

Lecture 25 & 26 combined

We will continue to learn about “Chemical Kinetics”

Suggested book: Physical Chemistry by Ira Levine

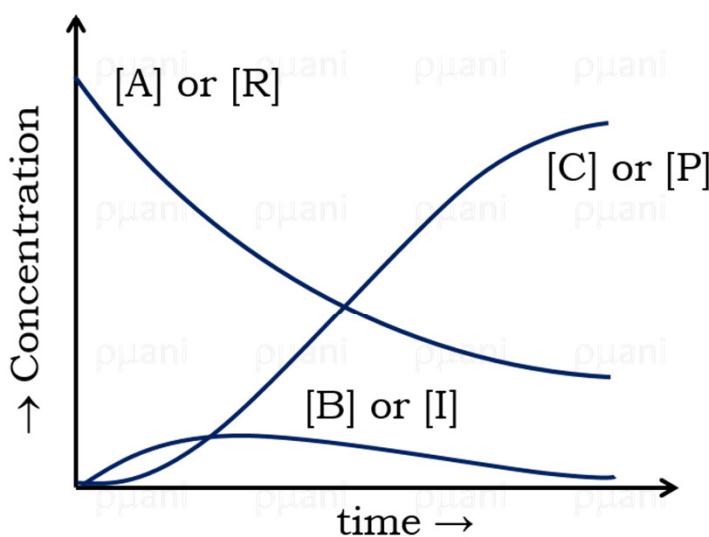
Steady State approximation:

In a multi-step reaction, many a time one or more intermediate species do appear. These intermediates are very (short lived and) reactive and therefore do not get accumulated in significant amount and they do not appear in overall equation.

Thus, $[I] \ll [R]$ and $[I] \ll [P]$ [where, R = reactant, I = intermediate, P = product]

We can assume that $[I]$ will increase starting at $t = 0$, then it will rise to maximum ($[I]_{\max}$) and then fall back to zero (as oscillations in concentration of a species during a reaction are very rare).

If $[I]$ remains small during a reaction, then $[I]_{\max}$ will be small compared to $[R]_{\max}$ and $[P]_{\max}$ and the curve will look like:



From the curve, except for the initial period (called induction period) where $[I]$ is increasing, the slope of curve for $[I]$ is much less than that for $[R]$ or $[P]$

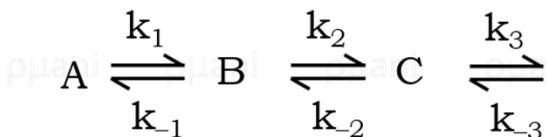
$$\text{i.e. } \frac{d[I]}{dt} \ll \frac{d[R]}{dt} \text{ and } \frac{d[I]}{dt} \ll \frac{d[P]}{dt}$$

Thus, it is therefore assumed that $\frac{d[I]}{dt} = 0$ for each of the reactive intermediate. This is a good approximation and known as Steady State or Stationary State approximation.

This assumes that rate of formation of I = rate of destruction of I so that a near constant steady state concentration is maintained.

"Rate determining step" approximation:

Let us assume the following reaction



consisting of one or more reversible reaction that stay close to equilibrium during most of the reaction, followed by a relatively slow rate-determining step which in turn is followed by one or more rapid reactions.

Assume here Step-2 i.e. $B \rightleftharpoons C$

is the rate-determining step (r.d.s.), if that is true then $k_{-1} \gg k_2$

This means B molecules will revert back to A rather than going in forward direction to C.

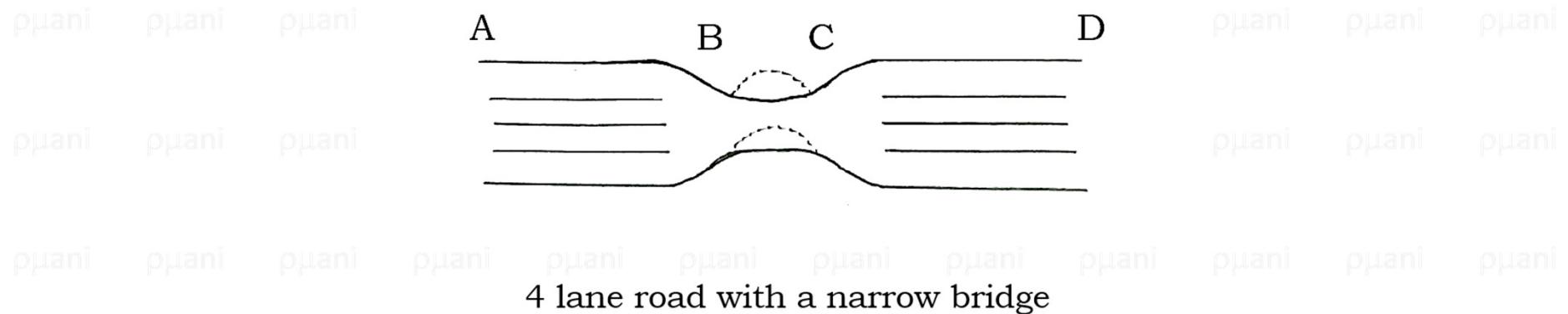
Thus, it ensures that Step-1, i.e. $A \rightleftharpoons B$

remains close to equilibrium.

We must have $k_3 \gg k_2$ and $k_3 \gg k_{-2}$ to ensure that Step-2 is the bottle neck and C molecules get converted to D rapidly.

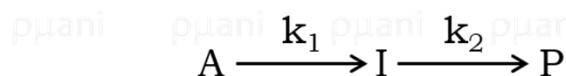
Thus overall rate is controlled by the 2nd step i.e. the rate-determining step

Rate determining step approximation:



Chemical reactions sometimes do follow above real-life examples.

Let us consider a consecutive elementary reaction



For the above reaction,

$$[I] = \left(\frac{k_1}{k_2 - k_1} \right) \times (e^{-k_1 \times t} - e^{-k_2 \times t}) \times [A]_0 \quad \dots \dots \dots \text{(i)}$$

$$\text{and } [P] = \left\{ 1 + \frac{(k_1 \times e^{-k_2 t}) - (k_2 \times e^{-k_1 t})}{(k_2 - k_1)} \right\} \times [A]_0 \quad \dots \dots \dots \text{(ii)}$$

Now, consider the case $k_2 \gg k_1$, this means whenever I is formed, it gets converted to P very fast.

Because, $e^{-k_2 \times t} \ll e^{-k_1 \times t}$, and $(k_2 - k_1) \approx k_2$

Then equation (ii) reduces to

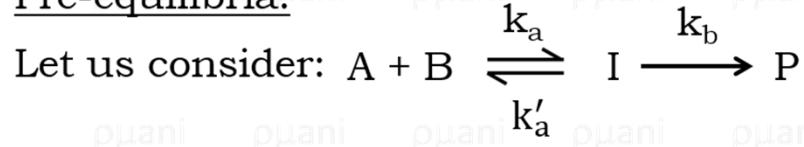
$$[P] \approx (1 - e^{-k_1 \times t}) \times [A]_0$$

Which shows that formation of final product P depends only on the smaller rate constant. That is, rate of formation of P depends on the rate at which I is formed and not on the rate at which I gets converted to P.

This $A \rightarrow I$ step is said to be rate determining step.

In general, rate determining step is the one with smallest rate constant.

Pre-equilibria:



Here the intermediate is in equilibrium with the reactants before going to the product.

A pre-equilibrium arises when rate of formation of intermediate and its decay back to reactants are much faster than the rate of formation of product.

i.e. when $k'_a \gg k_b$ (but not when $k_b \gg k'_a$)

As we assume A, B, I are in equilibrium

$$\text{So, } k = \frac{[I]}{[A][B]} \text{ and } k = \frac{k_a}{k'_a}$$

We also assume that rate of formation of P from I is too slow to affect the maintenance of the pre-equilibrium.

The rate of formation of P can be written as

$$\frac{d[P]}{dt} = k_b [I] = k_b \times k \times [A] \times [B]$$

This rate law has the form of a second order rate law with a composite rate constant.

$$\boxed{\frac{d[P]}{dt} = k'' \times [A] \times [B]} \text{ where } k'' = k_b \times k = k_b \times \frac{k_a}{k'_a}$$

When rate of formation of product is not that slow, then

$$\frac{d[P]}{dt} = k_b \times [I]$$

$$\frac{d[I]}{dt} = k_a \times [A] \times [B] - k'_a \times [I] - k_b \times [I]$$

$$\frac{d[I]}{dt} \approx 0 \text{ i.e. when } k_b \text{ is greater than } k_a \text{ or } k'_a$$

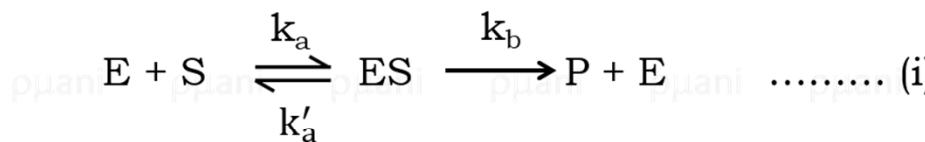
$$\Rightarrow [I] \approx \frac{k_a \times [A] \times [B]}{k'_a + k_b}$$

Thus,
$$\frac{d[P]}{dt} = k_b \times \frac{k_a \times [A] \times [B]}{k'_a + k_b}$$

Enzyme Kinetics:

An enzyme (E) is supposed to form a complex with substrate (S) and the complex (ES) gets converted to product (P) and enzyme (E).

Thus the overall reaction looks like



$$\text{Thus, } [ES] = \frac{k_a \times [E] \times [S]}{k'_a + k_b} \quad \dots \dots \dots \text{(ii)}$$

(where [E] and [S] are concentrations of free enzyme and substrate respectively)

Suppose $[E]_0$ is the total concentration of enzyme, then

$$[E]_0 = [E] + [ES] \quad \dots \dots \dots \text{(iii)}$$

Since very little concentration of enzyme is used, the free substrate concentration is almost the same as total substrate concentration and we can ignore the fact that [S] differs slightly from $[S]_{\text{total}}$

$$\text{Thus, } [ES] = \frac{k_a \times ([E]_0 - [ES]) \times [S]}{k'_a + k_b} \quad \dots \dots \dots \text{(iv)}$$

The above equation rearranges to,

$$[ES] = \frac{k_a \times [E]_0 \times [S]}{k'_a + k_b + (k_a \times [S])} \quad \dots \dots \dots \text{(v)}$$

The rate of formation of product is $k_b \times [ES]$

$$\text{where } k_b \times [ES] = \frac{k_b \times k_a \times [E]_0 \times [S]}{k'_a + k_b + (k_a \times [S])} = \frac{k_b \times [E]_0 \times [S]}{\left(\frac{k'_a + k_b}{k_a}\right) + [S]}$$

Rate of formation of product can also be written as

$$\frac{d[P]}{dt} = k \times [E]_0, \text{ where } k = \frac{k_b \times [S]}{\left(\frac{k'_a + k_b}{k_a}\right) + [S]} \dots\dots\dots (vi)$$

The parameter within the parenthesis i.e. $\left(\frac{k'_a + k_b}{k_a}\right)$ is known as **Michaelis constant (k_M)**

$$\text{where } k_M = \frac{k'_a + k_b}{k_a} \dots\dots\dots (vii-a)$$

$$\text{Thus, } k = \frac{k_b \times [S]}{k_M + [S]} \dots\dots\dots (vii-b)$$

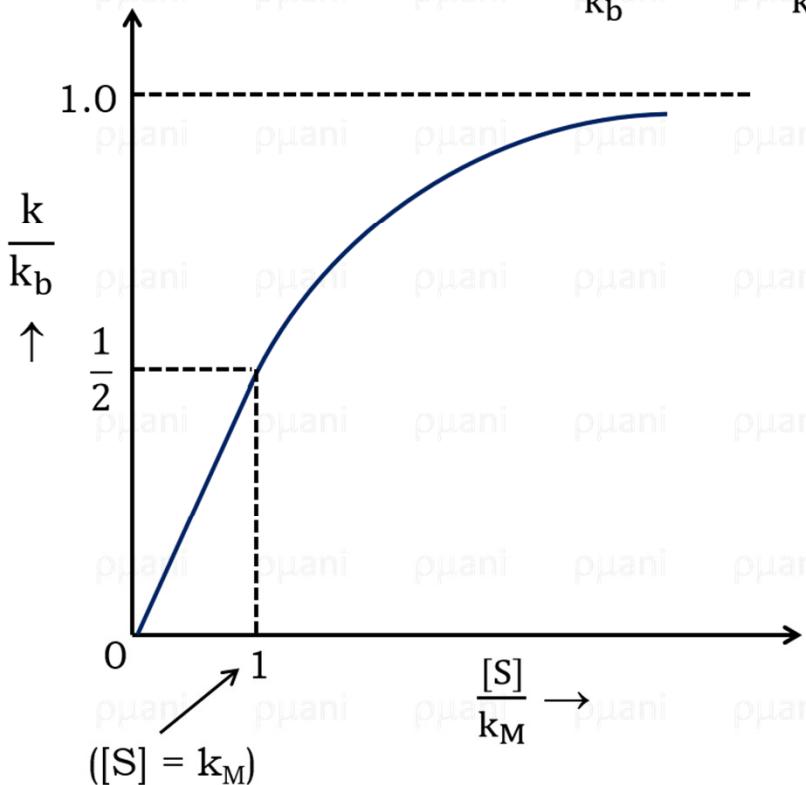
According to equation (vi), the rate of enzyme hydrolysis varies linearly with enzyme concentration.

When $[S] \gg k_M$ (in equation (vii b)) then equation (vi) reduces to $\frac{d[P]}{dt} = k_b \times [E]_0$ and zero order in $[S]$

From equation (vii-b), $\frac{k}{k_b} = \frac{p_{ua}[S]}{k_M + [S]} = \frac{\frac{[S]}{k_M}}{1 + \frac{[S]}{k_M}}$

In simple terms, it is of the general form, $y = \frac{x}{1+x}$ where $y = \frac{k}{k_b}$ and $x = \frac{[S]}{k_M}$

Now if we plot y vs. x i.e. $\frac{k}{k_b}$ against $\frac{[S]}{k_M}$, it yields the following plot:



Turnover number of enzyme varies from 10^{-2} to 10^{-6} molecules per second.

Typical values of $[E] \approx 10^{-9} \text{ mol dm}^{-3}$
 $[S] = 10^{-5} \text{ mol dm}^{-3}$

Rate of formation of product varies linearly with $[E]_0$ but in a complicated manner with $[S]$

The result means that under these conditions, rate is constant. There is so much [S] is present that it remains at effectively same concentration even though product is being formed.

Rate of formation of product is a maximum and ($k_b \times [E]_0$) is called maximum velocity of enzyme hydrolysis, k_b is termed as turnover number. (When $[S] \gg k_M$) ($\frac{d[P]}{dt} = \frac{k_b \times [S] \times [E]_0}{k_M + [S]}$)

When so little S is present that $[S] \ll k_M$, then the rate of formation of product is (using equation (vi))

$$\frac{d[P]}{dt} = \frac{k_b}{k_M} \times [E]_0 \times [S] \quad \dots \dots \text{(viii)}$$

Now the rate is proportional to both $[E]_0$ and $[S]$

From equation (viib), i.e.

$$k = \frac{k_b \times [S]}{k_M + [S]}$$

$$\Rightarrow \frac{1}{k} = \frac{k_M}{k_b \times [S]} + \frac{[S]}{k_b \times [S]}$$

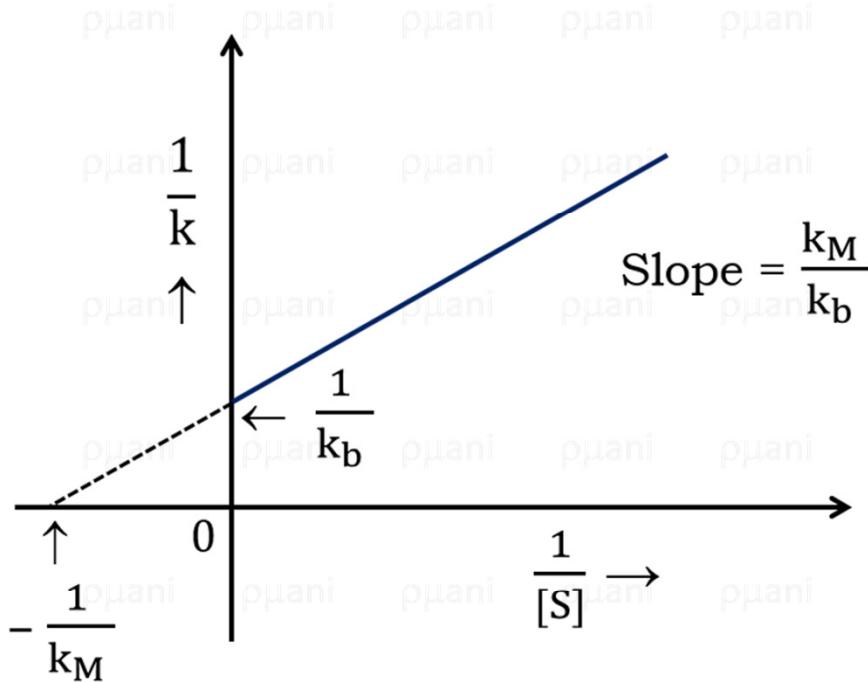
$$\Rightarrow \boxed{\frac{1}{k} = \frac{1}{k_b} + \frac{k_M}{k_b \times [S]}} \quad \dots \dots \text{(ix)}$$

See JACS 1934, 56, 658-666

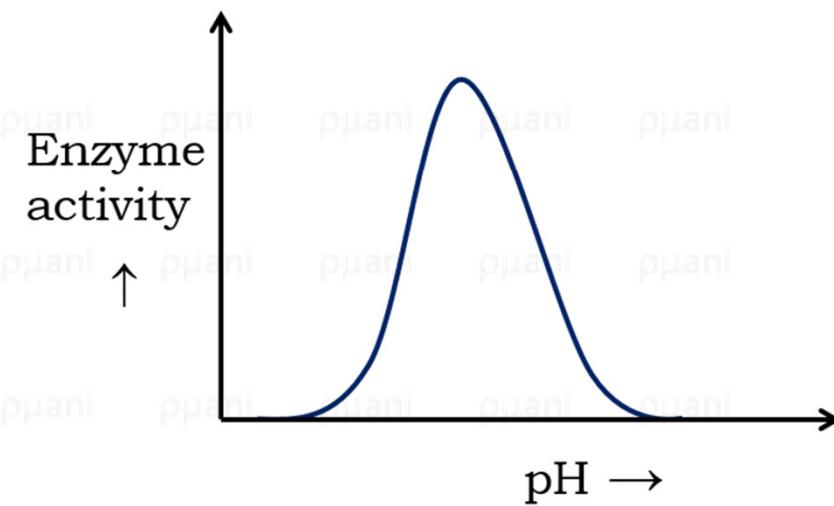
Hence a double reciprocal plot (Lineweaver-Burk plot) of $\frac{1}{k}$ against $\frac{1}{[S]}$ will give an intercept of $(\frac{1}{k_b})$ and from slope k_M will be obtained (provided k_b is known from intercept)

However, the plot can't give the individual values of k_a and k'_a that appear in k_M

Lineweaver - Burk plot



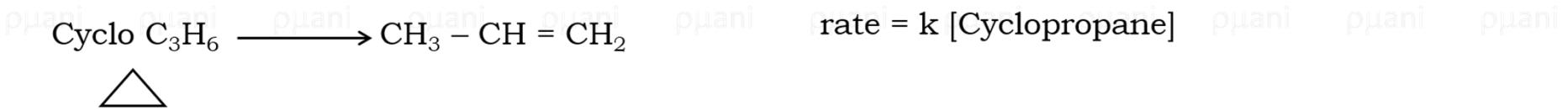
Enzyme activity with pH variation



Q. Assume the mechanism to be $\text{E} + \text{S} \rightleftharpoons \text{ES} \rightleftharpoons \text{E} + \text{P}$ or $\text{E} + \text{S} \rightleftharpoons \text{ES} \rightleftharpoons \text{EP} \longrightarrow \text{E} + \text{P}$
and then find out all rate related parameters.

Uni-molecular reactions:

A number of chemical reactions (gas-phase) follow first order rate kinetics. For example, isomerisation of cyclopropane.

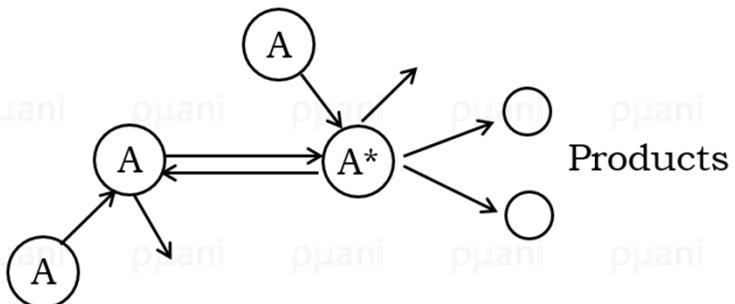


The problem with the interpretation of first order rate laws is that presumably one molecule acquires sufficient energy to react as a result of its collisions with other molecules. However, collisions are bimolecular, so the question that comes is that how can they result in first order rate law? **First order gas phase reactions** are called uni-molecular reaction as it involve an elementary molecular step in which the reactant molecule changes into product.

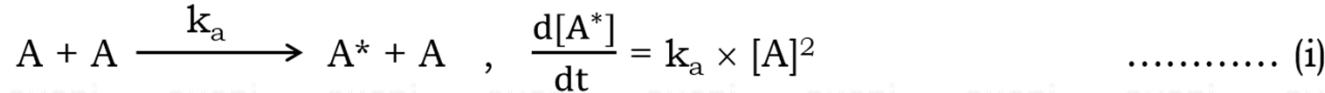
Lindemann-Hinshelwood mechanism:

(Lindemann discovered it in 1921 and Hinshelwood developed it further)

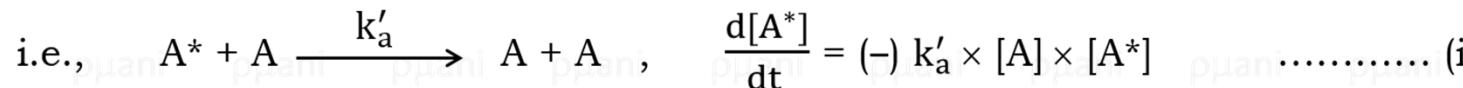
Lindemann and Hinshelwood could provide a model that could successfully explain the uni-molecular reaction.



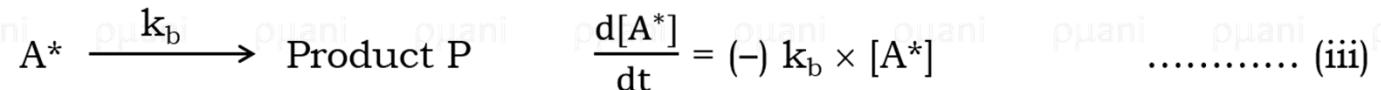
According to the model, it is supposed that a reactant molecule because of collision with another reactant molecule gets energetically excited



The energetic molecule may loose its excess energy because of collision with another molecule,



Alternatively because of collision, reactant may get converted to product.



If the uni-molecular step is slow enough to be rate-determining step, then the overall reaction will have first order kinetics, as observed. Applying steady state approximation to the net rate of formation of A^*

$$\frac{d[A^*]}{dt} = k_a \times [A]^2 - k'_a \times [A] \times [A^*] - k_b \times [A^*] \simeq 0 \quad \dots \dots \dots \text{(iv)}$$

$$\Rightarrow [A^*] = \frac{k_a \times [A]^2}{k'_a \times [A] + k_b} \quad \dots \dots \dots \text{(v)}$$

Rate law for the formation of product is

$$\frac{d[P]}{dt} = k_b \times [A^*] = \frac{k_a \times k_b \times [A]^2}{k'_a \times [A] + k_b} \quad \dots \dots \dots \text{(vi)}$$

At this state, **rate law is not of first order.**

Condition – I

However, if the rate of deactivation by $A^* - A$ collision is much greater than the rate of uni-molecular decay in the sense that $(k'_a \times [A^*] \times [A]) \gg (k_b \times [A^*])$ i.e. $(k'_a \times [A]) \gg k_b$, then from equation (vi) we get,

$$\frac{d[P]}{dt} = \frac{k_a \times k_b \times [A]^2}{k'_a \times [A]} = \frac{k_a \times k_b}{k'_a} \times [A] = k \times [A] \quad \dots \dots \dots \text{(vii)}$$

where $k = \frac{k_a \times k_b}{k'_a}$

Equation (vii) is a **first order rate law**.

Condition – II

Lindemann-Hinshelwood mechanism can be tested because it predicts that as the concentration of A is reduced then the reaction should switch to overall second order kinetics.

Thus, when $(k'_a \times [A]) \ll k_b$ then equation (vi) becomes

$$\frac{d[P]}{dt} \approx \frac{k_a \times k_b \times [A]^2}{k_b} = k_a \times [A]^2 \quad \dots \dots \dots \text{(viii)}$$

The physical reason for the change of order is that at low pressure, the rate-determining step is the bi-molecular formation of A^* .

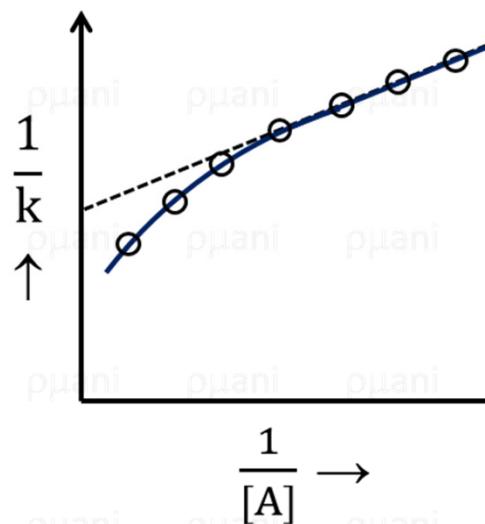
Equation (vi) can be written as $\frac{d[P]}{dt} = k \times [A]$ where $k = \frac{k_a \times k_b \times [A]}{k'_a \times [A] + k_b} \quad \dots \dots \dots \text{(ix)}$

$$\Rightarrow \frac{1}{k} = \frac{k'_a}{k_a \times k_b} + \frac{1}{k_a \times [A]} \quad \dots \dots \dots \text{(x)}$$

Thus, a test of the theory would be to plot $\frac{1}{k}$ vs. $\frac{1}{[A]}$.

According to equation (x) the plot should be a linear one.

A typical graph is shown below:



The curve at low $\frac{1}{[A]}$ value shows a clear curvature instead of a linear nature.

Thus at high $\frac{1}{[A]}$ value (i.e. low concentration of A) the curve is linear whereas for low $\frac{1}{[A]}$ (i.e. high concentration of A) curvature appears.

Thus L-H mechanism agrees in general with the switch of order of uni-molecular reaction, however, it does not agree in detail.

Activation energy of a composite reaction:

Generally the rate of each step of a complex reaction follow Arrhenius behaviour. But what about composite reaction?

To answer this question, we consider high pressure limit of the Lindemann-Hinshelwood mechanism as expressed in equation (vii), i.e. $k = \frac{k_a \times k_b}{k'_a}$ (under high pressure limit)

$$\begin{aligned}
 &= \frac{\left[A(a) \times e^{-\frac{E_a(a)}{RT}} \right] \times \left[A(b) \times e^{-\frac{E_a(b)}{RT}} \right]}{\left[A'(a) \times e^{-\frac{E'_a(a)}{RT}} \right]} \\
 &= \frac{A(a) \times A(b)}{A'(a)} \times e^{-\frac{[E_a(a) + E_a(b) - E'_a(a)]}{RT}} \quad \dots\dots\dots (xi)
 \end{aligned}$$

That is the **composite rate constant 'k'** has an Arrhenius like form with an activation energy (E_a)

$$E_a = E_a(a) + E_a(b) - E'_a(a) \quad \dots\dots\dots (xii)$$

From equation (xii) two cases may arise,

- When $[E_a(a) + E_a(b)] > E'_a(a)$, then activation energy is (+)ve and 'k' will increase with increase in temperature.
- When $[E_a(a) + E_a(b)] < E'_a(a)$, then activation energy is (-)ve and rate will decrease with increase in temperature. This means that the reverse reaction (corresponding to deactivation of A^*) is so sensitive to temperature that its rate increases sharply as the temperature is raised and depletes the steady state concentration of A^* .

