single molecule but Arrhenius on the complex molecules.

If the values of the predicted rate constants are compared with the values of known rate constants, it is noticed that collision theory fails to estimate the constants correctly, and the more complex the molecules are, the more it fails. The reason for this is that particles have been supposed to be spherical and able to react in all directions, which is not true, as the orientation of the collisions is not always proper for the reaction. To alleviate this problem, a new concept must be introduced: the steric factor ρ. It is defined as the ratio between the experimental value and the predicted one (or the ratio between the frequency factor and the collision frequency).

$$\rho = A_{observed}/Z_{calculated}$$

ρ is most often less than unity.

$$\text{Where: } 0 < \rho < 1$$

$$K = \rho.\ Z.\ e^{-(Ea/kT)}$$

3. Activated Complex Theory; Transition State Theory

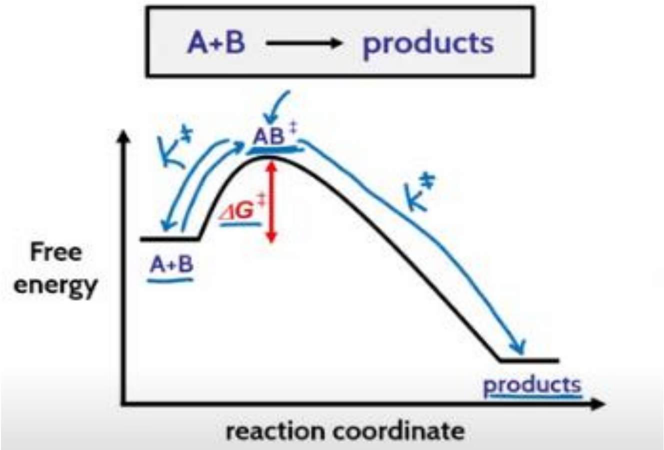
In this section, we will consider a further refinnement of our formulation of a reaction on the atomic level. Up to now, we have not entertained the possibility of short-lived, highly unstable intermediates appearing/ being generated upon the initial "collision" of reactive species. Eyring and co-workers postulated the presence of these highly unstable ، fleeting, transition states, and furthermore suggested an equilibrium between this transition state and the reactive species. The transition state is also considered an activated complex, hence the nomenclature **Activated Complex Theory (as well as Transition State Theory).**

$$\text{reactants} \rightleftharpoons \text{activated complex} \rightarrow \text{products}$$

Eyring equation

Both the **Arrhenius** and the **Eyring equation** describe the temperature dependence of reaction rate. Strictly speaking, the **Arrhenius equation** can be applied only to the kinetics of gas reactions. The **Eyring equation** is also used in the study of solution reactions and mixed phase reactions - all places where the simple **collision model** is not very helpful. The Arrhenius equation is founded on the empirical observation that rates of reactions increase with temperature. The **Eyring equation** is a theoretical construct, based on **transition state** model.

Derivation of the Eyring Equation:



The bimolecular reaction:

$$A + B \rightarrow \text{Product}$$

$$\text{Rate} = K_{simple}\,[A][B] \text{ ----1}$$

According to the transition state model, the reactants are getting over into an unsteady intermediate state on the reaction pathway.

$$A + B \overset{K_{equi.}}{\rightleftharpoons} AB^{\neq} \xrightarrow{K_{Tr.}} \text{Products}$$

$$\text{Rate} = K_{Tr.} [AB^{\neq}] \quad \text{---------} \ 2$$

$K_{Tr.}$ is rate constant of active complex

$$\text{If} : K_{equi.} = \frac{[AB^{\neq}]}{[A]\,[B]} \quad \text{---------} \ 3$$

$K_{equi.}$ is equilibrium constant

$$[AB^{\neq}] = K_{equi.} [A][B] \quad \text{-----} \ 4$$

Substituting equation 4 in equation 2, we get:

$$\text{Rate} = K_{Tr.} \, K_{equi.} [A][B] \ \text{------}5$$

From equation 1 and equation 5, we get:

$$k_{simple} \ \cancel{[A][B]} = K_{Tr.} \, K_{equi.} \cancel{[A][B]} \text{-------}6$$

$$k_{simple} = K_{Tr.} \, K_{equi} \ \text{------}7$$

Where; $K_{Tr.} = K_B \, T/h$ and $\Delta G^{\circ\neq} = -RT\ln K_{equi.}$ ⇨ $K_{equi.} = e^{-\Delta G\neq/RT}$

$$k_{simple} = (K_B T/h) \, e^{-\Delta G\neq/RT} \qquad \textbf{(Eyring equation)}$$

K_B = Boltzmann's constant [$1.381\text{x}10^{-23}$ J · K^{-1}],

Boltzmann constant $K_B = R/N_A$, N_A = Avogadro's number

T = absolute temperature in degrees Kelvin (K)

h = Plank constant [$6.626\text{x}10^{-34}$ J · s]

k_{simple} is called **universal constant for a transition state**

$K_{Tr.}$ is called **transition state constant.**

K_{equi} is called **equilibrium constant.**

$$k = \frac{k_\mathrm{B}T}{h}\mathrm{e}^{-\frac{\Delta G^\ddagger}{RT}}$$

$$k = \left(\frac{k_\mathrm{B}T}{h}\right)\exp\left(\frac{\Delta S^\ddagger}{R}\right)\exp\left(-\frac{\Delta H^\ddagger}{RT}\right)$$

$$\ln\frac{k}{T} = \frac{-\Delta H^\ddagger}{R}\cdot\frac{1}{T} + \ln\frac{k_\mathrm{B}}{h} + \frac{\Delta S^\ddagger}{R}$$

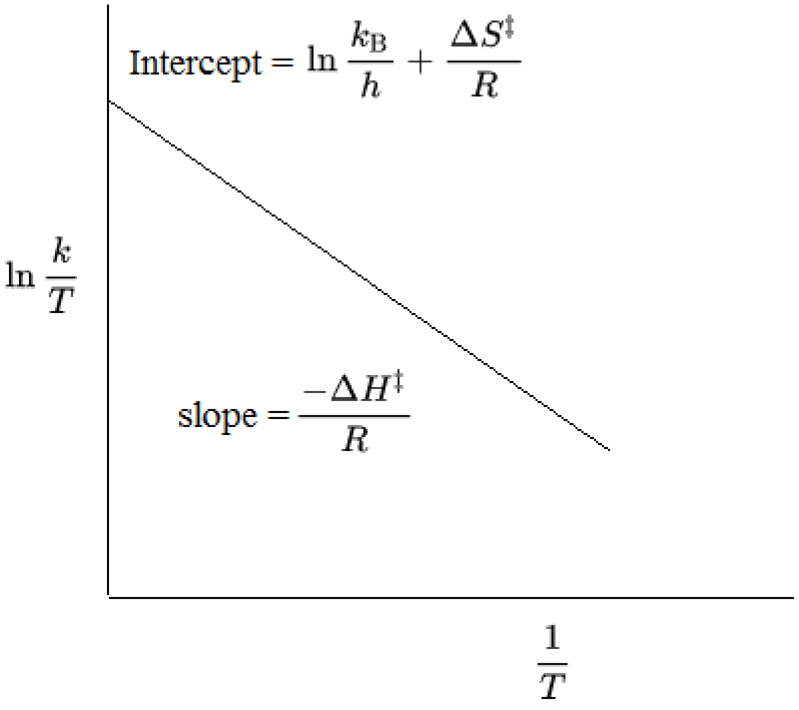
R = Gas Constant = 8.3145 J/mol K

$\Delta G^{\neq}$ = free activation enthalpy [kJ · mol^{-1}]

$\Delta S^{\neq}$ = activation entropy [J · mol^{-1} · K^{-1}]

$\Delta H^{\neq}$ = activation enthalpy [kJ · mol^{-1}]

$$\ln\frac{k}{T} = \frac{-\Delta H^\ddagger}{R}\cdot\frac{1}{T} + \ln\frac{k_\mathrm{B}}{h} + \frac{\Delta S^\ddagger}{R}$$



Physical Chemistry/ kinetics chemistry

(2025-2026)

Prof. Dr. Abdulqadier Hussien Alkhazraji

Lecture 7 14 / 01 / 2026

The kinetics of complex reactions

(Chain reactions , Consecutive reaction, Parallel reaction, Reversible reaction)

☒ Chain reactions

Chain reactions are examples of complex reactions, with complex rate expressions.

In a chain reaction, the intermediate produced in one step generates an intermediate in another step.This process goes on.

Intermediates are called chain carriers. Sometimes, the chain carriers are radicals; they can be ions as well. In nuclear fission they are neutrons.

There are several steps in a chain reaction.

1. **Chain initiation**

This can be by thermolysis (heating) or photolysis (absorption of light) leading to the breakage of a bond.

$$H_3C\text{-}CH_3 \rightarrow 2^{\cdot}CH_3$$

2. **Chain Propagation**

In this step the chain carrier makes another carrier.

$$^{\cdot}CH_3 + CH_3CH_3 \rightarrow CH_4 + {}^{\cdot}CH_2CH_3$$

3. Chain Inhibition

Chain carriers are removed by other processes, other than termination, say by foreign radicals.

$$CH_3CH_2^{\cdot} + {}^{\cdot}R \rightarrow CH_3CH_2R$$

4. Chain termination

Radicals combine and the chain carriers are lost.

$$CH_3CH_2^{\cdot} + CH_3CH_2^{\cdot} \rightarrow CH_3CH_2CH_2CH_3$$

Example;

$$2Br^- + H_2O_2 + 2H^+ \longrightarrow Br_2 + 2H_2O$$

Predicted Rate law;

$$\text{Rate} = d[Br_2]/dt = k\ [Br^-]\ [H_2O_2]\ [H^+]$$

Mechanism;

$$Br^- + H_2O_2 + H^+ \xrightarrow{k_1} HOBr + H_2O \quad \text{slow step}$$

$$HOBr + Br^- + H^+ \xrightarrow{k_2} Br_2 + 2H_2O \quad \text{fast step}$$

$$\text{Rate} = d[Br_2]/dt = k_2\ [HOBr]\ [H^+]\ [Br^-] \text{ ------ } 1$$

$$d[HOBr]/dt = \text{formation} - \text{disappearance}$$

According to the **steady-state approximation (SSA)**;

$$d[HOBr]/dt = 0$$

$$\text{Formation; } k_1\ [Br^-]\ [H_2O_2]\ [H^+]$$

$$\text{Disappearance; } k_2\ [HOBr]\ [H^+]\ [Br^-]$$

$$0 = k_1\ [Br^-]\ [H_2O_2]\ [H^+] - k_2\ [HOBr]\ [H^+]\ [Br^-]$$

$$[HOBr] = \frac{k_1\ \cancel{[Br^-]}\ [H_2O_2]\ \cancel{[H^+]}}{k_2\ \cancel{[H^+]}\ \cancel{[Br^-]}}$$

$$[HOBr] = \frac{k_1}{k_2}\ [H_2O_2] \text{ ------ } 2$$

Now substituting equation 2 in equation 1;

$$\text{Rate} = d[Br_2]/dt = \cancel{k_2}\ \frac{k_1}{\cancel{k_2}}\ [H_2O_2][H^+]\ [Br^-]$$

$$\text{Rate} = d[Br_2]/dt = k_1\ [H_2O_2][H^+]\ [Br^-]$$

That means; predicted rate law = derived rate law

Minimum necessary are, **Initiation**, **propagation** and **termination**.

Now, how do we calculate for the rate of laws of chain reactions?

A chain reaction can have a simple rate law. As a first example, consider the pyrolysis, or thermal decomposition in the absence of air, of acetaldehyde (ethanal, CH_3CHO), which is found to be three- halves order in CH_3CHO:

Overall reaction,

$$CH_3CHO_{(g)} \rightarrow CH_{4(g)} + CO_{(g)} \qquad \mathbf{d[CH_4]/dt = k[CH_3CHO]^{3/2}}$$

The mechanism for this reaction known as Rice-Herzfeld mechanism is as follows.

1. Initiation: $CH_3CHO \rightarrow \boldsymbol{\cdot CH_3} + \boldsymbol{\cdot CHO}$

   $R = k_I\,[CH_3CHO]$

2. Propagation: $CH_3CHO + \boldsymbol{\cdot CH_3} \rightarrow \boldsymbol{CH_3CO\cdot} + CH_4$

   $R= k_P\,[CH_3CHO][\cdot CH_3]$

   Propagation: $\boldsymbol{CH_3CO\cdot} \rightarrow \boldsymbol{\cdot CH_3} + CO$ ⟵ Product

   $R = K_{p\text{-}}[CH_3CO\cdot]$

3. Termination: $\boldsymbol{\cdot CH_3} + \boldsymbol{\cdot CH_3} \rightarrow CH_3CH_3$

   $R = k_T\,[\cdot CH_3]$

- The chain carriers $\boldsymbol{\cdot CH_3}$ and $\boldsymbol{\cdot CHO}$ are formed initially in the initiation step .
- To simplify the treatment, we shall **ignore** the subsequent reactions of $\boldsymbol{\cdot CHO}$.
- The chain carrier $\boldsymbol{\cdot CH_3}$ attacks other reactant molecules in the propagation steps, and each attack gives rise to a new carrier .
- Radicals combine and end the chain in the termination step .

To test the proposed mechanism we need to show that it leads to the observed rate law .

According to the **Steady-State Approximation (SSA)**, the net rate of change of the intermediates (${\cdot}CH_3$ and $CH_3CO{\cdot}$) may be set equal to zero, That is, the change in its concentration over time is equal to zero.

$$d[{}^{\cdot}CH_3]/dt = 0$$

$$d[{}^{\cdot}CH_3]/dt = \text{formation} - \text{disappearance}$$

$$d[{}^{\cdot}CH_3]/dt = k_I[CH_3CHO] - k_P[{}^{\cdot}CH_3][CH_3CHO] + k_{P-}[CH_3CO^{\cdot}] - 2k_T[{}^{\cdot}CH_3]^2 = 0$$

$$d[CH_3CO^{\cdot}]/dt = k_P[{}^{\cdot}CH_3][CH_3CHO] - k_{P-}[CH_3CO^{\cdot}] = 0$$

The sum of the two equations ($d[{}^{\cdot}CH_3]/dt + d[CH_3CO^{\cdot}]/dt$) is

$$K_I[CH_3CHO] - k_P[{}^{\cdot}CH_3][CH_3CHO] + k_{P-}[CH_3CO] - 2k_T[{}^{\cdot}CH_3]^2 = 0$$

$$+$$

$$K_P[{}^{\cdot}CH_3][CH_3CHO] - k_{P-}[CH_3CO] = 0$$

We get:

$$K_I[CH_3CHO] - 2k_T[{}^{\cdot}CH_3]^2 = 0$$

Which shows that the steady-state approximation also implies that the rate of chain initiation is equal to the rate of chain termination.

The steady-state concentration of ${}^{\cdot}CH_3$ radicals is

$$[{}^{\cdot}CH_3] = (K_I/2k_T)^{1/2}\,[CH_3CHO]^{1/2} \text{-------------}(1)$$

If follows that the rate of formation of CH_4 from Propagation step above is;

$$CH_3CHO + {\cdot}CH_3 \rightarrow CH_3CO{\cdot} + CH_4$$

$$d[CH_4]/dt = k_p[CH_3CHO]\,[{\cdot}CH_3]\text{-------}(2)$$

Substituting Eq. (1) in Eq (2), we get:

$$d[CH_4]/dt = k_p[CH_3CHO]\,(K_I/2k_T)^{1/2}\,[CH_3CHO]^{1/2}$$

$$d[CH_4]/dt = k_p\,(K_I/2k_T)^{1/2}\,[CH_3CHO]^{3/2}$$

$$k_p\,(K_I/2k_T)^{1/2} = k$$

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

Thus the mechanism explains the observed rate expression. It is sure that the true rate law is more complicated than that observed experimentally.

What is Steady-State Approximation (SSA);

$A \longrightarrow P$ Simple reaction

$A \longrightarrow B$ Intermediate

$B \longrightarrow P$

The intermediate compound forms rapidly and reacts or disappears just as quickly; therefore:

Rate of formation of intermediate = Rate of disappearance of intermediate

Example;

$$A \xrightarrow{k_1} I \xrightarrow{k_2} P$$

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

Use SSA:

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

$$0 = k_1[A] - k_2[I]$$

$$k_1[A] = k_2[I]$$

$$\Rightarrow [I] = \frac{k_1}{k_2}[A]$$

$$\text{Rate} = \frac{d[\mathrm{P}]}{dt} = k_2[I] = k_1[A]$$

Example; $\mathbf{A + B \longrightarrow P}$

Mechanism;

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C$$

$$C + B \xrightarrow{k_2} P \qquad \textbf{slow step}$$

$$\text{Rate} = -\,d[A]/dt = k_1\,[A]$$

$$\text{Rate} = -\,d[C]/dt = k_{-1}\,[C]$$

$$\text{Rate} = d[P]/dt = k_2\,[B]\,[C] \text{ ------ } 1$$

Using SSA;

Rate of formation of intermediate [C] = Rate of disappearance of intermediate [C]

$$K_1[A] = k_{-1}[C] + k_2[B][C]$$

$$K_1[A] = [C]\,\{k_{-1} + k_2[B]\}$$

$$[C] = \frac{K_1[A]}{k_{-1} + k_2[B]} \quad \text{------ } \mathbf{2}$$

Substituting equation 2 in equation 1;

$$\text{Rate} = k_2\,[B]\frac{K_1[A]}{k_{-1} + k_2[B]} \Rightarrow \text{Rate} = \frac{K_1\,k_2\,[A][B]}{k_{-1} + k_2[B]}$$

Case 1: if $k_{-1} \gg k_2[B]$ (This means that removing the intermediate is slower compared to the reverse, the reaction is second order)

Case 2 : if $k_2[B] \gg k_{-1}$ (This means converting the intermediate into product a very quickly, the reaction is first order)

$$\text{Rate} = \frac{K_1k_2\,[A][B]}{k_{-1} + k_2\,[\,B]}$$

$$k_{-1} >> k_2\,[B]$$

$$\text{Rate} = \frac{K_1k_2\,[A][B]}{k_{-1}}$$

$$\text{Rate} = K\,[A][B]\ \text{(second order reaction)}$$

$$\text{where } k = \frac{K_1}{k_{-1} + k_2}$$

$$k_2\,[B] >> k_{-1}$$

$$\text{Rate} = \frac{K_1\cancel{k_2}\,[A]\cancel{[B]}}{\cancel{k_2[\,B]}}$$

$$\text{Rate} = K_1[A]$$

(first order reaction)

KINETICS OF CONSECUTIVE REACTIONS

Consider the following series of first-order irreversible reactions, where species A reacts to form an intermediate species, B, which then reacts to form the product, C:

$$\mathbf{A} \xrightarrow[\text{First order reaction}]{K_1} \underset{\textbf{(Intermediate)}}{\mathbf{B}} \xrightarrow[\text{First order reaction}]{k_2} \mathbf{C}$$

$$\begin{array}{l} A \xrightarrow{k_1} \cancel{B} \\ \cancel{B} \xrightarrow{k_2} C \\ \hline A \longrightarrow C \end{array}$$

Initial conditions:

$$\begin{aligned} [A\,(t=0)] &= [A]_0 \\ [B\,(t=0)] &= 0 \\ [C\,(t=0)] &= 0 \end{aligned}$$

$$\begin{array}{cccc} & A \xrightarrow{k_1} & B \xrightarrow{k_2} & C \\ t=0 & [A]_0 & 0 & 0 \\ t=t & [A] & [B] & [C] \end{array}$$

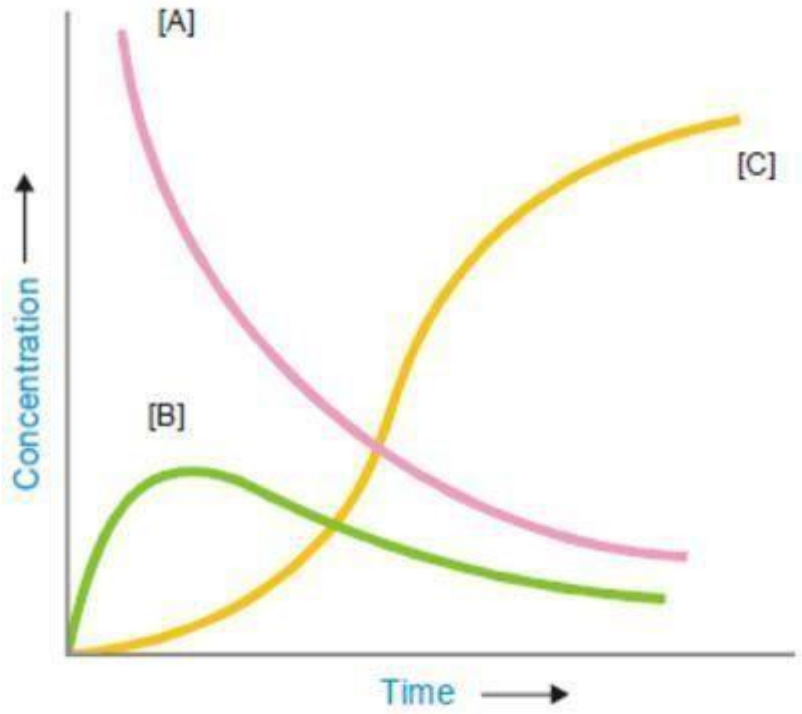
Mass balance equation is:

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

$$d[A]/dt = -k_1[A]$$

$$d[B]/dt = k_1[A] – k_2[B]$$

$$d[C]/dt = k_2[B]$$



First-order decay of [A]: $d[A]/dt = -k_1[A]$----- 1

$\ln A = -K_1 t + I$ ------- 2

At t=0 , $[A] = [A]_0$ $\ln [A]_0 = -K_1 \times 0 + I$------ 3

$$I = \ln [A]_0$$

$\ln A = -K_1 t + \ln [A]_0$------- 4

$\ln[A]/[A]_0 = -k_1 t$ -----5

$[A] = [A]_0 e^{-k1t}$ -------6

Substituting equation 6 in the equation 1, we get:

$d[A]/dt = -k_1[A]_0 e^{-k1t}$---------7

Rate of formation of B:

$$d[B]/dt = k_1[A] - k_2[B] \text{ ------8}$$

Substituting equation 6 in the equation 8, we get:

$$d[B]/dt = k_1[A]_0\, e^{-k1t} - k_2[B] \text{ ---- 9}$$

$$d[B]/dt + k_2[B] = k_1[A]_0\, e^{-k1t} \text{ ----10} \quad \text{(multiply Eq. 10 in } e^{+k2t}\text{)}$$

$$\{d[B]/dt + k_2[B]\}\, e^{+k2t} = k_1[A]_0\, e^{-k1t} .\, e^{+k2t} \text{ -------- 11}$$

$$d[B]/dt .\, e^{+k2t} + k_2[B].\, e^{+k2t} = k_1[A]_0\, e^{-k1t} .\, e^{+k2t} \text{ ------ 12}$$

For recall;

$$[A]/[A]_0 = e^{-k1t} \text{ , and } [B]/[B]_0 = e^{-k2t} \Rightarrow [B]_0 /[B] = e^{+k2t}$$

$$[B]_0 = [B]\, e^{+k2t} \text{ ---13}$$

At t = 0 the initial concentration of $[B]_0 = 0$

$$0 = [B].\, e^{+k2t} \text{-------- 14}$$

Substituting equation 14(it value 0) in the equation 12, we get:

$$d[B]/dt .\, e^{+k2t} = k_1[A]_0\, e^{-k1t} .\, e^{+k2t} \text{ ------------------------ 15}$$

$$d[B]\, e^{+k2t} = k_1[A]_0\, e^{-(k1-k2)\,t}\, dt \text{---------------- 16}$$

$$e^{+k2t}\ {}_0\!\int^{[B]} d[B] = k_1[A]_0\ {}_0\!\int^{t} e^{-(k1-k2)t}\, dt \text{ -------17}$$

$$[B]e^{+k2t} = k_1[A]_0\ {}_0\!\int^{t} e^{-(k1-k2)t}\, dt \text{ -----18}$$

Now, solve the exponential integral (for $k_1 \neq k_2$), the right integral from eq. (18):

$$k_1[A]_0\ {}_0\!\int^{t} e^{-(k1-k2)\tau}\, dt = k_1[A]_0\, [-(k_1 - k_2)^{-1}].\, e^{-(k1-k2)t}$$

Eq. 18 became;

$$[B]\, e^{+k2t} = k_1[A]_0\, [-(k_1 - k_2)^{-1}].\, e^{-(k1-k2)t} + I \text{----- 19}$$

Now to find I integration constant;

At t = 0 ; [B] = 0 substituting in equation 19;

$$0 * e^{+k2 *0} = k_1\, [A]_0\, [-(k_1 - k_2)^{-1}].\, e^{-(k1-k2)\,0} + I$$

$$0 = k_1\, [A]_0\, [-(k_1 - k_2)^{-1}].\, e^{0} + I$$

$$I = -\, k_1\, [A]_0\, [-(k_1 - k_2)^{-1}].\, e^{0}$$

Where $e^0 = 1$;

$$I = -k_1 [A]_0 [-(k_1 - k_2)^{-1}] \text{-----}\ 20$$

Substituting equation 20 in equation 19;

$$[B]\, e^{+k2t} = k_1 [A]_0 [-(k_1 - k_2)^{-1}].\, e^{-(k1-k2)t} - k_1[A]_0 [-(k_1 - k_2)^{-1}] \text{------}\ 21$$

$$[B]\, e^{+k2t} = k_1 [A]_0 \left[\frac{e^{-(k1-k2)t}}{-(k_1 - k_2)} - \frac{1}{-(k_1 - k_2)} \right]$$

$$[B]\, e^{+k2t} = \frac{k_1 [A]_0}{k_2 - k_1} [e^{-(k1-k2)t} - 1]$$

Divide by e^{+k2t} we get;

$$[B] = \frac{k_1 [A]_0}{k_2 - k_1} \left[\frac{e^{-(k1-k2)t}}{e^{+k2t}} - \frac{1}{e^{+k2t}} \right]$$

$$[B] = \frac{k_1 [A]_0}{k_2 - k_1} [e^{-k1t \cancel{+k2t}} . \cancel{e^{-k2t}} - e^{-k2t}]$$

$$[B] = \frac{k_1 [A]_0}{k_2 - k_1} [e^{-k1t} - e^{-k2t}]$$

The concentration of B at $k_1 \# k_2$ can be written as:

$$\mathbf{[B] = \frac{k_1 [A]_0}{k_2 - k_1} [e^{-k_1t} - e^{-k_2t}] \text{-----}\ 22}$$

The concentration of B at $k_1 = k_2 = k$ can be written as:

$$\mathbf{[B] = k [A]_0 e^{-kt} \text{----------} 23}$$

Then, solving for [C], we find that mass balance equation is:

$$[A]_0 = \mathbf{[A]} + \mathbf{[B]} + [C]$$

$$[A]_0 = \mathbf{[A]_0 e^{-k1t}} + \mathbf{k_1 [A]_0 / k_2 - k_1 (e^{-k1t} - e^{-k2t})} + [C]_t$$

Where: $[A] = [A]_0 e^{-k1t}$ from equation 6; and $[B]_t = k_1 [A]_0 / k_2 - k_1 (e^{-k1t} - e^{-k2t})$ from equation 22 we get:

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

$$[C] = [A]_0 - \mathbf{[A]_0 e^{-k1t}} + \mathbf{k_1 [A]_0 / k_2 - k_1 (e^{-k1t} - e^{-k2t})}$$

$$[C] = [A]_0 \{1 - e^{-k1t} + k_1 / k_2 - k_1 (e^{-k1t} - e^{-k2t})\}$$

$$[C] = [A]_0 \{1 - \{e^{-k1t} + k_1 / k_2 - k_1 e^{-k1t} - k_1 / k_2 - k_1 e^{-k2t} \}\}$$

$$[C] = [A]_0 \{1 - \{\ e^{-k1t} + \frac{k_1 e^{-k1t}}{k_2 - k_1} - \frac{k_1 e^{-k2t}}{k_2 - k_1}\}\}$$

$$[C] = [A]_0 \{1 - \{\frac{(k_2 - k_1) e^{-k1t} + k_1 e^{-k1t} - k_1 e^{-k2t}}{(k_2 - k_1)}\}\}$$

$$[C] = [A]_0 \{1 - \{\frac{k_2 e^{-k1t} \cancel{- k_1 e^{-k1t}} \cancel{+ k_1 e^{-k1t}} - k_1 e^{-k2t}}{(k_2 - k_1)}\}\}$$

$$[C] = [A]_0 \{1 - \{\frac{k_2 e^{-k_1 t} - k_1 e^{-k_2 t}}{(k_2 - k_1)}\}\} \text{ --------23}$$

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

$$\mathbf{[A] = [A]_0\, e^{-k1t}} \text{---------6}$$

$$\mathbf{[B] = k_1 [A]_0 / k_2 - k_1 (e^{-k1t} - e^{-k2t})} \text{ ----- } \mathbf{22}$$

$$[C] = [A]_0 \{1 - \{\frac{k_2 e^{-k_1 t} - k_1 e^{-k_2 t}}{(k_2 - k_1)}\}\} \text{ --------23}$$

$$[A]_0 = \mathbf{[A]_0\, e^{-k1t}} + \mathbf{k_1 [A]_0 / k_2 - k_1 (e^{-k1t} - e^{-k2t})} +$$

$$[C] = [A]_0 \{1 - \{\frac{k_2 e^{-k_1 t} - k_1 e^{-k_2 t}}{(k_2 - k_1)}\}\}$$

$$\boxed{[A]_0 = [A]_0 [\ e^{-k1t} + k_1 / k_2 - k_1 (e^{-k1t} - e^{-k2t}) + 1 - \{\frac{k_2 e^{-k1t} - k_1 e^{-k2t}}{(k_2 - k_1)}\}}$$

We can calculate the maximum B and maximum time by equation:

If $k_1 \neq k_2$

$$t_{\max} = \frac{\ln \frac{k_2}{k_1}}{k_2 - k_1}$$

$$B_{\max} = [A_0] \left(\frac{k_2}{k_1}\right)^{\frac{k_2}{k_1 - k_2}}$$

If $k_1 = k_2 = k$

$$t_{max} = 1 / k$$

$$[B]_{max} = [A]_0\, e^{-1}$$

Because of at $t_{max} = 1 / k$;

$$[B]_{max} = [A]_0 e^{-k\, t_{max}} = [A]_0 e^{-k\, 1/k} = [A]_0\, e^{-1}$$

Notes:

- If $k_2 >> k_1$(Meaning B quickly convert to C) B does not accumulate much and small $[B]_{max}$ and t_{max}.
- If $k_1 >> k_2$ that meaning B accumulate at long period and increased $[B]_{max}$.

Example: how much time would be required for the B to reach maximum concentration for the reaction:

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

$K_1 = 12$ and $k_2 = 2$ [t in min]

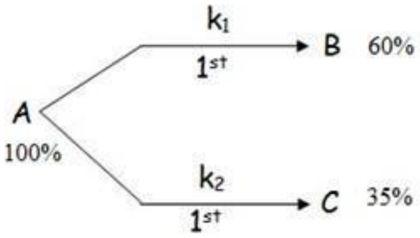
Answer:

$$t_{max} = (\ln k_1/k_2)^* (k_1\text{-}k_2)^{-1}$$

$$= (\ln 12/2)^*(12\text{-}2) = 0.179 \text{ min}$$

☒ Kinetic of Parallel or Side Reactions

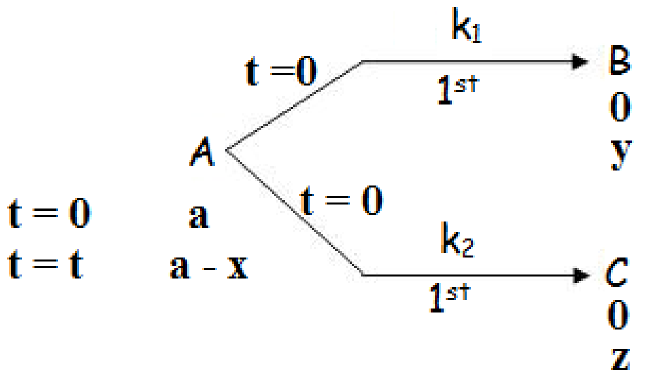
The reactions in which a substance reacts or decomposes in more than one way are called parallel or side reactions.



$K_1 > K_2$

At t = 0
$[A] = [A]_0$
$[B] = 0$
$[C] = 0$

If we assume that both of them are first order, we get.



$x = y + z$

$$-d[A]/dt = k_1[A] + k_2[A]$$

$$-d[A]/dt = (k_1+k_2)[A]$$

Where $[A] = (a-x)$, $[A]_0 = a$, $[B] = y$, and $[C] = z$

$$-\frac{d}{dt}(a-x) = k_1(a-x) + k_2(a-x)$$

$$-\underset{=0}{\cancel{\frac{da}{dt}}} + \frac{dx}{dt} = (k_1+k_2)(a-x)$$

$$\frac{dx}{dt} = (k_1+k_2)(a-x)$$

$$\int_0^x \frac{dx}{(a-x)} = \int_0^t (k_1+k_2)\,dt$$

$$\left[\ln\frac{1}{a-x}\right]_0^x = k_1+k_2\,[\,t\,]_0^t$$

$$\ln\frac{1}{a-x} - \ln\frac{1}{a-0} = (k_1+k_2)(t-0)$$

$$\ln\frac{1}{a-x} - \ln\frac{1}{a} = (k_1+k_2)\,t$$

$$\ln\frac{a}{a-x}=(k_1+k_2)\,t$$

$$-\ln\frac{a-x}{a}=(k_1+k_2)\,t$$

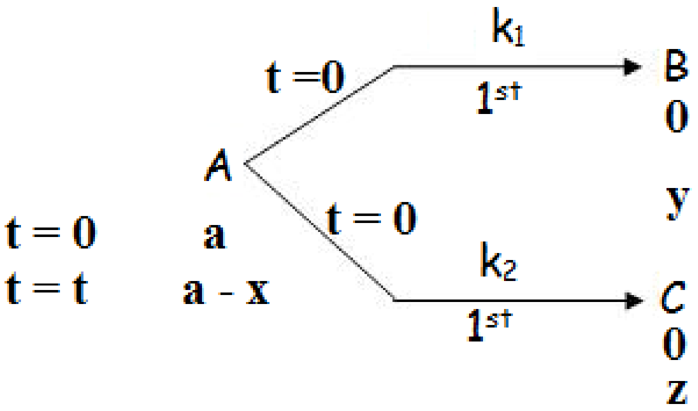
$$\ln\frac{a-x}{a}=-(k_1+k_2)\,t$$

$$\frac{a-x}{a}=e^{-(k_1+k_2)t}$$

Where $[A]_0 = a$, $[A] = (a\text{-}x)$

$$\frac{[A]}{[A]_0}=e^{-(k_1+k_2)t}$$

$$\boxed{[A]\;=\;[A]_0\,e^{-(k_1+k_2)t}}$$



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

$$\frac{d[B]}{dt}=k_1\,[A]_0\,e^{-(k_1+k_2)t}$$

$$\int_0^y d[B]\;=\int_0^t k_1\,[A]_0\,e^{-(k_1+k_2)t}\,dt$$

$$\int_0^y d[B]\;=k_1\,[A]_0\int_0^t e^{-(k_1+k_2)t}\,dt$$

$$[B]_0^y = k_1 [A]_0 \int_0^t e^{-(k_1+k_2)t}\,dt$$

Mathematically $\int e^{x}\,dx = \frac{e^{-x}}{-1}$

$$[B] = k_1 [A]_0 \left[\frac{e^{-(k_1+k_2)t}}{-(k_1+k_2)}\right]_0^t$$

$$[B] = \frac{k_1 [A]_0}{-(k_1+k_2)} \left[e^{-(k_1+k_2)t} - e^0\right]$$

$$[B] = \frac{k_1 [A]_0}{-(k_1+k_2)} \left[e^{-(k_1+k_2)t} - 1\right]$$

$$[B] = \frac{k_1}{(k_1+k_2)} [A]_0 \left[1 - e^{-(k_1+k_2)t}\right]$$

$$\boxed{[B] = y = \frac{k_1}{(k_1+k_2)} [A]_0 \left[1 - e^{-(k_1+k_2)t}\right]}$$

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

$$\boxed{[C] = z = \frac{k_2}{(k_1+k_2)} [A]_0 \left[1 - e^{-(k_1+k_2)t}\right]}$$

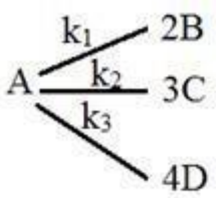
$$\frac{[B]}{[C]} = \frac{y}{z} = \frac{k_1}{k_2}$$

Ratio of concentration of B and C is constant for all time.

If $k_1 > k_2$ then;

$A \rightarrow B$ is main reaction

$A \rightarrow C$ is side reaction



$$1.\ A = A_0\, e^{-(k1+k2+k3)\,t}$$

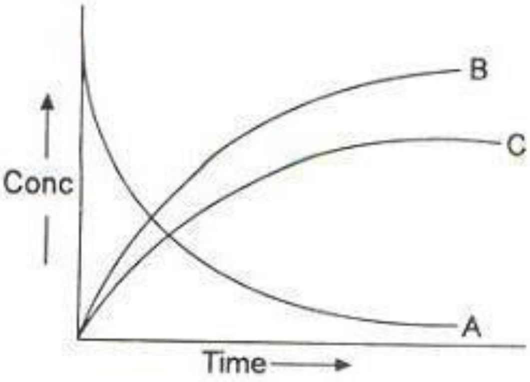
$$2.\ B = \frac{2k_1}{k_1+k_2+k_3}[A_0 - A\ ]$$

$$B = \frac{2k_1}{k_1+k_2+k_3}[A_0 - e^{-(k1+k2+k3)t}]$$

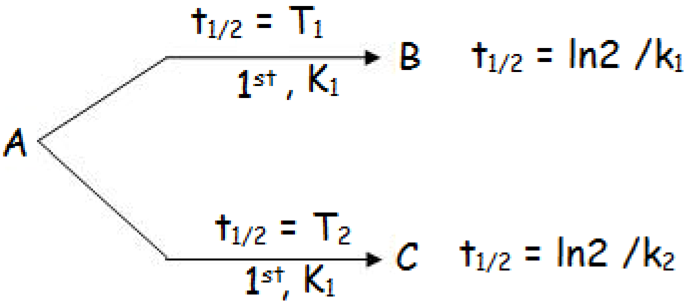
$$3.\ D = \frac{4\,k_1}{k_1+k_2+k_3}[A_0 - A_0\, e^{-(k1+k2+k3)t}]$$

$$4.\ \frac{B}{D} = \frac{k_B}{k_D} = \frac{2k_1}{4k_3}$$

$$5.\ \%B = \frac{2k_1}{2k_1+3k_2+4k_3} \text{ x } 100$$



Effective half-life:



Two independent cases with half-lives; we have two processes or mechanisms that occur together:

$T_1 = \ln 2/k_1$ ⇨ $k_1 = \ln 2/\ T_1$

And $T_2 = \ln 2/\ k_2$ ⇨ $k_2 = \ln 2/T_2$

Where T is Half-life , k is decay constant

When both processes occur together (active decomposition), the resulting decomposition has a total decomposition constant:

$$K_f = k_1 + k_2$$

Effective half-life is T_f;

$$T_f = \ln 2/k_f \Rightarrow k_f = \ln 2/T_f$$

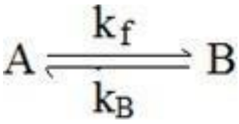
$$K_f = k_1 + k_2$$

$$\ln 2/T_f = \ln 2/T_1 + \ln 2/T_2$$

$$1/T_f = 1/T_1 + 1/T_2$$

According to this equation, when there are two independent decomposition processes, the effective half-life is smaller than each one separately because the combined influence of the two processes causes decomposition to happen more quickly.

☒ The kinetics of reversible reaction



$$A \underset{k_B}{\overset{k_f}{\rightleftharpoons}} B$$

$t = 0$	A_0	0
$t = t$	$A_0 - x$	x
$t = t_{eq}$	$A_0 - xe$	xe
	$[A]_{eq}$	$[B]_{eq}$

Rate of forward reaction = $k_f\,[A]$

Rate of backward reaction = $k_B\,[B]$

At equilibrium;

Rate of forward reaction = Rate of backward reaction

$$k_f\,[A]_{eq} = k_B\,[B]_{eq}$$

$$k_f\,(A_0 - xe) = k_B\,xe$$

$$k_f A_0 - k_f\,xe = k_B\,xe$$

$$k_f\, A_0 = k_B\, xe + k_f\, xe$$

$$k_f\, A_0 = (k_B + k_f\,)\, xe$$

$$\boxed{\frac{k_f}{k_f + k_B}\, A_0 = xe = [B]_{eq}}$$

$$[A]_{eq} = A_0 - xe$$

$$[A]_{eq} = A_0 - \left[\ \frac{k_f}{k_f + k_B}\ A_0\ \right]$$

$$[A]_{eq} = A_0 \left[\ 1 - \frac{k_f}{k_f + k_B}\ \right]$$

$$[A]_{eq} = A_0 \left[\frac{\cancel{k_f} + k_B - \cancel{k_f}}{k_f + k_B}\right]$$

$$\boxed{[A]_{eq} = A_0 \left[\frac{k_B}{k_f + k_B}\right]}$$

Conclusion:

① $[A]_{eq} = A_0 \left[\frac{k_B}{k_f + k_B}\right]$

② $[B]_{eq} = \frac{k_f}{k_f + k_B} A_0$

$kt = \ln \frac{A_0}{[A]} \Rightarrow kt = \ln \frac{A_0}{A_0 - xe}$, where $[A] = A_0 - xe$

③ $(k_f + k_B)t = \ln \frac{xe}{xe - x}$

Expression for $t_{1/2}$

$$t = t_{1/2}\ ,\ x = xe/2$$

$$(k_f + k_b)t_{1/2} = \ln \frac{xe}{xe - xe/2}$$

$$(k_f + k_b)\,t_{1/2} = \ln \frac{\cancel{xe}}{\cancel{xe}/2}$$

$$(k_f + k_b)t_{1/2} = \ln 2 \Rightarrow t_{1/2} = \frac{\ln 2}{k_f + k_b}$$

④ $t_{1/2} = \dfrac{0.693}{k_f + k_b}$

⑤ $[B] = x$

$$(k_f + k_b)t = \ln \frac{xe}{xe - x}$$

$$e^{(kf + kb)t} = \frac{xe}{xe - x}$$

$$xe - x = xe\, e^{-(kf + kb)t}$$

$$x = xe - xe\, e^{-(kf + kb)t}$$

$$[B] = x = xe - xe\, e^{-(kf + kb)t}$$

⑥ $[A] = A_0 - x$

$$[A] = A_0 - xe - xe\, e^{-(kf + kb)t}$$

$$[A] = A_0 - xe\,[-\, e^{-(kf + kb)t}]$$

Physical Chemistry/ kinetics chemistry

(2025-2026)

Prof. Dr. Abdulqadier Hussien Alkhazraji

Lecture 8   21 / 01/ 2026

Surface reaction mechanisms and kinetics

The study of **physical** and **chemical** phenomena that occur at the **interface** of two **phases**, including **solid-liquid** interfaces, **solid-gas** interfaces, **solid-vacuum** interfaces, and **liquid-gas** interfaces.

Interface is the boundary between two or more phases exist together.

Possible interfaces:

- Solid- (solid, liquid, gas/vapour)
- Liquid- (liquid, gas/vapour)
- Gas-gas not possible.

Surface reactions are the heart of catalysis, where molecules meet solid surfaces. Adsorption, reaction, and desorption steps work together to create new compounds. Understanding these processes is key to designing better catalysts and improving chemical reactions. Kinetics and mechanisms help us unravel how surface reactions unfold. From Langmuir-Hinshelwood to Eley-Rideal, different pathways lead to product formation. Factors like surface structure and reaction conditions play crucial roles in determining reaction rates and outcomes.

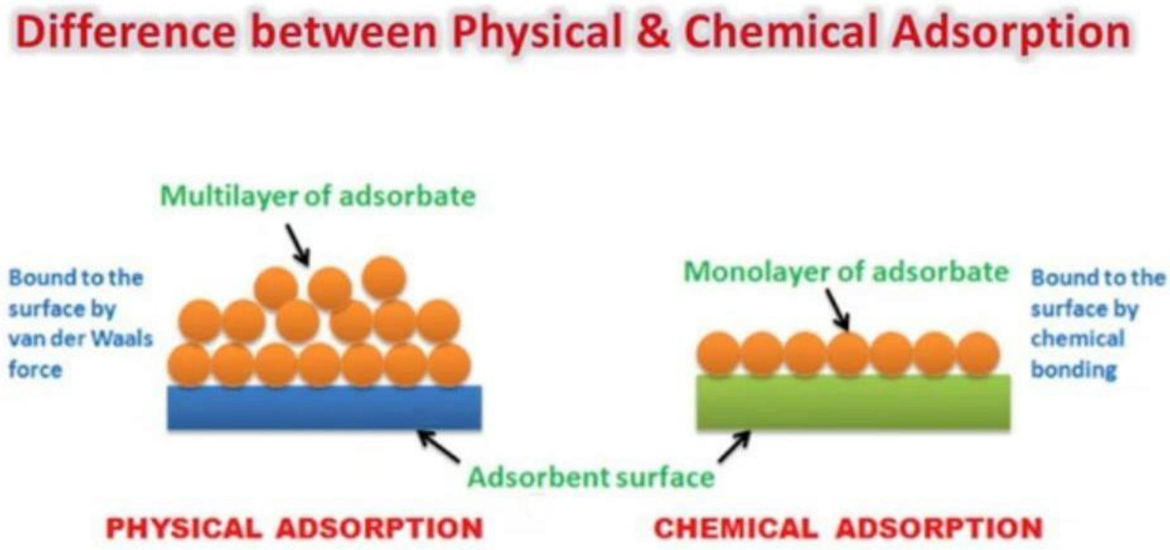
Surface reaction steps

Adsorption and desorption processes

Surface reactions involve the interaction of gas-phase molecules with solid surfaces, typically resulting in the adsorption, reaction, and desorption of species.

Adsorption is a phenomenon in which substance **(adsorbates)** accumulates on the surface typically gas or liquid material on the solid material **(adsorbent),** hence it is the process by which molecules from the gas phase bind to the surface, either through **physisorption** (weak van der Waals interactions) or **chemisorption** (strong chemical bonds)

Depending upon the nature of forces between adsorbate and adsorbent, adsorption of two types



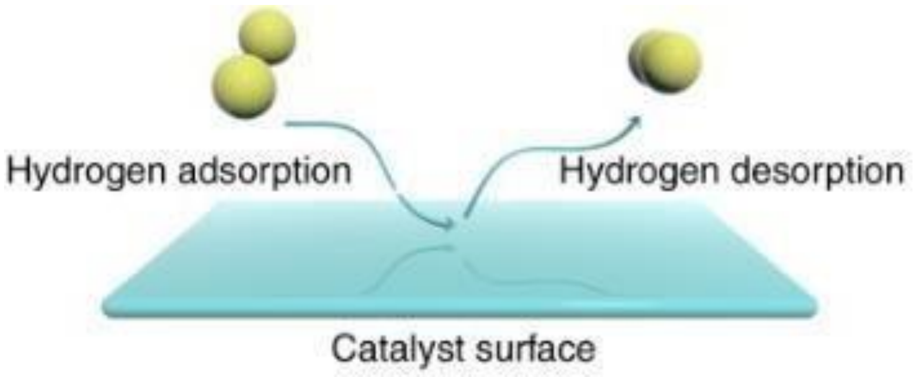
Physisorption examples: noble gases on metal surfaces, organic molecules on graphite.

Chemisorption examples: hydrogen on metal surfaces, oxygen on metal oxides.

Desorption is the process by which the products of the surface reaction are released from the surface back into the gas phase

Desorption can be induced by increasing the **temperature** or reducing the **pressure**.

Adsorption and desorption molecules process.



Absorption: It is a phenomenon in which one substance enters into another substance and gets uniformly distributed throughout the BULK of another substance.

Sorption : when both adsorption & absorption take place, the term sorption is used.

Elementary steps in surface reactions

Surface reactions can occur between **adsorbed species**, between an **adsorbed species and a gas-phase molecule**, or between an **adsorbed species and the surface itself**;

- Adsorbed reaction example (**adsorbed species**): CO oxidation on platinum surfaces:

$$CO_{ads} + O_{ads} \xrightarrow{Pt} CO_{2gas}$$

- Gas-adsorbed reaction example **(adsorbed species and a gas-phase molecule)**: hydrogen abstraction from a hydrocarbon by an adsorbed oxygen atom
- Adsorbed-surface reaction example (**adsorbed species and the surface itself**): oxidation of a metal surface by dissociative adsorption of oxygen

☒ The overall rate of a surface reaction is determined by the relative rates of adsorption, reaction, and desorption steps

☒ The slowest step in the reaction sequence is called the **rate-determining step** and controls the overall reaction rate

Kinetics of surface reactions

Rate equations and adsorption isotherms

- The kinetics of surface reactions can be described using rate equations that relate the reaction rate to the concentrations of reactants and products, as well as the rate constants for each elementary step.
- Adsorption isotherms, such as the Langmuir isotherm, describe the relationship between the surface coverage of adsorbed species and the pressure of the gas phase at a constant temperature.
- The rate of a surface reaction can be expressed in terms of the surface coverage of the reactants, which can be determined from the adsorption isotherms.

Factors influencing surface reactions

Surface structure and composition effects

- The surface structure and composition play a crucial role in determining the rates of surface reactions, as they affect the adsorption and activation of reactants.
- The presence of surface defects, such as steps, kinks, and vacancies, can provide sites with enhanced reactivity compared to the flat terraces
- The electronic structure of the surface, particularly the density of states near the Fermi level, can influence the adsorption and activation of reactants.

The Fermi level is an imaginary energy level used in materials physics and quantum mechanics to describe the distribution of electrons within matter (especially metals and semiconductors).

Simply put:

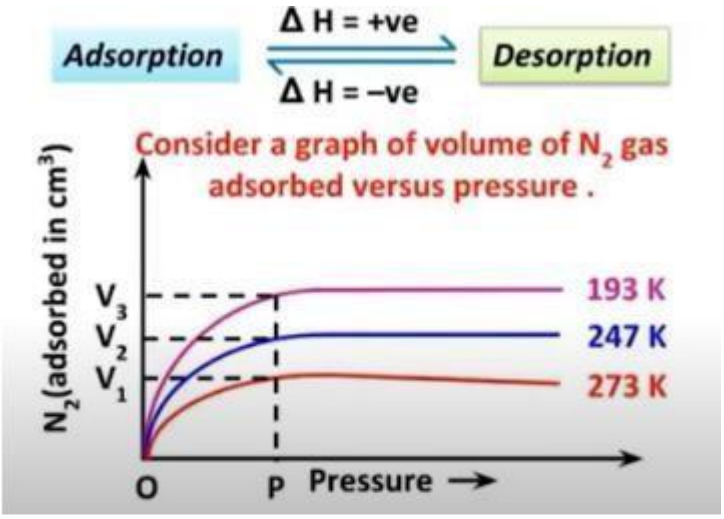
- It is the highest energy level where electrons exist at absolute zero (0 Kelvin).
- At ordinary temperatures, it gives you an idea of where most electrons are found and how they can transition to higher energy levels (such as electrical conductivity or electron transport).

Reactant properties and reaction conditions

- The nature of the reactants, including their molecular structure, size, and polarity, can affect their adsorption and reaction on the surface
- The reaction conditions, such as temperature and pressure, can influence the rates of adsorption, desorption, and reaction steps, as well as the overall selectivity of the process

Adsorption **decreases with increase in temperature**. Adsorption is an exothermic process and it is a favored at low temperature.

Graph below explain, the temperature increases from 193k to 273k at a constant p, the volume of gas adsorbed decreases from v_3 to v_1.



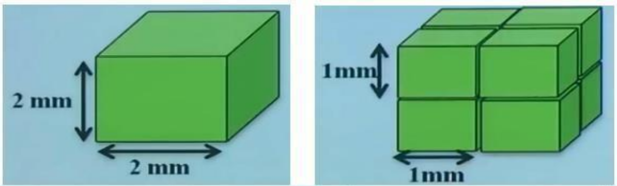
- The presence of co-adsorbed species, such as promoters or poisons, can modify the electronic and geometric properties of the surface, leading to changes in the reaction rates and selectivity

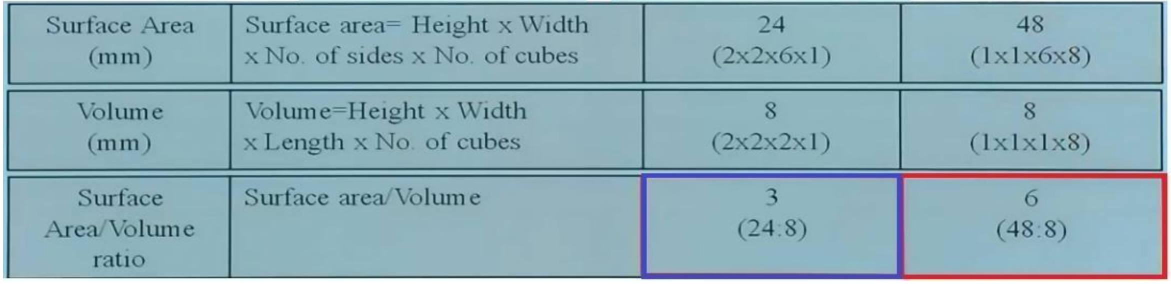
Nature of adsorbent is observed that same gas is adsorbed to different extent by different solids at the same temperature.

Adsorption is a surface phenomenon. It depended upon surface area of adsorbent.

Surface area α Rate of Adsorption

Surface area – to- volume ratio





Surface Area (mm)	Surface area= Height x Width x No. of sides x No. of cubes	24 (2x2x6x1)	48 (1x1x6x8)
Volume (mm)	Volume=Height x Width x Length x No. of cubes	8 (2x2x2x1)	8 (1x1x1x8)
Surface Area/Volume ratio	Surface area/Volume	3 (24:8)	6 (48:8)

Finally divided substance, are good adsorbent as they provide larger surface area for a given mass.

Adsorption kinetics

Studying the kinetics of the adsorption process is very significant for understanding the adsorption rate onto the particle surface, since adsorption kinetics show the influence of different conditions on the speed of the process by using models that could describe this reaction. In addition, adsorption kinetics determines the mechanism of materials adsorption onto the adsorbent material.

Pseudo-First-Order Model (Lagergren Model)

This kinetic model determines the relationship between the change in time and the adsorption capacity with order of one.

The Lagergren Model is based on the assumption that the rate of change of the amount of adsorbed material over time is directly proportional to the difference between the two values q_t and q_e.

It is expressed by Equation (1):

$$\frac{dq_t}{dt} = k_1 (q_e - q_t) \qquad (1)$$

$$\frac{dq_t}{(q_e - q_t)} = k_1 \, dt \qquad (2)$$

Integration of both parties from t = 0 at qt = 0 to t = t at qt = qe

$$\int_{q_t}^{q_e} \frac{dq_t}{(q_e - q_t)} = k_1 \int_0^t dt \qquad (3)$$

$$lnqe + ln\,(qe - qt) = kt \qquad (4)$$

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \qquad (5)$$

The nonlinear equation for a pseudo-first-order reaction is

$$q_t = q_e(1 - e^{-k_1 t}) \qquad (6)$$

Where qe and qt are the adsorption capacity at equilibrium time and time t (mg g^{-1}), respectively, k_1 is the pseudo first order rate constant (min^{-1}) and t is the time (min). The values of qe and k_1 can be determined from the intercept and the slope of the linear plot of log ($q_e - q_t$) versus t.

Calculation of the adsorption capacity at any time and equilibrium as follows:

$$\text{Adsorption Capacity} \left(\frac{mg}{g}\right), q_t = \frac{Co - Ct}{W} X \; V \qquad (7)$$

$$\text{Adsorption Capacity} \left(\frac{mg}{g}\right), qe = \frac{Co - Ce}{W} X \; V \qquad (8)$$

Where W is the weight of adsorbent (g), and V is the volume of the solution (L). C_0 and C_e (mg/L) are the initial and equilibrium concentrations, respectively.

For calculate the equilibrium concentration (Ce):

Ce = Absorbance/ molar extinction coefficient (ε)

The Lagergren pseudo-first-order (PFO) model is often associated with **physical adsorption** (**physisorption**), particularly when the rate-limiting step is diffusion.

Physical adsorption depend on van der Waals forces, which are weak and rapid, therefore the process is very fast at the beginning and then gradually slows down as the system approaches equilibrium, that because the rate of reaction decreases as the surface approaches saturation.

Pseudo-Second-Order Model (Ho and Mckay Model)

The pseudo-second-order kinetic model is expressed by Equation (9), which shows the relationship of the adsorption capacity and concentration with second order.

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \qquad (9)$$

$$\frac{dq_t}{(q_e - q_t)^2} = k_2\, dt \qquad (10)$$

$$\int \frac{dq_t}{(q_e - q_t)^2} = k_2 \int_0^t dt \qquad (11)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (12)$$

The nonlinear equation for a pseudo-second-order reaction is

$$q_t = q_e(1 - \frac{1}{1 + k_2 q_e t}) \qquad (13)$$

Initial adsorption rate h = $k_2q_e^2$, this gives a measure of the initial adsorption rate (mg $g^{-1}min^{-1}$).

If the value of "h = $k_2q_e^2$" is large, this indicates rapid initial adsorption.

Half-life ($t_{0.5}$) is the time when it arrives $q_t = q_e/2$

$$t_{0.5} = 1/\, k_2q_e^2 \qquad (14)$$

The pseudo-second-order model is often associated with **chemical adsorption (chemisorption)**, or processes that exhibit a strong dependence on residual surface area.

Elovich Model

This model is an interesting one for describing the activated **chemisorption** process on the heterogeneous surfaces, since it is generally applicable for chemisorption kinetics. It is assumed that the adsorption rate decreases exponentially with increasing amounts of adsorbed material on the surface, because the repulsion energy or availability of effective sites decreases with coverage.

The rate of adsorption (dq_t/dt) is assumed to decrease exponentially with the amount adsorbed (q_t) on a heterogeneous surface. This leads to the differential equation:

$$dq_t/dt = \alpha \exp(-\beta q_t) \qquad (15)$$

Here, α is the initial adsorption rate and β is constant related to the activation energy of adsorption.

To find the relationship between adsorption and time; Rearrange it to separate variables (dt and dq_t):

$$dq_t / \exp(-\beta q_t) = \alpha\, dt \qquad (16)$$

Integrate both sides from time $t = 0$ to $t = t$ and from $qt = 0$ to $q_t = q_t$

$$\int_0^{q_t} \exp(\beta q_t) dq_t = \int_0^t \alpha\, dt$$

$$[\frac{1}{\beta} \exp(\beta q_t)]_0^{q_t} = [\alpha t]_0^t$$

$$\frac{1}{\beta} (\exp(\beta q_t) - \exp(0)) = \alpha t$$

Now, solve for qt:

$$\frac{1}{\beta}(\exp(\beta q_t) - 1) = \alpha t$$
$$\exp(\beta q_t) - 1 = \alpha \beta t$$
$$\exp(\beta q_t) = \alpha \beta t + 1$$
$$\beta q_t = \ln(\alpha \beta t + 1)$$
$$q_t = \frac{1}{\beta} \ln(\alpha \beta t + 1)$$
$$q_t = \frac{1}{\beta} \ln(1 + \alpha \beta t)$$

This can also be written as:

$$qt = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta} \ln t \qquad (17)$$

Elovich Model is valid for the heterogeneous adsorbent surfaces and expressed by Equation (17).

Where α is the initial adsorption rate constant (mg g^{-1} min^{-1}), β is the desorption constant related to the chemisorption activation energy and the surface coverage (g mg^{-1}), and qt is the adsorbed material (mg g^{-1}) at time *t* (min). By plotting qt versus *ln t*, a straight line is obtained where values of α and β can be obtained.

Notes:

- The Alpha constant (α , mg g^{-1} min^{-1} or mol g^{-1} s^{-1}) represents the initial adsorption rate, and the higher value of alpha, that mean the initial adsorption very quickly , and meaning the surface contains a large number of active sites.

Alpha constant (α**)** increase with increased temperature, concentration adsorbent and number of active sites.

- The Beta constant (β) expresses how much the adsorption rate decreases with increasing amounts of adsorbed material. The beta constant (β, mg g-1) represents the effect of surface covring on adsorption rate.

- A large beta value (β) indicates that the adsorption rate decreases rapidly as adsorption increases, meaning that the surface sites have lower or higher adsorption energy.
- A small beta value (β) means that the adsorption rate remains high even when a large portion of the surface is covered.

Adsorption isotherm;

An adsorption isotherm is a graphical or mathematical model that describes the relationship between the amount of a substance (adsorbate) on a solid surface (adsorbent) and its concentration in the surrounding fluid (gas or liquid) at a constant temperature. It quantifies the extent of adsorption at equilibrium, providing insights into the material's surface properties, pore structure, and adsorption

At constant temperature , the graph between x/m and the pressure (p) of a gas at constant temperature is called **adsorption isotherm**.

Adsorbate: The substance that is adsorbed onto the surface.

Adsorbent: The solid material onto which the adsorbate is adsorbed.

Equilibrium: The point where the rate of adsorption equals the rate of desorption.

Constant temperature: Temperature is held constant because it significantly affects the equilibrium of the adsorption process.

We have a five types of physisorption isotherms are found over all solids:

Where: I , II and III ⟶ **Non porous** , but IV and V⟶ **porous**

Type I adsorption isotherm is a typical Langmuir isotherm because the adsorption leads to monolayer formation. The curve represents that after certain value of P, there is no change in x/m with the increase of pressure. i.e., it shows limiting or saturation state after certain value of P (Fig.1). Rapid increase followed by horizontal saturation microporous, monolayer adsorption,

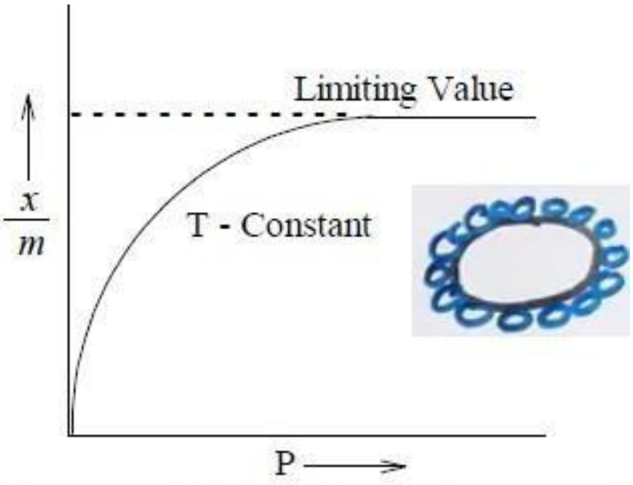


Fig. 1: Type I Adsorption Isotherm

Type II represents a a multi-molecular layer physical adsorption on non-porous materials. The curve shows that there is a transition point, B that represents the pressure at which the formation of monolayer is complete and that of multilayer is being started (Fig.2). It like S letter; non-porous, multilayer adsorption.

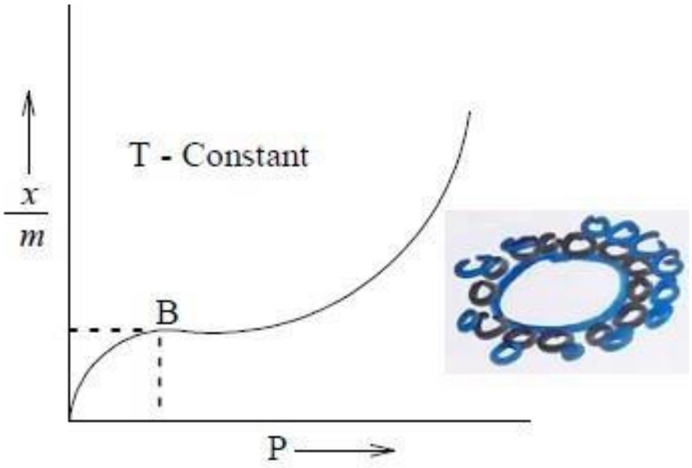


Fig. 2: Type II Adsorption Isotherm

Type III represents a case of physical adsorption on porous materials. The curve represents that multi molecular layer formation starts even before the completion of monomolecular layer formation (Fig.3).

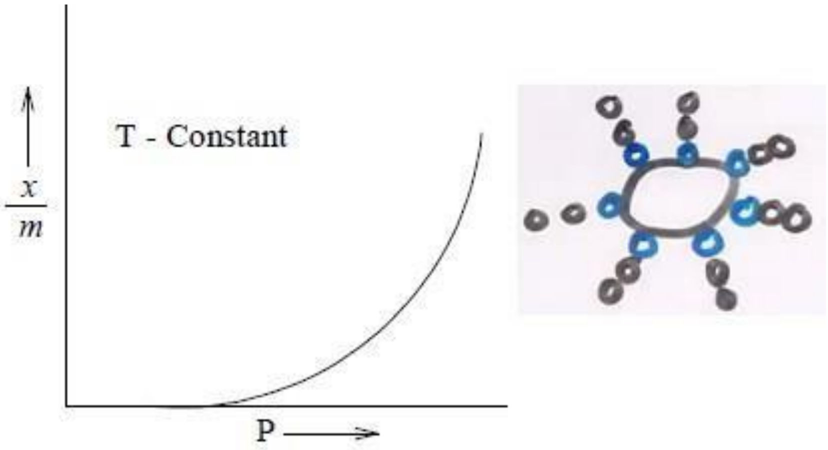


Fig. 3: Type III Adsorption Isotherm

Type V also represents a case of physical adsorption on porous materials accompanied by capillary condensation. This isotherm indicates that there is a tendency for saturation state to be reached in the multi molecular region (Fig.4). staged adsorption (first monolayer then build-up of additional layers). Multilayer adsorption + capillary condensation, mesoporous, The V type is like II.

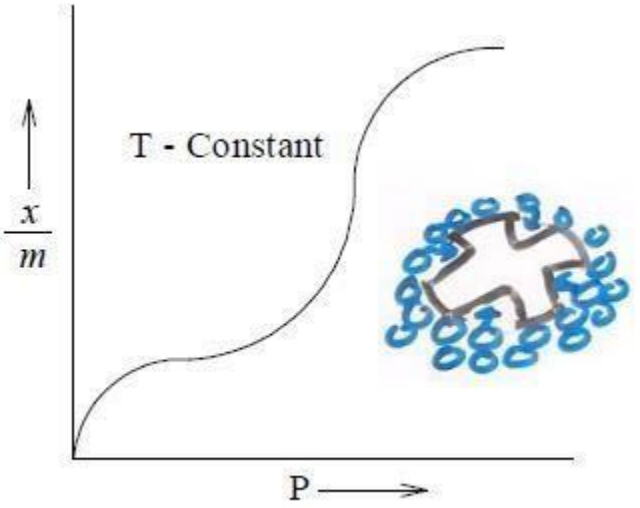


Fig. 4: Type IV Adsorption Isotherm

Type IV also represents a case of physical adsorption on porous material. It indicates that the formation of multi molecular layer starts in the beginning (Fig.5). The V type is like III, weak adsorption + capillary condensation, porous materials with cohesive force between adsorbate molecules and adsorbent being greater than that between adsorbate molecules.

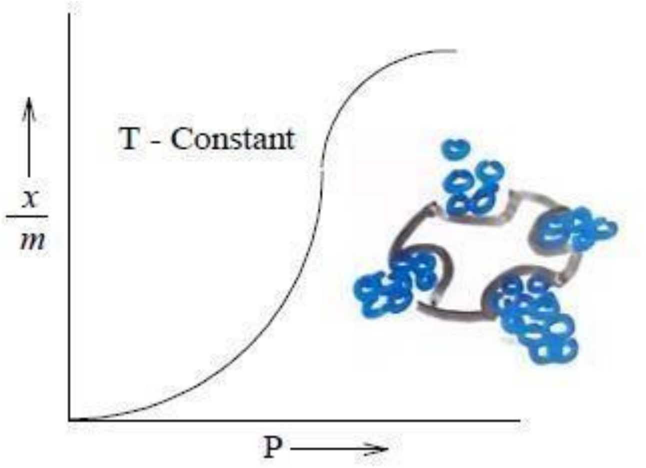


Fig. 5: Type V Adsorption isotherm

Isotherm models:

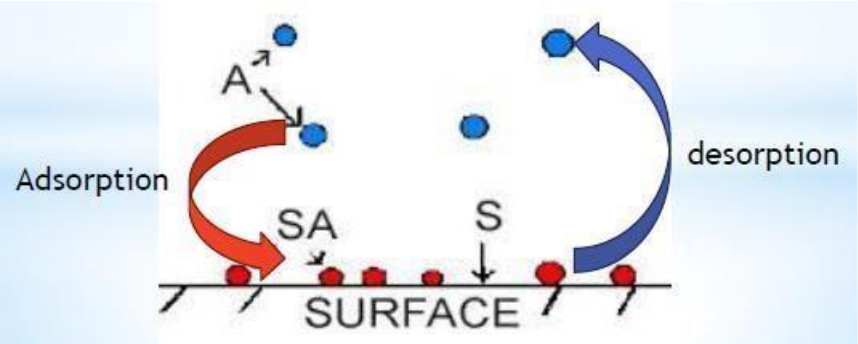
The process of adsorption is usually studied through graphs know as adsorption isotherm. It is the graph between the amounts of adsorbate (x) adsorbed on the surface of adsorbent (m) and pressure (P) at constant temperature.

LANGMUIR ADSORPTION ISOTHERM

In 1916, Irving Langmuir proposed another adsorption Isotherm which explained the variation of adsorption with pressure.

Assumptions of Langmuir Isotherm

- All surface active regions have the same energy.
- At low pressure, the adsorbed gases on the solid surface form monolayer.
- Absorbed gas behave ideally
- No lateral interaction.
- Absorbed molecules are localized.
- The adsorption process is a dynamic adsorption state that contains two opposite processes.



Derivation of Langmuir Adsorption Isotherm

Langmuir Equation depicts the relationship between the extent of adsorption and pressure. Langmuir proposed that dynamic equilibrium exists between adsorbed gaseous molecules and the free gaseous molecules. Using the equilibrium equation, equilibrium constant can be calculated.

- Consider an adsorbing surface of area 1 square centimeter is exposed to a gas (Figure. 1) Molecules of the gas will strike the surface and stick for an appreciable time due to condensation while other gas molecules will evaporate from the surface due to thermal agitation.
- If θ is the fraction of surface area covered by gas molecules at any instant, then the fraction of the remaining surface available for adsorption is (1−θ).

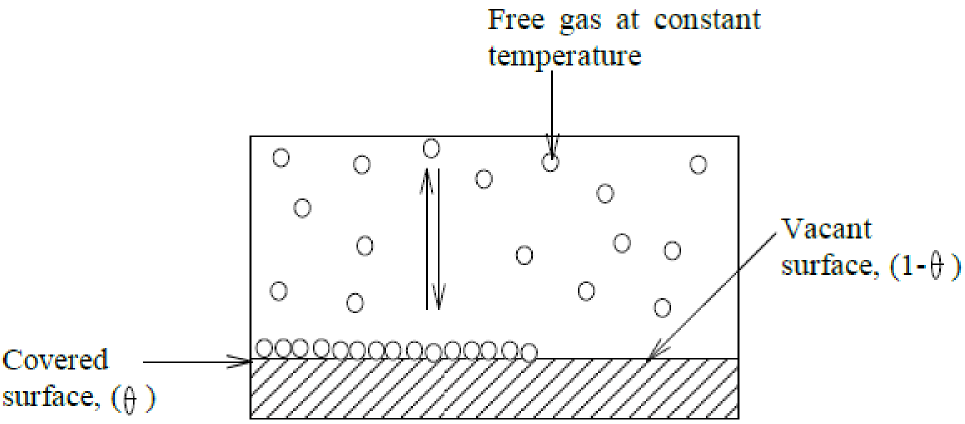


Figure 1: Equilibrium between free molecules and adsorbed molecules

- If P is the pressure of the gas, then the rate of condensation (adsorption) molecules is expected to

be the proportional to the pressure, P and fraction of uncovered surface, (1−θ). Hence, The rate of adsorption = $k_1 (1-\theta)P$ (18)

- The rate at which gas molecules evaporates from the surface (desorption) will depend on the fraction of the surface covered by the gas molecules, (θ). Hence,

The rate of evaporation of gas molecules = $k_2\theta$ (19)

Where k_1 and k_2 are proportionality constants for a given system.

- At equilibrium, the rate of adsorption and the rate of evaporation are equal, then,

$$k_1(1-\theta)P = k_2\theta$$

$$k_1P - k_1P\theta = k_2\theta$$

$$k_1P = k_2\theta + k_1P\theta$$

$$k_1P = \theta(k_2 + k_1P)$$

$$\theta = \frac{k_1P}{k_2 + k_1P} \qquad (20)$$

- Dividing the numerator and denominator of the right-hand side of equation (20) by k_2, we get:

$$\theta = \frac{\left(k_1/k_2\right)P}{1+\left(k_1/k_2\right)P}$$

$$\theta = \frac{bP}{1+bP} \qquad (21)$$

Where $b = k_1/k_2$ and is called adsorption coefficient.

- If x is the amount of gas adsorbed on the mass m of the adsorbent, then x/m is the amount of gas adsorbed per unit mass of the adsorbent.

- Since the amount of gas adsorbed per unit mass of adsorbent (*x/m*) is proportional to the fraction (θ) of the surface covered, then

$$\frac{x}{m} \ \alpha \ \theta$$

$$\frac{x}{m} = k\,\theta$$

$$\theta = \frac{x}{km} \qquad (22)$$

Where *k* is proportionality constant.

- Substituting the value of θ in equation (21), we have

$$\frac{x}{km} = \frac{\mathrm{b}P}{1+\mathrm{b}P}$$

$$\frac{x}{m} = \frac{\mathrm{kb}P}{1+\mathrm{b}P}$$

$$\frac{x}{m} = \frac{\mathrm{a}P}{1+\mathrm{b}P} \qquad (23)$$

Where the constant a = kb.

- Equation (23) relates the amount of gas adsorbed to the pressure of the gas at constant temperature and is known as the **Langmuir adsorption isotherm**.
- The constant a and b depend on the nature of the system and on the temperature. In order to test this isotherm, the equation (23) is divided by P on both sides, we get:

$$\frac{\left(x/m\right)}{P} = \frac{1}{P}\left[\frac{\mathrm{a}P}{1+\mathrm{b}P}\right] \qquad (24)$$

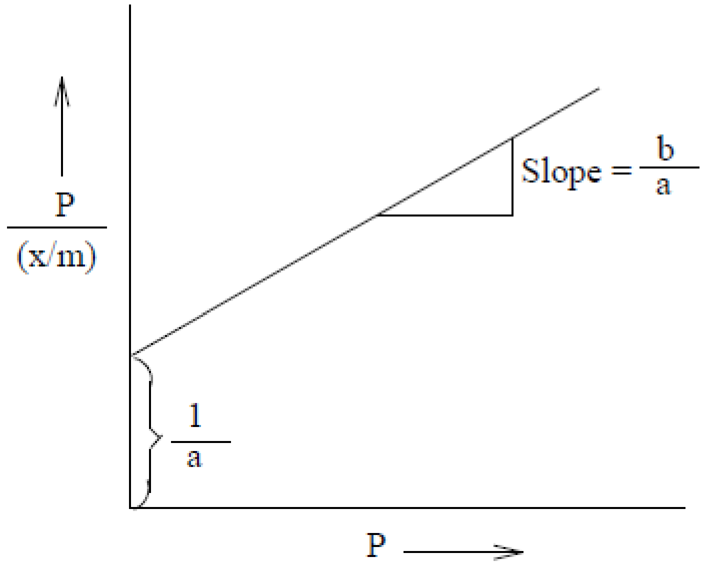
- Further taking reciprocals, we get:

$$\frac{P}{\left(x/m\right)} = \frac{P(1+bP)}{aP}$$

$$\frac{P}{\left(x/m\right)} = \frac{(1+bP)}{a}$$

$$\frac{P}{\left(x/m\right)} = \frac{1}{a} + \left(\frac{b}{a}\right) P \qquad (25)$$

This equation is similar to an equation for a straight line (y = mx +c). Hence if *P / (x/ m)* is plotted against *P*, a straight line should be obtained with a slope equal to *(b/a)* and intercept equal to *(1/a).*



Langmuir Adsorption Isotherm

Testing of Langmuir Adsorption Isotherm

We shall now consider three special cases of Langmuir isotherm.

$$\frac{P}{\left(x/m\right)} = \frac{1+bP}{a} \qquad (24)$$

Case 1: At very low pressures, bP can be neglected in comparison with unity (i.e: bP <<1) and hence,

$$\frac{P}{\left(x/m\right)} = \frac{1}{a}$$

$$\frac{x}{m} = a\,P$$

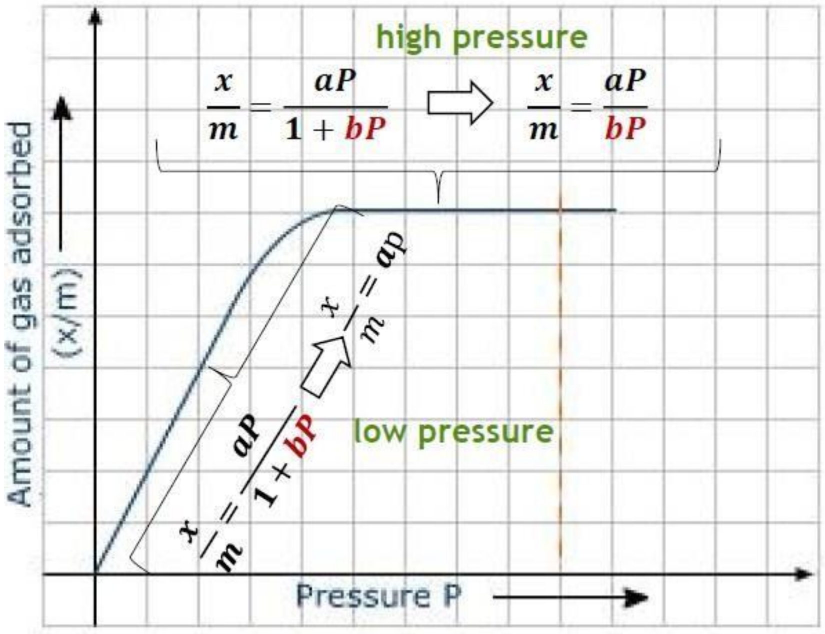
At very low pressures, the amount of gas adsorbed is directly proportional to the pressure.

Case 2: At high pressures bP>>1, and hence 1 can be neglected in comparison with bP.

$$\frac{P}{\left(x/m\right)} = \left(\frac{b}{a}\right) P$$

$$\frac{x}{m} = \frac{a}{b} \qquad (25)$$

At very high pressures, the extent of adsorption at a given temperature is independent of pressure of the gas. This condition arises when the surface of the adsorbent is completely covered by the unimolecular layer of gas molecules.



Case 3: At intermediate pressure, Langmuir equation becomes Freundlich equation.

At very low pressure,

$$\frac{x}{m} \ \alpha \ P$$

$$\frac{x}{m} = k \ P$$

At very high pressure,

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

At intermediate pressure, the equation becomes:

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

Where the value n lies between 0 and 1. This equation is known as Freundlich equation.

The mass of the gas adsorbed per gram of the adsorbent is related to the equilibrium pressure.

According to the following equation,

$$\frac{x}{m} = \frac{aP}{1 + bP}$$

Where, **a** and **b** are constants

Whose values depend upon-

1. The nature of the gas adsorbed.
2. The nature of the gas adsorbent.
3. Temperature

Freundlich Adsorption Isotherm

In the year 1909, the scientist Freundlich proposed a model to explain isothermic adsorption via an equation that relates the amount of gas adsorbed on the solid surface with pressure and the equation is called an equation **Freundlich Equation**;

$x/m \alpha P^{1/n}$, where $n \geq 1$

$$\frac{x}{m} = kP^{\frac{1}{n}} \quad \text{---------} \quad \textbf{Freundlich Equation}$$

Where:

x is the amount of adsorbate (mg/g)

m is the mass of adsorbent

P is pressure extent of adsorption of a gas

K and **n** are constant depend of matter type and temperature.

x/m is amount of adsorption of a gas.

At constant Temperature:

Adsorption α **pressure of gas (p)**

A graph drawn between extent of adsorption and the pressure of gas at constant temperature called **Adsorption Isotherm**.

The extent of adsorption of a gas per unit mass of adsorbent upon the pressure of the gas.

The extent of adsorption increases with pressure and becomes **maximum.**

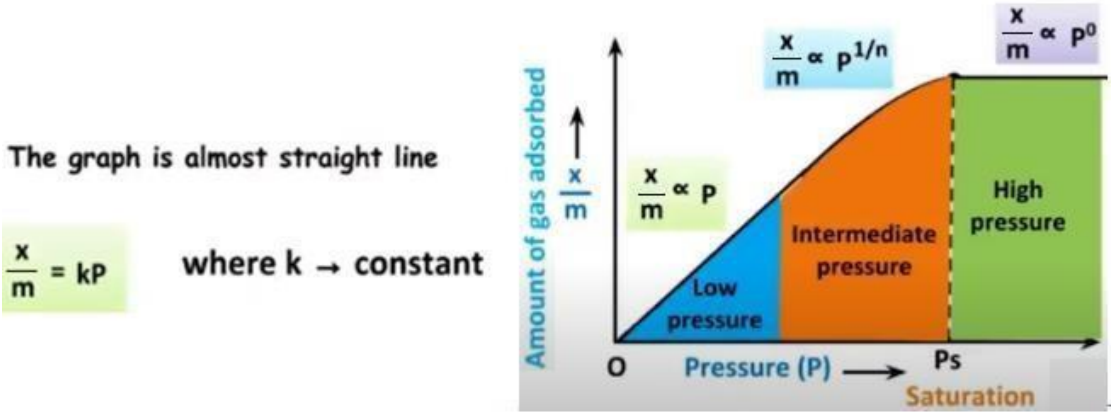
x/m (1 to 0)

(i) Low pressure: $n = 1$

At low pressures, the number of gas molecules is very small compared to the number of adsorption sites on the surface, so most of the sites remain empty, and there is no saturation or competition between molecules on the surface.

$$x/m \propto P \Rightarrow x/m = k\,p^{1/n} \Rightarrow x/m = k\,p^{1/1} \Rightarrow x/m = k\,p \Rightarrow$$

$$x/m = k\,p^{1/n}$$



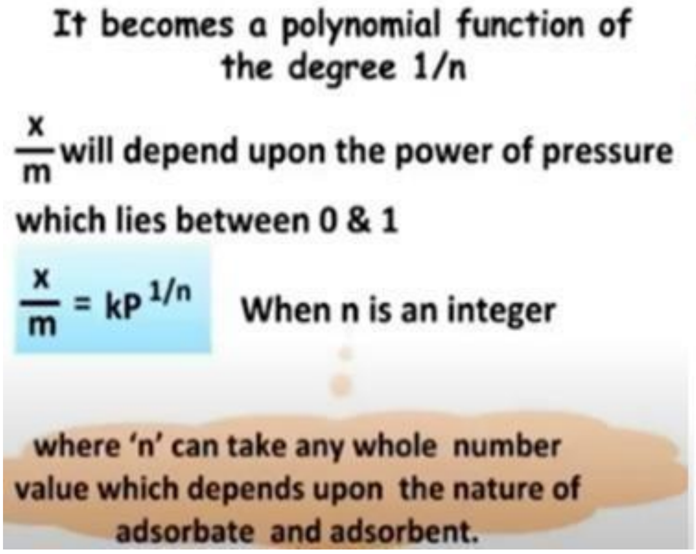
The graph is almost straight line

$\frac{x}{m} = kP$ where k → constant

(ii) Intermediate pressure: $n = n$

$$x/m = k\,p^{1/n}$$

$$n > 1$$

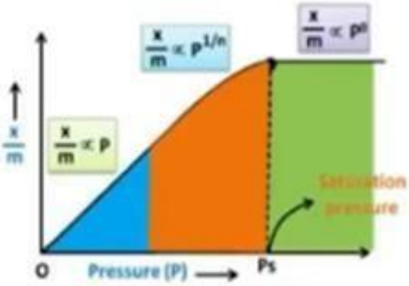


It becomes a polynomial function of the degree 1/n

$\frac{x}{m}$ will depend upon the power of pressure which lies between 0 & 1

$\frac{x}{m} = kP^{1/n}$ When n is an integer

where 'n' can take any whole number value which depends upon the nature of adsorbate and adsorbent.



(iii) High pressure: $n = \infty$

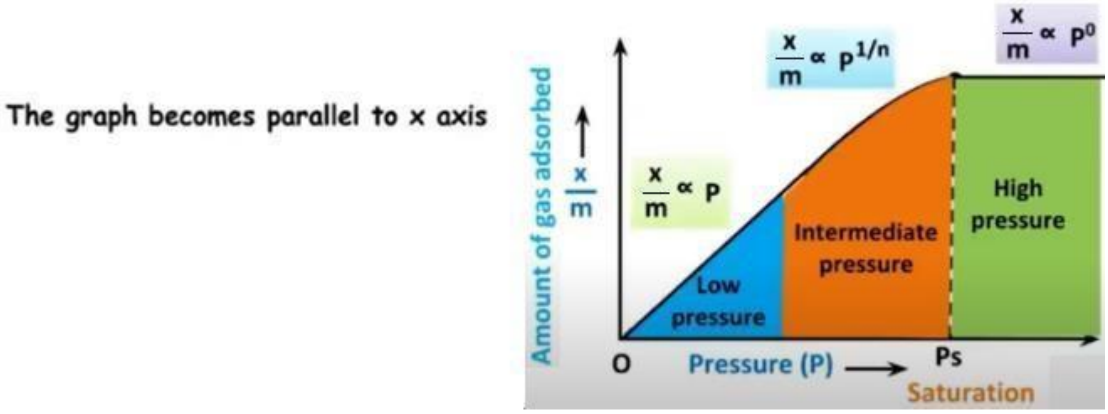
$$x/m = k\,p^{1/n}$$

$$x/m = k\,p^{1/\infty}$$

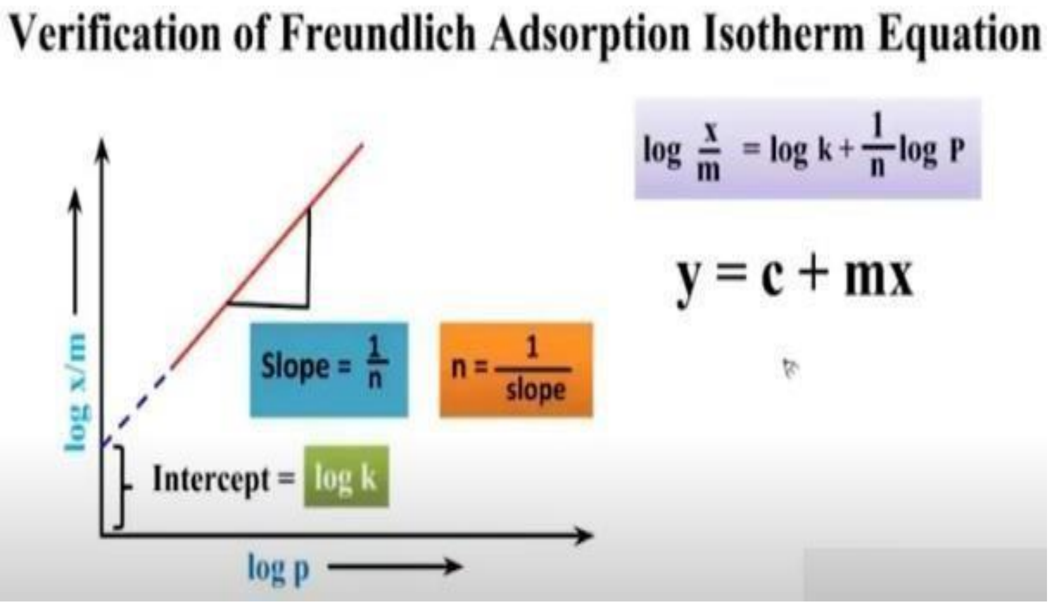
$$x/m = k\,p^{0}$$

$$x/m = k\,(1)$$

$$x/m = k$$



In order to obtain the constants value (K and n) in the Freundlich equation we take the natural logarithm to both sides of the equation to get as follows:



We can express concentration in the Freundlich equation if we replace pressure with concentration, but it should be Concentration in units of mol / liter, so the equation becomes as follows:

$$\log \frac{x}{m} = \log k + \frac{1}{n} \log C$$

C : is concentration (mol/L)

Disadvantages of Freundlich equation:

1. Invalid at high pressure and concentrations due to the diffraction occurring in a curve adsorption.
2. The values of the constants k, n depend on the temperature.
3. It is considered a hypothetical equation and without a theoretical basis from which it is derived.

The BET Equation for Multilayer Adsorption

The three scientists (Paul Emmett, Stephen Brenner and Edward Teller) put forth a theory to explain the multi-layer adsorption, it has been called (BET isotherm).

So, this is a more general, multi-layer model. It assumes that a Langmuir isotherm applies to each layer and that no transmigration occurs between layers. It also assumes that there is equal energy of adsorption for each layer except for the first layer.

Depending on a number of assumptions, they are as follows:

1. Gaseous molecules behave ideally
2. Multilayers are formed.
3. Each adsorbed molecule provides a site for the adsorption of the molecule in the layer above it
4. Adsorption at one site dose not effect adsorption at another site
5. All sites on the surface are equivalent
6. Heat of adsorption in succeeding layer = Energy of liquification ($\Delta H_{ads}=\Delta H_{liq}$)
7. surface area for nth layer α θ_{n-1}
8. The heat of adsorption $(\Delta Hads)_n$ is constant for all layers after the first $(\Delta Hads)_1$

The adsorption involves the formation of multimolecular layer of adsorbate molecules on the surface of solid adsorbent.

The multilayer adsorption takes place the following manner:

Vapour + Free surface of adsorbent → Monolayer
Vapour + Monolayer → Bimolecular layer
Vapour + Bimolecular layer → Trimolecular layer
Vapour + Trimolecular layer → Multimolecular layer

Langmuir assumption applies to each layer and there is sa dynamic equilibrium exits between the successive layer. Further, the rate of from the first layer is equal to the rate of condensation of preceding layer.

The heat of adsorption in each layer (except the first layer) is involved in each of the evaporation process. After the formation of first layer, the heat of adsorption is equal to the latent heat of condensation of vapours.

BET equation

$$\frac{p}{v(p_0 - p)} = \frac{1}{v_m C} + \frac{C-1}{v_m C} \cdot \frac{p}{p_0}$$

Where:

P: partial vapour pressure of adsorbate gas in equilibrium with the surface in pascals

P_o: saturated pressure of adsorbate gas, in pascals

v: volume of gas adsorbed at standard temperature and pressure (STP) [273.15Kand atmospheric pressure (1.013×105Pa)], in millilitres

v_m: volume of gas adsorbed at STP to produce an apparent monolayer on the sample surface, inmillilitres

C: dimensionless constant that is related to the enthalpy of adsorption of the adsorbate gas on the powder sample.

it calculate:

$$C = exp^{\left(\frac{(\Delta H_{ads} - \Delta H_{liq})}{RT}\right)}$$ (constant for given gas)

ΔH_{ads}: heat of adsorption 1st layer

ΔH_{liq}: heat of liquification

BET Plot and Determination of Surface Area

The BET equation can be rearranged into a linear form:

$$\frac{p}{v(p_0 - p)} = \frac{1}{v_m C} + \frac{C-1}{v_m C} \cdot \frac{p}{p_0}$$

Surface Area Calculation

From the monolayer absorbed gas volume (v_m), we can determine total and specific surface area

$$S = \frac{v_m N A_s}{V}$$

S is surface area of sample material

v_m is monolayer absorbed gas volume

N is Avogadro's number = 6.02×10^{23} molecules/mol

As is cross-sectional area of adsorbed gas molecule

V is molar volume of adsorbed gas

$$S_{BET} = \frac{S}{a}$$

S_{BET} = specific surface area

a= mass of sample

Derivation BET adsorption isotherm

We can represent the formation of multilayer of gas molecules on the surface of adsorbent can be explained with following equilibrium equations:

$$\mathrm{M + S \longrightarrow MS}$$
$$\mathrm{M + MS \longrightarrow M_2S}$$
$$\mathrm{M + M_2S \longrightarrow M_3S}$$
$$\mathrm{M + M_{n\text{-}1}S \longrightarrow M_nS}$$

Where M is the unadsorbed gas molecules and S is the active sites on the adsorbent surface; MS is the single layer formed; M2S is the second layer formed and so on. There is always an equilibrium exists between the adsorbate and adsorbent.

The equilibrium constant can be written as:

$$k_1 = \frac{[MS]}{[M][S]}; \qquad k_2 = \frac{[M_2S]}{[M][MS]}; \qquad k_2 = \frac{[M_3S]}{[M][M_2S]} \quad and\ so\ on \qquad (1)$$

We know that P is the pressure of gas molecules and M is the un-adsorbed molecules. Further, let θ_o be free surface area available for adsorption; θ_1 is fraction of free surface area available after formation of monolyer; θ_2 is fraction of free surface area available after formation of second layer; $\theta_3$is fraction of free surface area available after formation of third layer and so on.

Therefore, the adsorption of unadsorbed molecule on the surface of adsorbent, [S] α P and;

$[M]=]\theta_o$; $[MS] = \theta_1$; $[M_2S]= \theta_2$; $[M_3S] = \theta_3$ and so on.

Substituting the above θ values in equation (1), we have:

$$k_1 = \frac{\theta_1}{P\theta_o}; \quad k_2 = \frac{\theta_2}{P\theta_1}; \quad k_3 = \frac{\theta_3}{P\theta_2} \qquad (2)$$

The value of k1 is usually very large as compared to the other equilibrium constant. This is due to the increase in distance from the adsorbent surface and the interaction gas molecules and solid adsorbent.

- Therefore, k_2, k_3, k_4 *etc*. much smaller than k_1.

$$\text{So, } k_2 \approx k_3 \approx k_L, \qquad (3)$$

where kL is the equilibrium constant corresponding to saturated vapour liquid equilibrium system and it may be represented mathematically as:

$$k_L = \frac{1}{P_o} \qquad (4)$$

$$M + S \xrightarrow{k_1} MS \qquad k_1 = \frac{\theta_1}{\theta_0 p} \Rightarrow \theta_1 = k_1 p \theta_0 \qquad (5)$$

A_g is gas molecule, S active site , AS is the molecule adsorbed onto the surface, θ_0 is the unadsorbed part of the surface, θ_1 is the part covered by a single layer of molecules.

$$M + MS \xrightarrow{k_2} M_2S \qquad k_2 = \frac{\theta_2}{\theta_1 p} \Rightarrow \theta_2 = k_2 p \theta_1 = \theta_1 \frac{p}{p^0} \qquad (6)$$

In multilayer adsorption at saturation pressure B, the gas begins to condense into a liquid on the preceding layer, therefore, it can be written:

$$\theta_2 = \theta_1 \frac{p}{p^0} \qquad (7)$$

$$M + M_2S \xrightarrow{k_3} M_3S \qquad k_3 = \frac{\theta_3}{\theta_2 p} \Rightarrow \theta_3 = k_3 p \theta_2 = \theta_2 \frac{p}{p^0} \qquad (8)$$

$$M + M_3S \xrightarrow{k_4} M_4S \qquad k_3 = \frac{\theta_4}{\theta_3 p} \Rightarrow \theta_4 = k_4 p \theta_3 = \theta_3 \frac{p}{p^0} \qquad (9)$$

$$M + M_{n-1}S \xrightarrow{k_n} M_nS \qquad k_n = \frac{\theta_n}{\theta_{n-1} p} \Rightarrow \theta_n = k_n p \theta_{n-1} = \theta_{n-1} \frac{p}{p^0} \qquad (10)$$

Adsorption is usually stronger in the first layer than in the layers that follow it, therefore:

$$K_1 >>>> k_2 > k_3 > k_4 >> k_n = k_L$$

But when adsorption becomes similar to condensation (from gas to liquid), the constant remains constant and takes on a value of:

$$K_L = \text{constant for reaction } \underset{\substack{\text{saturated}\\ \text{vapour}\\ (p^0)}}{M_{(g)}} \rightleftharpoons \underset{\text{liquid}}{M_{(liq)}}$$

$$K_L = \frac{[M_{(liq)}]}{[M_{(g)}]} \Rightarrow \boxed{K_L = \frac{1}{p^0}} \text{ (Important)} \qquad (11)$$

$$K_2 = k_3 = k_4 \dots = k_n = k_L = 1/p^0$$

Because the layers after the first one condense like liquids, we replace all the $K_2 = k_3 = k_4 \dots = k_n = k_L$ values with $1/p^0$ value.

Now from equations 1, 2, 3, 4 , we get:

$$\theta_1 = k_1 p\, \theta_0 \left(\frac{p}{p^0}\right)^0$$

$$\theta_2 = \theta_1 \frac{p}{p^0} = k_1 p\, \theta_0 \left(\frac{p}{p^0}\right)^1$$

$$\theta_3 = \theta_2 \frac{p}{p^0} = k_1 p\, \theta_0 \left(\frac{p}{p^0}\right)^2$$

$$\theta_4 = \theta_3 \frac{p}{p^0} = k_1 p\, \theta_0 \left(\frac{p}{p^0}\right)^3$$

$$\theta_n = \theta_{n-1} \frac{p}{p^0} = k_1 p\, \theta_0 \left(\frac{p}{p^0}\right)^{n-1}$$

Sum of all surface states = 1

$$\theta_0 + \theta_1 + \theta_2 + \theta_3 + \theta_4 \dots\dots \theta_n = 1$$

We compensate for each θ:

$$\theta_0 + k_1 p\, \theta_0 \left(\frac{p}{p^0}\right)^0 + k_1 p\, \theta_0 \left(\frac{p}{p^0}\right)^1 + k_1 p\, \theta_0 \left(\frac{p}{p^0}\right)^2 + k_1 p\, \theta_0 \left(\frac{p}{p^0}\right)^3 \dots\dots = 1$$

$$\theta_0 \left[\, 1 + k_1 p + k_1 p \left(\frac{p}{p^0}\right)^1 + k_1 p \left(\frac{p}{p^0}\right)^2 + k_1 p \left(\frac{p}{p^0}\right)^3 \dots\dots = 1\right.$$

$$\theta_0 \left[\, 1 + k_1 p \left\{ 1 + \left(\frac{p}{p^0}\right)^1 + \left(\frac{p}{p^0}\right)^2 + \left(\frac{p}{p^0}\right)^3 \right\} \dots\dots = 1\right.$$

mathematically when $(1 + x + x^2 + x^3 + x^4 \dots) = \dfrac{1}{(1-x)}$

Where $x = \dfrac{p}{p^0}$

$$1 + \left(\frac{p}{p^0}\right)^1 + \left(\frac{p}{p^0}\right)^2 + \left(\frac{p}{p^0}\right)^3 = \frac{1}{1 - \frac{p}{p^0}}$$

$$\theta_0 \left[\, 1 + k_1 p \left(\frac{1}{1 - \frac{p}{p^0}}\right) \right] = 1 \Rightarrow \theta_0 \left[\, 1 + \frac{k_1 p}{\left(1 - \frac{p}{p^0}\right)} \right] = 1$$

$$\theta_0 \left[\frac{(1-\frac{p}{p^0}) + k_1 p}{(1-\frac{p}{p^0})} \right] = 1$$

$$\left[\frac{(1-\frac{p}{p^0}) + k_1 p}{(1-\frac{p}{p^0})} \right] = \frac{1}{\theta_0}$$

$$\theta_o = \frac{1-\left(P/P_o \right)}{1-\left(P/P_o \right) + k_1 P} \qquad (12)$$

Let V_{tot} be the total number of molecules adsorbed by unit mass of adsorbent and V_m be the total number of surface sites occupied by the adsorbed molecules per unit mass of the adsorbent.

Further $V_m\theta_1$ is the number of sites carrying one molecule thick, $V_m\theta_2$ is the number of sites carrying two molecules thick and so on and hence,

$$\therefore V_{tot} = V_m \left(\theta_1 + 2\theta_2 + 3\theta_3 + \ldots \right) \qquad (13)$$

Substituting θ_1, θ_2, θ_3 values in equation (13), we have

$$\therefore V_{tot} = V_m \left[k_1 P \theta_o \left\{ 1 + 2\left(P/P_o \right) + 3\left(P/P_o \right)^2 + \ldots \right\} \right] \qquad (14)$$

$$V_{tot} = V_m \left[k_1 P \theta_o \frac{1}{\left(1 - \frac{P}{P_o} \right)^2} \right] \qquad \therefore 1 + 2x + 3x + \ldots = \frac{1}{(1-x)^2} \qquad (15)$$

Substituting θ_o,in (15), we get

$$V_{tot} = V_m \left[\frac{k_1 P}{\left(1 - \frac{P}{P_o} \right)^2} \times \frac{\left(1 - \frac{P}{P_o} \right)}{\left(1 - \frac{P}{P_o} \right) + k_1 P} \right] \qquad (16)$$

$$V_{tot} = V_m \left[\frac{k_1 P}{\left(1 - \frac{P}{P_o}\right)\left(1 - \frac{P}{P_o}\right) + k_1 P} \right] \qquad (17)$$

Expansion of *P* in terms of partial pressure can be written as:

$$P = P \times \frac{P_o}{P_o} = P_o \left({}^{P}\!/_{P_o} \right) = \frac{1}{k_L} \left({}^{P}\!/_{P_o} \right) \qquad \therefore k_L = {}^{1}\!/_{P_o}$$

Replacing *P* by 1/k$_L$ (*P/P$_o$*) in equation (17), we get

$$V_{tot} = V_m \left[\frac{\left({}^{k_1}\!/_{k_L} \right)\left({}^{P}\!/_{P_o} \right)}{\left(1 - \frac{P}{P_o}\right)\left(1 - \frac{P}{P_o}\right) + \left({}^{k_1}\!/_{k_L} \right)\left({}^{P}\!/_{P_o} \right)} \right] \qquad (18)$$

$$V_{tot} = \left[\frac{V_m \, c \left({}^{P}\!/_{P_o} \right)}{\left(1 - \frac{P}{P_o}\right)\left[1 - \left({}^{P}\!/_{P_o} \right) + c \left({}^{P}\!/_{P_o} \right)\right]} \right] \quad \text{where } c = \left({}^{k_1}\!/_{k_L} \right) \qquad (19)$$

Equation (19) is the required equation for adsorption of gaseous molecules on adsorbent surface and it is known as BET adsorption equation for multi-molecular layer formation.

Determination of surface area covered using BET adsorption equation (Testing of BET adsorption equation)

- Let P/Po as x and hence BET equation may be represented as:

$$V_{tot} = \left[\frac{V_m\ cx}{(1-x)\left[1-x+cx\right]} \right] \qquad (20)$$

$$\frac{V_{tot}(1-x)}{x} = \left[\frac{V_m\ c}{1-x+cx} \right] \qquad (21)$$

$$\frac{x}{V_{tot}(1-x)} = \frac{1-x+cx}{V_m\ c}$$

$$\frac{x}{V_{tot}(1-x)} = \frac{1+x\left[-1+c\right]}{V_m\ c}$$

$$\frac{x}{V_{tot}(1-x)} = \frac{1}{V_m c} + \frac{x\left[c-1\right]}{V_m\ c}$$

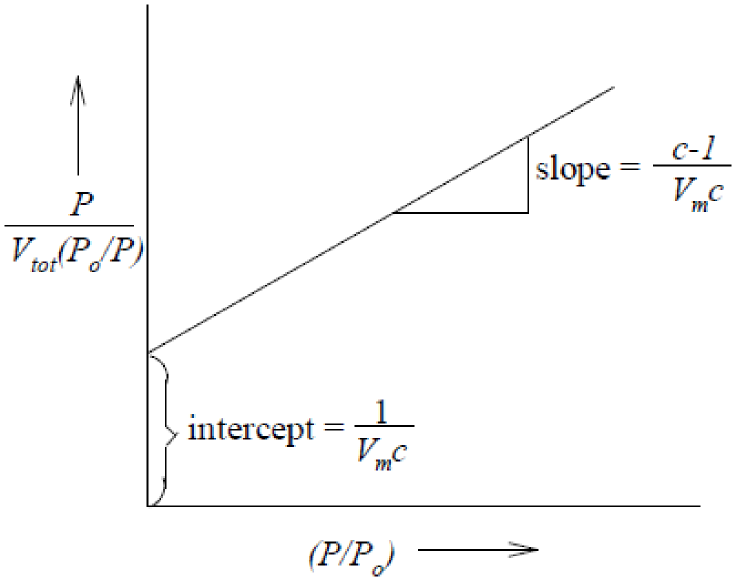
$$\frac{x}{V_{tot}(1-x)} = \frac{1}{V_m c} + \frac{x\left[c-1\right]}{V_m\ c}$$

$$\left({}^{P}\!/_{P_o} \right) \frac{1}{V_{tot}\dfrac{(P_o-P)}{P}} = \frac{1}{V_m c} + \frac{\left[c-1\right]}{V_m\ c}\left({}^{P}\!/_{P_o} \right)$$

$$\frac{P}{V_{tot}(P_o-P)} = \frac{1}{V_m c} + \frac{\left[c-1\right]}{V_m\ c}\left({}^{P}\!/_{P_o} \right) \qquad (22)$$

Equation (22) is the BET Equation, Where P/Po is the relative pressure of the adsorbate; Vtot is the total number of gas molecules adsorbed; Vm is the total number of sites occupied by adsorbed molecules per unit mass of the adsorbent; and c is the characteristic constant which depends on nature of adsorbent and adsorbate.

If we plot $\frac{P}{V_{tot}(P_o - P)}$ versus $\left(P/P_o\right)$, we get slope $= \frac{[c-1]}{V_m\ c}$ and intercept $= \frac{1}{V_m c}$.



Adding slope and intercept, we get:

$$\text{slope} + \text{intercept} = \frac{[c-1]}{V_m\ c} + \frac{1}{V_m c}$$

$$\text{slope} + \text{intercept} = \frac{c-1+1}{V_m\ c}$$

$$V_m = \frac{1}{\text{slope} + \text{intercet}}$$

At standard temperature and pressure,

22.4 L will have = N_A molecules

$$V_m \text{ L will have} = \frac{V_m N_A}{22.4} \qquad (23)$$

Let one molecule of an adsorbate occupies an surface area = σ

Total number of molecules present in one volume will occupy surface area,

$$S = \frac{\sigma V_m N_A}{22.4}$$

Physical Chemistry/ kinetics chemistry

(2025-2026)

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Lecture 9 28 / 01/ 2026

Kinetics of Polymerisation

1. KINETICS OF FREE RADICAL POLYMERISATION

Kinetics of free radical polymerization involves three steps:

Step 1: Chain Initiation

It consists of two steps: In the first step, the initiator I dissociates into two molecules of primary free radicals (R•);

$$I \xrightarrow{k_d} 2R^\bullet$$

The rate of dissociation of the initiator, I is given by:

$$\frac{-d[I]}{dt} = k_d[I] \quad \ldots(1)$$

Or) the rate of formation of free radical is given as:

$$\frac{+d[R^\bullet]}{dt} = 2k_d[I] \quad \ldots(2)$$

Since the reaction takes place by two events.

In the second step, the primary free radical combines with the first monomer M to give chain initiating carrier.

$$R^\bullet + M \xrightarrow{k_i} M^\bullet$$

Further, the rate of formation of chain carrier is given by:

$$\frac{d[M^\bullet]}{dt} = k_I[R^\bullet][M] \quad \ldots(3)$$

Applying steady state approximation (SSA) with respect to R•, we have:

The rate of formation of R• = The rate of conversion of R• into M•

$$2k_d[I] = k_I[R^\bullet][M]$$

$$\frac{d[M^\bullet]}{dt} = 2k_d[I]$$

Therefore, the rate of chain initiation is given as:

$$R_i = 2k_d[I] \quad \ldots(4)$$

Step 2: Chain Propagation

It involves the growth of chain initiating carrier by successive addition of large number of monomers one by one.

$$M^\bullet + M \overset{k_p}{\rightarrow} M_1^\bullet$$

$$M_1^\bullet + M \overset{k_p}{\rightarrow} M_2^\bullet$$

$$M_2^\bullet + M \overset{k_p}{\rightarrow} M_3^\bullet$$

$$M^\bullet + M \overset{k_p}{\rightarrow} M_n^\bullet$$

Since the chain growth is independent of chain length, all these steps take place with a rate constant of k_p.

Therefore, the rate of propagation is given as:

$$R_p = k_p[M^\bullet][M] \quad \ldots(5)$$

Step 3: Chain Termination

It takes place by mutual combination of chain carriers, and it proceeds with the rate constant, k_t.

$$M^\bullet + M^\bullet \overset{k_t}{\rightarrow} P$$

Therefore, the rate of chain termination is given as:

$$R_t = 2k_t[M^\bullet]^2 \quad \ldots(6)$$

In any number of terminations, two number of chain carriers are involved.

Applying SSA to M• in order to evaluate in terms of measurable quantities, we have:

Rate of formation of M• = Rate of termination of M•

$$R_i = R_t$$

$$2k_d[I] = 2k_t\,[M^\bullet]^2$$

$$[M^\bullet]^2 = \frac{k_d[I]}{k_t}$$

$$[M^\bullet] = \left(\frac{k_d}{k_t}\right)^{\frac{1}{2}}[I]^{\frac{1}{2}} \quad \ldots(7)$$

But, the rate of polymerisation depends upon the rate of propagation, and hence:

The rate of polymerisation =$[M\bullet][M]$

$$R_P = k_p\left(\frac{k_d}{k_t}\right)^{\frac{1}{2}}[I]^{\frac{1}{2}}[M]$$

(or)

$$R_P = k_p\left(\frac{k_d}{k_t}\right)^{\frac{1}{2}} f^*[I]^{\frac{1}{2}}[M] \quad \ldots(8)$$

2. KINETICS OF ANIONIC POLYMERISATION

The monomers like vinyl chloride, acrylonitrile follow anionic polymerisation. The Lewis base like $NaNH_2$ or KNH_2 acts as the catalyst. The kinetics of anionic polymerisation also involves three steps.

Step 1: Chain Initiation

In the first step Lewis base dissociates to give the active species. The active species in turn attacks the the first monomer to give a carbanion chain carrier.

$$\underset{\text{Lewis base}}{AB} \rightarrow \underbrace{A^+ + B^-}_{\text{Active species}}$$

$$B^- + M \xrightarrow{k_i} BM^-$$

Where, BM^- is a carbanion chain carrier.

Therefore, the rate of initiation is given by:

$$R_i = k_i[B^-]\,[M] \quad \ldots(1)$$

Step 2: Chain Propagation

It consists of the growth of anionic chain carrier by successive addition of large number of monomers one by one.

$$M^- + M \rightarrow M - M^-$$
$$M - M^- + M \rightarrow M - M - M^-$$
$$M - M - M^- + M \rightarrow M - M - M - M^-$$

(or)

$$M_n^- + M \overset{k_p}{\rightarrow} M_{n+1}^-$$

Therefore, the rate of propagation is given by:

$$R_p = k_p[M_n^-]\,[M] \quad \ldots(2)$$

Step 3: Chain Termination

The growing chain can be terminated by using excess of suitable solvent.

$$M_n^- + B \overset{k_t}{\rightarrow} M_n + B^-$$

Therefore, the rate of termination is given by:

$$R_t = k_t[M_n^-]\,[B] \quad \ldots(3)$$

Applying SSA to the intermediate species $□_{□}^{-}$, we have:

The rate of formation of $□_{□}^{-}$ = The rate of termination of $□_{□}^{-}$

$$k_i[B^-]\,[M] = k_t[M_n^-]\,[B]$$

$$[M_n^-] = \frac{k_i}{k_t}\frac{[B^-]}{[B]}[M] \quad \ldots(4)$$

We know that,

The rate of polymerisation = The rate of propagation

$$R_p = k_p[M_n^-]\,[M] \quad \ldots(5)$$

Substituting $[M_n^-]$ in equation (5), we get:

$$R_p = k_p\frac{k_i}{k_t}\frac{[B^-]}{[B]}\,[M]^2 \quad \ldots(6)$$

The kinetic chain length of polymers is defined as the average number of monomers reacting with active species to form a polymer from initiation to termination.

(or)

$$\text{The kinetic chain length} = \frac{\textbf{Rate of polymerisation}}{\textbf{Rate of initiation}}$$

$$\boldsymbol{KCL = \frac{k_p \frac{k_i}{k_t} \frac{[B^-]}{[B]} [M]^2}{k_i [B^-]\, [M]}}$$

$$\boldsymbol{KCL = \frac{k_i}{k_t} \frac{[M]}{[B]}}$$

3. KINETICS OF CATIONIC POLYMERISATION

The monomers like propylene, styrene follow anionic polymerisation. The Lewis acid like $AlCl_3$ or BF_3 acts as catalyst and water is used as co-catalyst. The kinetics of cationic polymerisation involves three steps.

Step 1: Chain Initiation

In the first step Lewis acid reacts with the cocatalyst to give the active species. The active species in turn attacks the first monomer to give a carbonium ion chain carrier.

$$\underset{\text{Lewis acid}}{\boldsymbol{A}} + \underset{\text{Co-catalyst}}{\boldsymbol{RH}} \overset{\boldsymbol{k}}{\rightarrow} \underset{\text{Active species}}{\boldsymbol{H^+ - AR^-}}$$

$$\boldsymbol{H^+ - AR^- + M \overset{k_i}{\rightarrow} HM^+ - AR^-}$$

Where, $\boldsymbol{HM^+ - AR^-}$ is a carbonium ion chain carrier.

Therefore, the rate of initiation is given by:

$$\boldsymbol{R_i = k_i [H^+ - AR^-]\, [M]}$$

(or)

$$\boldsymbol{R_i = k_i k [A]\, [RH][M]} \quad \dots(\mathbf{1})$$

Step 2: Chain Propagation

It consists of the growth of cationic chain carrier by successive addition of large number of monomers one by one.

$$HM^+ - AR^- + M \to H - M - M^+ - AR^-$$

$$H - M - M^+ + M \to H - M - M - M^+ - AR^-$$

(or)

$$M_n^+ - AR^- + M \xrightarrow{k_p} M_{n+1}^+ - AR^-$$

Therefore, the rate of propagation is given by:

$$R_p = k_p[M_n^+ - AR^-]\,[M] \quad \ldots(2)$$

Step 3: Chain Termination

It involves the transfer of H^+ ion from the end of growing chain to AR^-.

$$M_n^+ - AR^- \xrightarrow{k_t} M_n + H^+AR^-$$

Therefore, the rate of termination is given by:

$$R_t = k_t[M_n^+ - AR^-] \quad \ldots(3)$$

Applying SSA to the intermediate species $M_n^+ - AR^-$, we have:

The rate of formation of $M_n^+ - AR^-$ = The rate of termination of $M_n^+ - AR^-$

$$k_i k[A]\,[RH][M] \quad = k_t[M_n^+ - AR^-]$$

$$[M_n^+ - AR^-] = \frac{kk_i}{k_t}[A]\,[RH][M] \quad \ldots(4)$$

We know that,

The rate of polymerisation = The rate of propagation

$$R_p = k_p[M_n^+ - AR^-]\,[M] \quad \ldots(5)$$

Substituting $M_n^+ - AR^-$ in equation (5), we get:

$$R_p = k_p\frac{kk_i}{k_t}[A]\,[RH][M]^2 \quad \ldots(6)$$

The kinetic chain length of polymers is defined as the average number of monomers reacting with active species to form a polymer from initiation to termination.

(or)

$$\text{The kinetic chain length} = \frac{\textit{Rate of polymerisation}}{\textit{Rate of initiation}}$$

$$KCL = \frac{k_p \frac{kk_i}{k_t}[A]\,[RH][M]^2}{k_i k[A]\,[RH][M]}$$

$$KCL = \frac{k_p}{k_t}[M]$$

Kinetics of Enzyme Catalysis (Michaelis – Menten Equation)

⇒ The general mechanism for the kinetics of enzyme-catalysed reaction was first proposed by L.Michaelis and Mary Menten in 1913.

⇒ The mode of action of an enzyme in Michaelis-Menten mechanism is as follows:

(i) Formation of the Enzyme-substrate complex.

$$E + S \underset{k_2}{\overset{k_1}{\Leftrightarrow}} ES$$

$$\textit{Forward rate} = k_1[E][S]$$

$$\textit{Backward rate} = k_2[ES]$$

(ii) Decomposition of the complex.

$$ES \xrightarrow{k_3} P + E$$

Where *E* is the enzyme, *S* is the substrate, *ES* is the enzyme-substrate complex, (intermediate activated complex) and *P* is the end product.

⇒ The rate of formation of the product is given by:

$$\frac{d[P]}{dt} = r = k_3[ES] \qquad \ldots(1)$$

⇒ In order to solve the equation (1), it is necessary to know the concentration of *ES*. This can be calculated through steady-state principle.

⇒ According to this "when a short-lived reaction intermediate exists at low concentration in a system, the rate of formation of intermediate can be considered to be equal to its rate of disappearance".

⇒ Applying steady-state principle,

$$k_1[E][S] = k_2[ES] + k_3[ES]$$

$$k_1[E][S] = [ES](k_2 + k_3)$$

$$[ES] = \frac{k_1[E][S]}{(k_2 + k_3)} \qquad \ldots(2)$$

Since the enzyme exists either in free form *E*, or the combined form *ES*, the total concentration of the enzyme, E_o originally added can be obtained from the material balance equation.

$$[E_0] = [E] + [ES]$$

$$[E] = [E_0] - [ES] \qquad \ldots(3)$$

⇒ Inserting the value [*E*] in equation (2), we get

$$[ES] = \frac{k_1\{[E_0] - [ES]\}[S]}{(k_2 + k_3)}$$

$$(k_2 + k_3)[ES] = k_1[E_0][S] - k_1[ES][S]$$

$$(k_2 + k_3)[ES] + k_1[ES][S] = k_1[E_0][S]$$

$$[ES]\{(k_2 + k_3) + k_1[S]\} = k_1[E_0][S]$$

$$[ES] = \frac{k_1[E_0][S]}{k_1[S] + (k_2 + k_3)} \qquad \ldots(4)$$

⇒ Substituting [*ES*] in equation (1), we get:

$$\frac{d[P]}{dt} = r = \frac{k_3 k_1 [E_0][S]}{k_1[S] + (k_2 + k_3)} \qquad \ldots(5)$$

⇒ Dividing the numerator and denominator of equation (5) by k_1 gives:

$$\frac{d[P]}{dt} = r = \frac{k_3[E_0][S]}{[S] + \left(\frac{k_2 + k_3}{k_1}\right)}$$

$$r = \frac{k_3[E_0][S]}{[S] + k_m} \qquad \ldots(6)$$

where

$$k_m = \left(\frac{k_2 + k_3}{k_1}\right)$$

⇒ $\boldsymbol{k_m}$ is called Michaelis constant and *equation (6) is known as **Michaelis-Menten equation.***

Significance of k_m (Michaelis Constant)

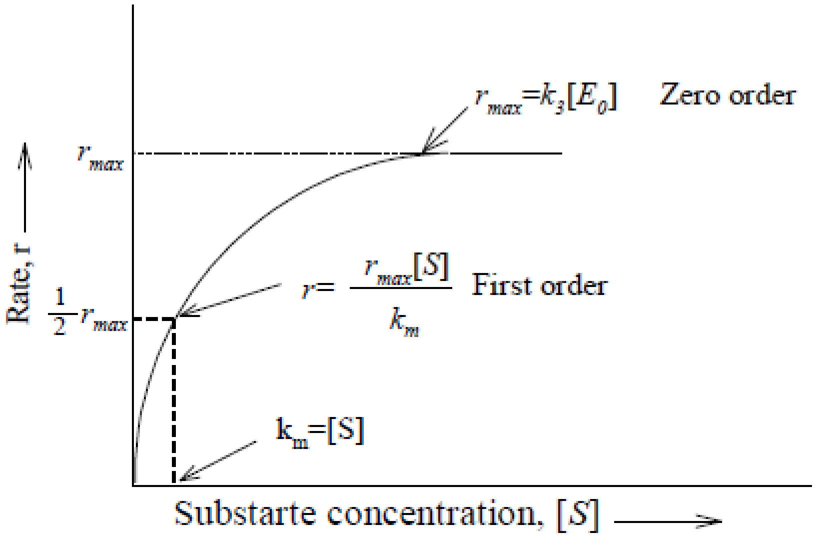
⇒ When all the enzyme has reacted with substrate at high concentration, the reaction will be going at maximum rate. No free enzyme will remain, so that $[E_o] = [ES]$. Hence from equation (1), we have

$$\frac{d[P]}{dt} = r_{\max} = k_3[E_0] \qquad \ldots(7)$$

where r_{max} is the maximum rate.

⇒ The Michaelis-Menten equation can now be written as:

$$r = \frac{r_{\max}[S]}{k_m + [S]} \qquad \therefore\ r_{\max} = k_3[E_o]$$



⇒ ***Case 1:*** If Michaelis constant, *km* is equal to substrate concentration, [*S*] i.e.: $k_m = [S]$, then

$$r = \frac{r_{\max}[S]}{[S]+[S]}$$

$$r = \frac{1}{2}r_{\max} \qquad \ldots(8)$$

⇒ The Michaelis constant is a measure of enzyme activity and can be shown to be equal to $(k_2 + k_3) / k_1$. It is also equal to the substrate concentration at one half the maximum rate.

⇒ ***Case 2:*** At low concentration of substrate, when $[S] << k_m$, then

$$r = \frac{k_3[E_0][S]}{k_m}$$

$$r = \frac{r_{\max}[S]}{k_m} \qquad \ldots(9)$$

⇒ So, the rate of the reaction will be of first order with respect to the substrate and enzyme.

⇒ ***Case 3:*** At high concentration of substrate, when $[S] >> k_m$**,** then

$$r = \frac{k_3[E_0][S]}{[S]}$$

$$r = k_3[E_0]$$

$$r = r_{\max} \qquad \ldots(10)$$

⇒ So, the rate of the reaction will be zero order with respect to substrate for a given amount of enzyme.

It is clearly understand that the reaction of an enzyme catalyzed reaction changes from first order to zero order as the substance concentration is increased. This is because each enzyme molecule has one or more active sites at which the substrate must be bound in order that the catalytic action may occur.

Lineweaver-Burke Plots (Determination of k_m)

⇒ Lineweaver-Burk Equation (Reciprocal form of Michaelis-Menten equation) is used to calculate Michaelis constant.

⇒ A plot of $\frac{1}{r}$ vs $\frac{1}{[S]}$ gives a straight line whose intercept is $1/r_{max}$ and whose slope is k_m/r_{max}. Hence Michaelis constant which is characteristic for an enzyme with a substrate can be determined

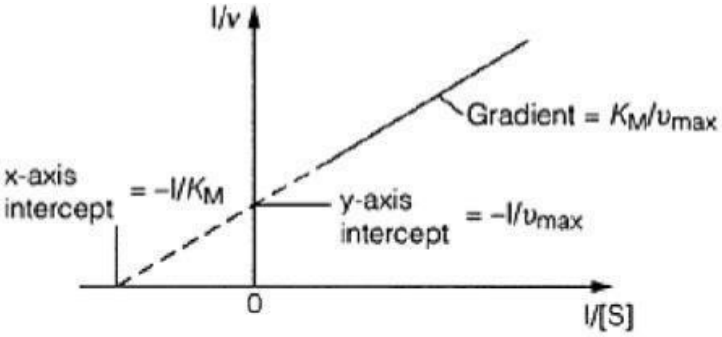


Figure is the Lineweaver-Burke plot for enzyme kinetics: The reciprocal of reaction rate(v) is plotted against the reciprocal of substrate concentrations[S] for experiments using the same total enzyme concentration

Turnover Number: The constant k_3 is called the turnover number of the enzyme. It is defined as “the ability of one molecule of enzyme to form the complex with number of molecules of substrate and to convert it into products”.