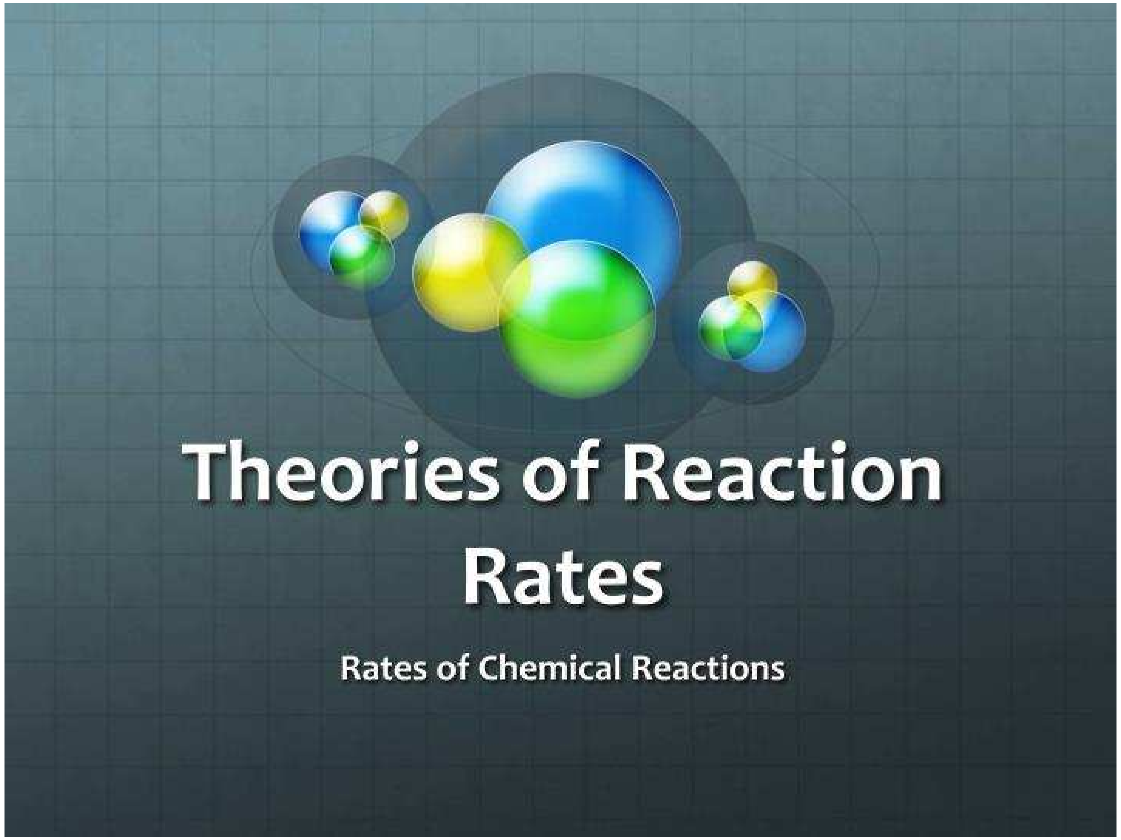

Theories of Reaction Rates

Rates of Chemical Reactions

PART-II

By-

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2) Transition State Theory:

The **transition state** or **Activated complex theory** was developed by ***Henry Erying*** (1935). This theory is also called the **Absolute rate theory.**

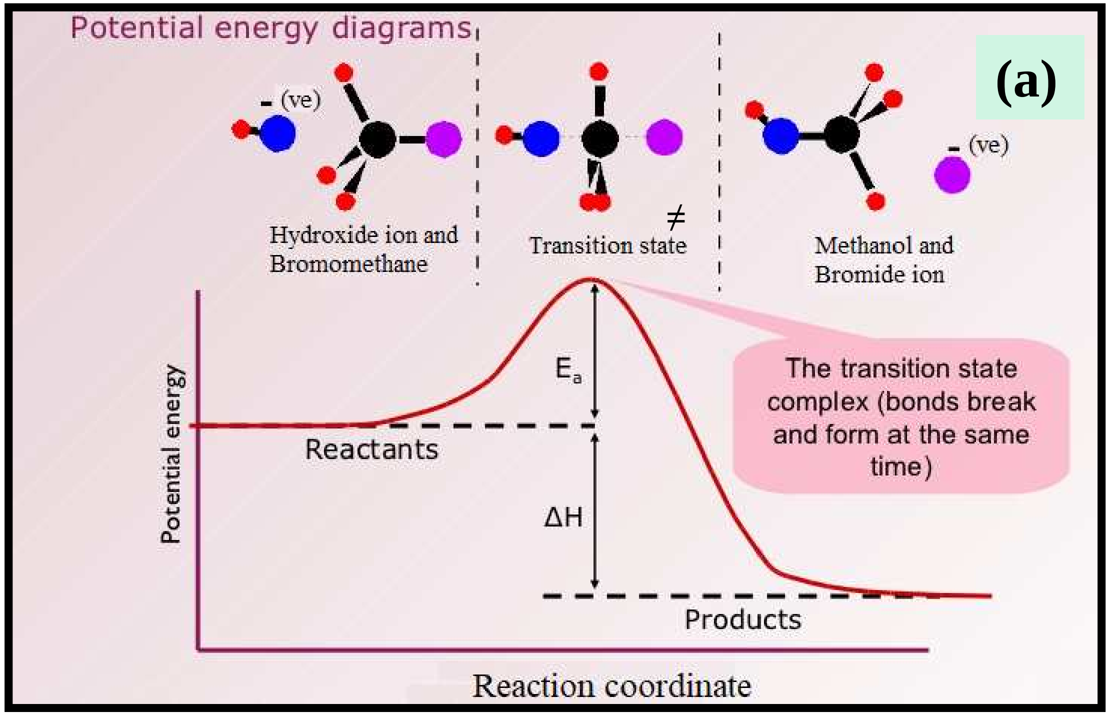

Potential energy diagrams
(a)
- (ve)
Hydroxide ion and Bromomethane
≠
Transition state
Methanol and Bromide ion
- (ve)
Potential energy
E_a
Reactants
ΔH
Products
The transition state complex (bonds break and form at the same time)
Reaction coordinate

Fig.(a)- *Formation of product via the formation of an activated complex or transition state.*

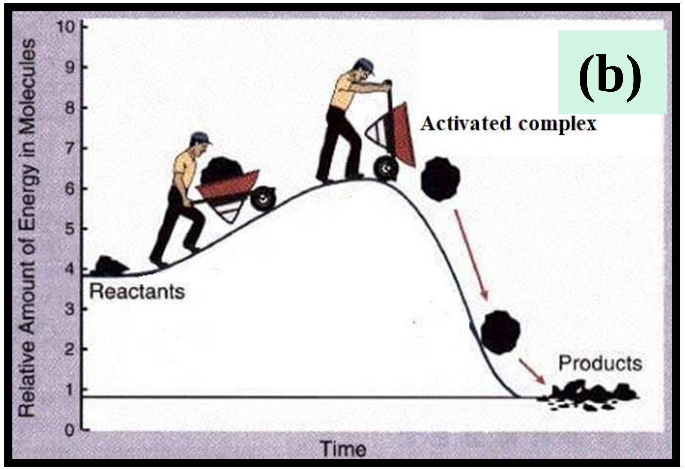

(b)
Relative Amount of Energy in Molecules
10
9
8
7
6
5
4
3
2
1
0
Activated complex
Reactants
Products
Time

Fig.(b)- *Significance of activation energy.*

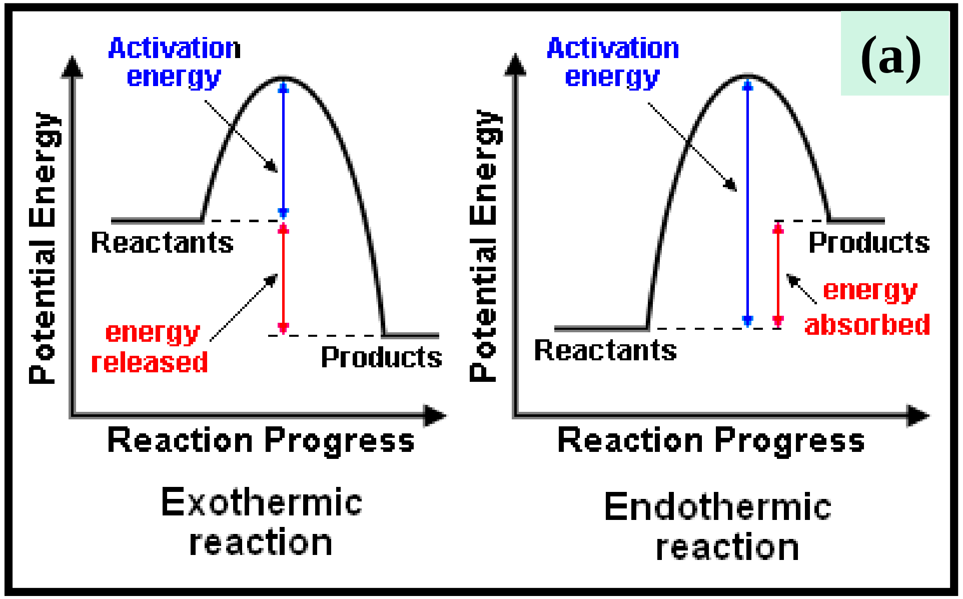

(a)
Potential Energy
Activation energy
Reactants
energy released
Products
Reaction Progress
Exothermic reaction
Potential Energy
Activation energy
Products
energy absorbed
Reactants
Reaction Progress
Endothermic reaction

Fig.- *General energy profile diagram for a reaction (exothermic and endo-thermic).*

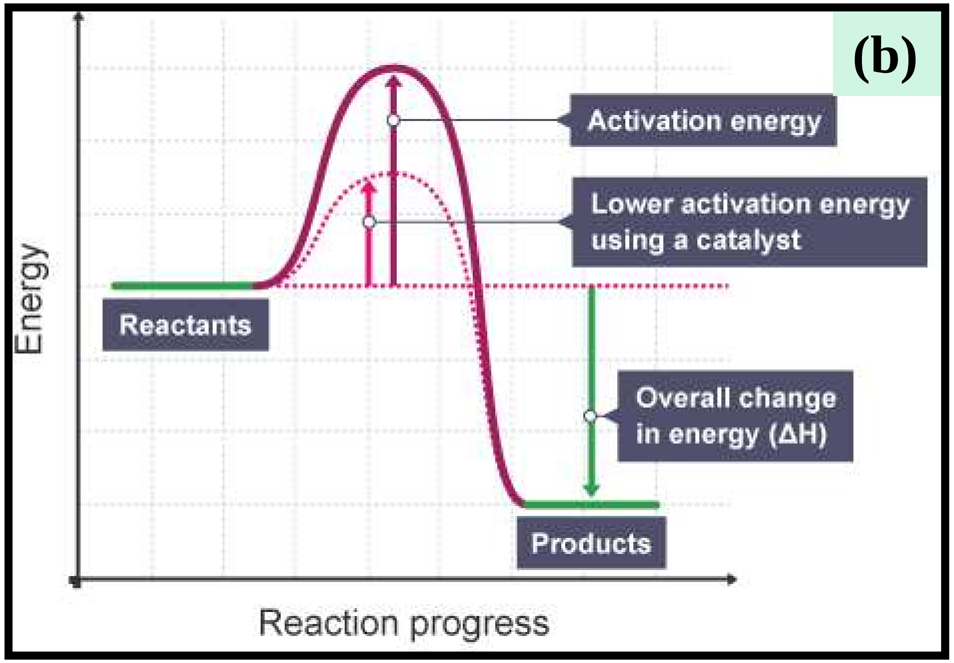

(b)
Energy
Activation energy
Lower activation energy using a catalyst
Reactants
Overall change in energy (ΔH)
Products
Reaction progress

Fig.- *Graphical explanation of effect of catalyst on activation energy.*

3) Lindeman’s Theory of Unimolecular Reaction

Proposed by ***Frederick Lindemann*** in 1922 and subsequently developed by ***Cyril Hinshelwood*** so also called as ***Lindemann-Hinshelwood theory,*** followed by ***Rice-Rampsberger-Kassel (RRK) Theory*** and ***Rice-Rampsberger-Kassel-Marcus (RRKM) Theory*****.**

•In 1922, Lindeman explained this anomaly by assuming that **there existed a time lag between activation and reaction of molecules.** During this time lag, the activated molecules could either react or be deactivated. Thus,

- $A + A \rightarrow A + A^*$ *activation* ...(1)
- $A + A^* \rightarrow A + A$ *deactivation* ...(2)
- $A^* \rightarrow$ products *reaction* ...(3)

•If the time lag is long, step (3) is slow, the reaction should follow first order kinetics. However, if *A* reacts as soon as formed, step (2) is the slow step, then the reaction should be second order.

In order to study the kinetics and mechanism of complex reaction we use two approximations:

1. The Equilibrium Approximation. Consider a reaction in which reactant R gives rise to product P through the formation of a series of consecutive intermediates I_1, I_2, I_3, ……, I_n, as follows:

$$R \xrightarrow{k_0} I_1 \xrightarrow{k_1} I_2 \xrightarrow{k_2} I_3 \xrightarrow{k_3} \cdots\cdots\cdots \xrightarrow{k_{n-1}} I_n \xrightarrow{k_n} P$$

The whole reaction sequence may be described in terms of a single reaction coordinate composing the coordinates of the individual steps, as illustrated in Fig. 8. The intermediates are supposed to be stable, occupying points on the energy valley.

In order to derive the rate equation for the reaction, we assume that a rate-determining step exists. *This rate-determining step is the slowest in a sequence of steps*. It is further assumed that all the steps preceding the rate-determining step are in equilibrium, that is,

$$R \overset{K_0}{\rightleftharpoons} I_1 \overset{K_1}{\rightleftharpoons} I_2 \overset{K_2}{\rightleftharpoons} \cdots\cdots \overset{K_{n-1}}{\rightleftharpoons} I_n \overset{K_n}{\rightleftharpoons} P$$

where the K_is are the various equilibrium constants.

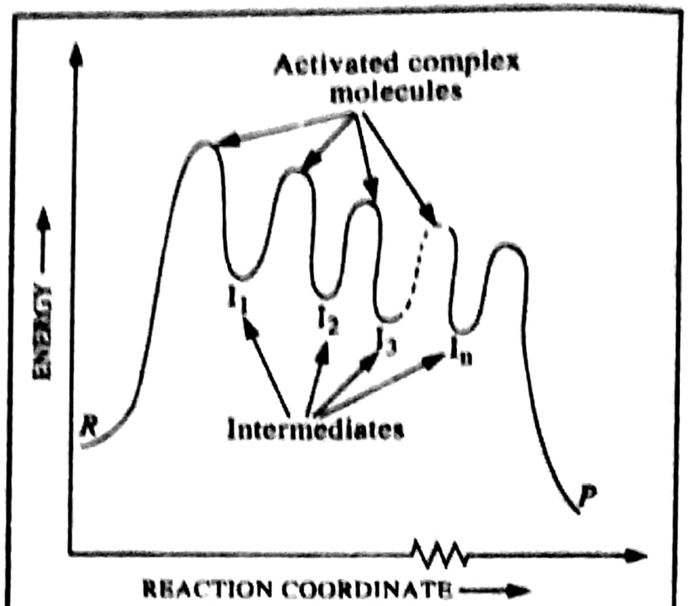


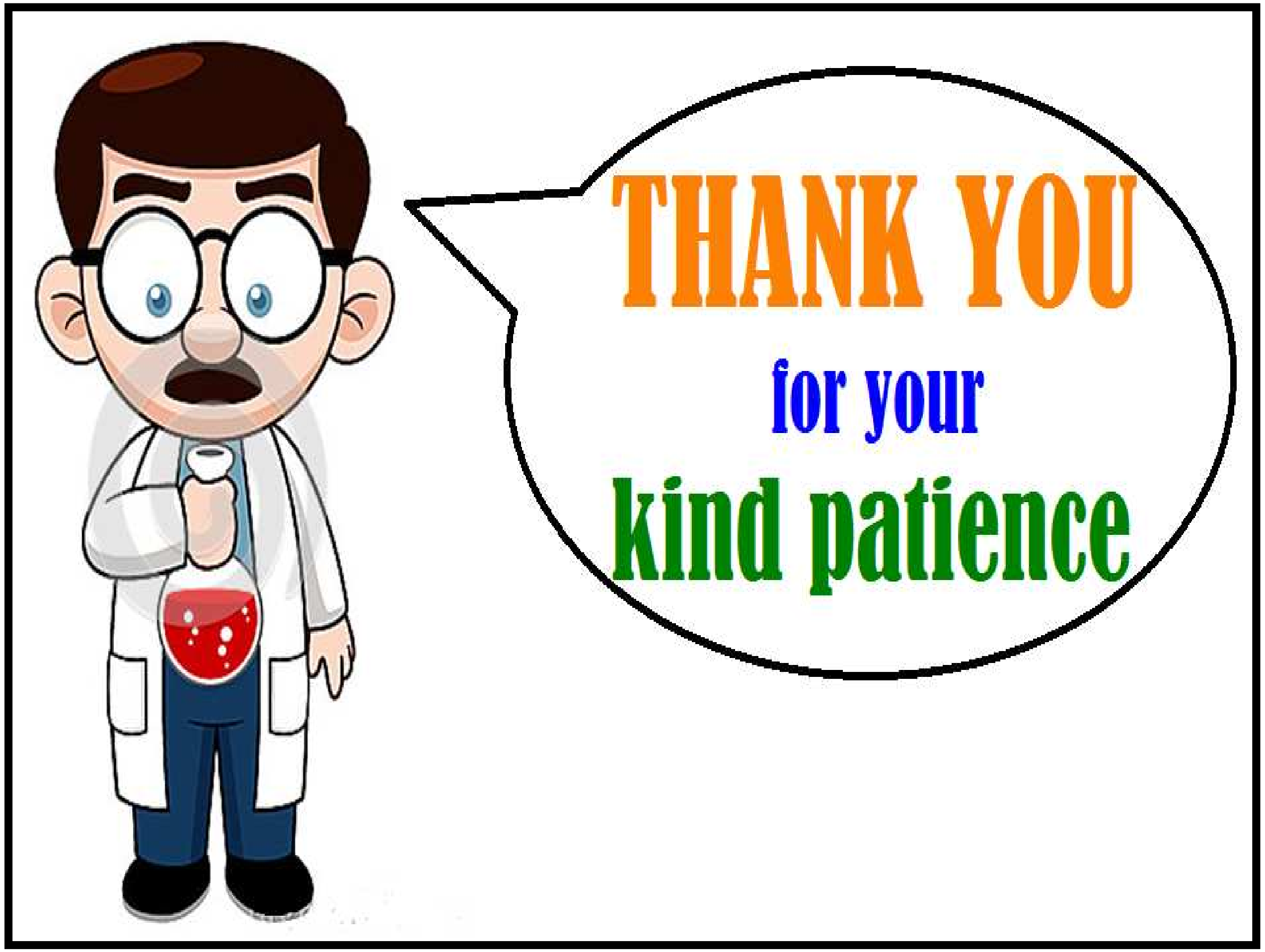
Fig. 8. Energy *versus* reaction coordinate profile for a complex reaction.

2. The Steady State Approximation. In a case where the reactions are investigated under such conditions that the slowest rate-determining step does not exist, one assumes the *steady state approximation* (*s.s.a*) for the transient, *i.e.*, short-lived, intermediate. In such a mechanism, as shown below

$$R \xrightarrow{k_0} I_1 \xrightarrow{k_1} I_2 \xrightarrow{k_2} I_3 \xrightarrow{k_3} \cdots\cdots \xrightarrow{k_{n-1}} I_n \xrightarrow{k_n} P,$$

the rate of formation of an intermediate is equal to the rate of its decomposition so that

$$\frac{d[I_1]}{dt} = \frac{d[I_2]}{dt} \cdots\cdots = \frac{d[I_n]}{dt} = 0$$


THANK YOU
for your
kind patience