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| Principal Investigator | | Co- Principal Investigator and Technical Coordinator |
|---|---|---|
| **Prof. A.K.Bakhshi**<br>Sir Shankar Lal Professor,<br>Department of Chemistry<br>University of Delhi | | **Dr. Vimal Rarh**<br>Deputy Director, Centre for e-Learning<br>and Assistant Professor,<br>Department of Chemistry, SGTB Khalsa College, University of Delhi<br><br>*Specialised in : e-Learning and Educational Technologies* |
| **Paper Coordinator** | **Content Writer** | **Reviewer** |
| **Prof. A.K.Bakhshi**<br>Sir Shankar Lal Professor,<br>Department of Chemistry<br>University of Delhi | **Prof. A.K.Bakhshi**<br>Sir Shankar Lal Professor,<br>Department of Chemistry<br>University of Delhi<br><br>**Dr. Priyanka Thakral**<br>Assistant Professor<br>Shradhanand College<br>University of Delhi | **Prof. D.V.S. Jain**<br>Emeritus Professor<br>Department of Chemistry<br>Panjab University<br>Chandigarh |
| Anchor Institute : SGTB Khalsa College, University of Delhi | | |


| Chemistry | PAPER No. 6: PHYSICAL CHEMISTRY-II (Statistical Thermodynamics, Chemical Dynamics, Electrochemistry and Macromolecules) |
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## 1. Learning Outcomes

After studying this module you shall be able to

- Learn about Limitations Lindemann Mechanism for unimolecular gaseous reactions.
- Learn about Hinshelwood modification
- Learn about RRK theory
- Learn about RRKM theory

## 2. Introduction

In the last module, we did discuss in detail the theory of unimolecular reaction rates provided by Lindemann. Lindemann mechanism was the first attempt to understand the rates of unimolecular reaction. The observed first order kinetics of many unimolecular reactions was satisfactorily explained by this mechanism.

Lindemann assumed that there is time lag between activation and reaction during which the activated or energized molecules may either react to give product or be de-energized (deactivated) to ordinary molecules. Only under the given conditions, the behavior of unimolecular reactions can be explained on the basis of bimolecular collisions.

Lindemann hypothesized a situation where "A reactant molecule A becomes energetically excited due to collision with another molecule of reactant A".

$$A + A \rightarrow A^* + A \qquad (Energization)$$

Where *A* represents inactive molecule while $A^*$ represents activated molecule. The rate for reaction (1) becomes,

$$Rate = \frac{d[A^*]}{dt} = k_1[A]^2$$

This energized molecule $A^*$ can lead to two situations:

- **Situation I**: The energized molecule $A^*$ might lose its energy due to collision with another molecule of A.

  $$A^* + A \rightarrow A + A \qquad (de-energization)$$

  The rate for reaction becomes,

$$Rate = -\frac{d[A^*]}{dt} = k_{-1}[A^*][A]$$

- **Situation II**: The energized molecule $A^*$ might lead to product formation i.e., it might undergo unimolecular decay.

$$A^* \rightarrow P \qquad (Product\ formation)$$

The rate for reaction becomes,

$$Rate = -\frac{d[A^*]}{dt} = \frac{d[P]}{dt} = k_2[A^*]$$

If the unimolecular step is slow enough to be the rate determining step, then the overall reaction will follow first order kinetics.

## 3. Limitations of Lindemann's Theory

Lindemann approach breaks down for two reasons:

- The bimolecular step does not account for the activation energy dependence, the internal degrees of freedom of the molecule are ignored and this theory underestimates the rate of activation.
- The unimolecular step does not account for the involvement of one particular form of molecular motion (for example rotation around a double bond) in a unimolecular reaction.

To resolve the above issues, two theories with some improvisations were proposed. These theories are:

1. Hinshelwood theory which offered solution to the first problem. Hinshelwood modified Lindemann Mechanism by stating that "every energized molecule will not enter into product formation but will go into activated molecule.

2. RRK theory addresses the second problem. RRK theory recognized that for a unimolecular reaction to take place, a minimum amount of energy must be localised in specific modes of molecular motion. An additional step in the Lindemann mechanism is the one where the excited molecule A* gets converted into a specifically excited 'activated complex' $A^{\ddagger}$

The qualitative approach towards understanding of Hinshelwood modification and RRKM theory forms a part of discussion of this module. Over here, we will only look into these models qualitatively without going in mathematical details.

## 4. Hinshelwood modification

Hinshelwood modified Lindemann Mechanism by stating that "every energized molecule will not enter into product formation but will go into activated molecule. And these activated molecules will lead to product formation"

$$A + A \overset{k_1}{\rightarrow} A^* + A \qquad (Energization)$$

$$A^* + A \overset{k_{-1}}{\longrightarrow} A + A \qquad (De-energization)$$

$$A^* \overset{k_2}{\rightarrow} A^{\#} \qquad (Activation)$$

$$A^{\#} \overset{k_3}{\rightarrow} P \qquad (Product\ formation)$$

## 5. RRKM theory

The Rice-Ramsperger-Kassel-Marcus (RRKM) theory is a theory of chemical reactivity. This was developed by Rice and Ramsperger in 1927 and then by Kassel in 1928, which altogether is referred to as RRK Theory. And this was generalized into RRKM theory 1952 by Marcus who took into consideration the transition state theory.

The main assumptions of this model are as follows:

- It was assumed that the molecule consists of connected harmonic oscillators which can exchange energy with each other.
- The energy of excitation of the molecule *E*, enables the reaction to occur.
- The energy distribution intra-molecularly was assumed to be faster than that of the reaction itself.

RRK theory addresses the second problem. RRK theory recognized that for a unimolecular reaction to take place, a minimum amount of energy must be localised in specific modes of molecular motion. An additional step in the Lindemann mechanism is the one where the excited molecule A* gets converted into a specifically excited 'activated complex' $A^{\ddagger}$.

$$A^* \overset{k_a}{\rightarrow} A^{\ddagger} \overset{k^{\ddagger}}{\rightarrow} P$$

$k^{\ddagger}$ is of the vibrational frequency order, and $k_a$ is generally very small. This implies that conversion of A* to $A^{\ddagger}$ is the rate determining step, and $k_a$ is, thus, the overall rate coefficient for conversion of A* to products. Because $k_a << k^{\ddagger}$ , $[A^{\ddagger}]$ is very small and we can use the steady state approximation to find $k_a$, giving

(**Steady State Approximation / Principle**. This principle states that when a short lived reaction intermediate such as $A^*$ exists at low concentration in a system, the rate of formation of the intermediate can be considered to be equal to its rate of disappearance. Applying this to $[A^*]$ gives, $\frac{d[A^*]}{dt} = -\frac{d[A^*]}{dt}$)

$$k_a = k^{\ddagger}[A^{\ddagger}]/[A^*]$$

RRK theory takes into account that the flow of energy is free from one vibrational mode to another within the molecule, which is also fairly reasonable with anharmonic molecular vibrations (and are therefore coupled).

**RRKM THEORY**: This was developed using the results of Hinshelwood and RRK theory. The reaction mechanism was rewritten taking into consideration the energy dependence of the rates of collisional activation and unimolecular dissociation.

$$A + M \xrightarrow{dk_1(E)} A^*(E) + M$$

$$A^*(E) + M \xrightarrow{k_{-1}} A + M$$

$$A^*(E) \xrightarrow{k_2(E)} P$$

Applying the steady state approximation to [A*(E)] gives the unimolecular rate constant for the energy range from E to E+dE.

Over here, the energy of the molecule is categorized into two components: fixed and non-fixed components where only the non-fixed component E* contributes to the reaction where free flow across the various modes of motion of the molecule is allowed.

In the general sense, RRKM theory predicts equilibrium between A* and $A^{\ddagger}$ , but not between A* and A. However, at high pressures, A* and A are also found to be in equilibrium. Transition state theory assumes thermal equilibrium between the activated complex $A^{\ddagger}$ and the reactants. This is very much equivalent to assuming that the thermal Boltzmann distribution is maintained

at all energies, which is true at sufficiently high pressures. At high pressures the RRKM model approaches the transition state model, and thus, the results of the two theories coincide.

## 5. Summary

- Lindemann approach is the simplest theory of unimolecular reaction rates and Lindemann was the first to successfully explain the observed first order kinetics of many unimolecular reactions.
- Lindemann approach breaks down for two reasons:
  - The bimolecular step does not account for the activation energy dependence, the internal degrees of freedom of the molecule are ignored and this theory underestimates the rate of activation.
  - The unimolecular step does not account for the involvement of one particular form of molecular motion (for example rotation around a double bond) in a unimolecular reaction.
- Hinshelwood modified Lindemann Mechanism by stating that "every energized molecule will not enter into product formation but will go into activated molecule.
- RRK theory recognized that for a unimolecular reaction to take place, a minimum amount of energy must be localised in specific modes of molecular motion. An additional step in the Lindemann mechanism is the one where the excited molecule A* gets converted into a specifically excited 'activated complex' $A^{\ddagger}$.