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The exact treatment of Marcus's extension and its analysis is beyond the scope of this course. However, we can state that the agreement between the theory and the experiment is better than the earlier theories, yet more modifications are being done to make it still better. Let us now sum up what we have learnt about unimolecular reactions in this unit. However, before that answer the following simple questions to assess your understanding.

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### SAQ 7

What are two important features of the expression for rate of activation as per RRK theory?

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### SAQ 8

What is the difference between the active and inactive modes of activated molecules in RRKM formalism?

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## 8.6 SUMMARY

Unimolecular reactions are the simplest kind of elementary reaction in gas phase in which a single reactant molecule passes into the activated complex and gives the product. These reactions show first order kinetics, and the first order rate constant is observed to be independent of pressure at high pressures. However, at moderate or intermediate pressures the first order rate constant is observed to depend on pressure. Further, at intermediate pressures the reaction shows complex kinetics with no simple order. However, at low pressures, the reaction shows second order kinetics.

To explain these experimental characteristics a number of theories have been proposed. The first of these, called Lindemann-Christiansen theory proposed a three-step mechanism for unimolecular reactions. In the first step, the reactant molecules undergo collisions amongst themselves to give energised molecules,  $A^*$  having sufficient energy to undergo reaction. However, these do not decompose immediately, there is a time lag. During this time, the energised molecule may undergo deactivation. Using this mechanism, Lindemann showed that the experimental observations could be explained at least qualitatively. However, there were limitations in terms of quantitative agreement. The Lindemann-Christiansen's theory underestimates the rate of energisation as it does not consider the energy dependence of the energisation step and neglects the internal degrees of freedom of the molecule.

The second theory proposed by Hinshelwood extended the Lindemann's approach by considering that the vibrational energies of the energised molecule are distributed internally amongst various vibrational modes to supply sufficient energy to the bond being broken. This approach addressed one of the limitations of Lindemann's theory and there was better agreement between theory and experiment.

The third theory, discussed in the unit, is called RRK theory. It proposed that a species will not undergo a unimolecular reaction unless one of its vibrational modes contains a certain minimum internal energy, called critical energy  $E^*$ . An energised molecule having a specific normal mode of vibration having critical amount of energy becomes an activated complex that undergoes the unimolecular reaction. Any molecule having acquired this energy, unless it is deenergised by collision, will pass through the activated state into final state. In other words, a new step, conversion of energised molecule to activated molecule, was introduced in the Lindemann's mechanism.

The RRK formalism was extended by R. A. Marcus by explicitly considering the individual vibrational frequencies of the energised and activated species. These have been designated either as active i.e., the ones that freely exchange energy and or inactive (adiabatic) modes that remain in the same quantum states during the reaction. The theory is called RRKM theory and provides much better agreement with the experimental observations.

## 8.7 TERMINAL QUESTIONS

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1. Differentiate between true and apparent unimolecular reactions.
2. How does Lindemann—Christiansen mechanism for unimolecular reactions gets altered in presence of excess inert gas?
3. Give the limitation of Lindemann—Christiansen mechanism.
4. Briefly describe the Hinshelwood's modification to Lindemann—Christiansen mechanism.
5. In what way did RRK theory improve on the Lindemann-Hinshelwood theory?
6. What was Marcus's modification of RRK theory?

## 8.8 ANSWERS

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### Self-Assessment Questions

1. The most crucial aspect of the mechanism of unimolecular reactions as proposed by Lindemann-Christiansen theory was the suggestion of a time lag between the activation and reaction steps.
2. Under high pressure conditions the energisation step of Lindemann-Christiansen's mechanism is rate determining step.
3. The Lindemann-Christiansen's theory underestimates the rate of energisation as it does not consider the energy dependence of the energisation step and neglects the internal degrees of freedom of the molecule.

4. Hinshelwood corrected the shortcoming of Lindemann-Christiansen's theory by proposing that the energy of the energised molecule to be distributed initially among the  $s$  degrees of freedom, in number of possible ways.
5. Two important features for the rate of activation as per RRK theory are:
  - I. It predicts that the rates are a function of the number of vibrational oscillators  $s$  and
  - II. The rate increases rapidly with excess energy,  $(E-E_0)$ .
6. In RRKM formalism active modes are the ones that exchange energy freely whereas the inactive mode remains in the same quantum states during the reaction.

### Terminal Questions

1. In true unimolecular reactions the energy for activation is provided by the electromagnetic field, and the reaction does not occur in the absence of light. On the other hand, in apparent unimolecular reactions the activation of molecules is achieved by inelastic collisions with other molecules.
2. In presence of excess of inert gas, the energisation and deactivation steps primarily involve the collisions between the gas molecule (normal or energised) with the molecules of inert gas.
3. There are two limitations of Lindemann-Christiansen mechanism. These are:
  - i. In a plot of  $k_1^{\text{obs}}$  against  $[A]$  the first-order rate constant falls off at a much higher pressure than experimentally observed.
  - ii. In the inverse plot between  $1/k_1^{\text{Obs}}$  against  $1/[A]$  the experimental curve shows significant departure from the predicted line at low pressures.
4. Hinshelwood extended the Lindemann's approach by considering that the vibrational energies of the energised molecule are distributed internally amongst various vibrational modes to supply sufficient energy to the bond being broken.
5. RRK theory proposed that a species will not undergo a unimolecular reaction unless one of its vibrational modes contains a certain minimum internal energy, called critical energy  $E^*$ . An energised molecule having a specific normal mode of vibration having critical amount of energy becomes an activated complex that undergoes the unimolecular reaction. In other words, a new step, conversion of energised molecule to activated molecule, was introduced in the Lindeman's mechanism.
6. The RRK formalism was extended by R. A. Marcus by explicitly considering the individual vibrational frequencies of the energised and activated species. These have been designated either as active i.e., the ones that freely exchange energy and or inactive (adiabatic) modes that remain in the same quantum states during the reaction.