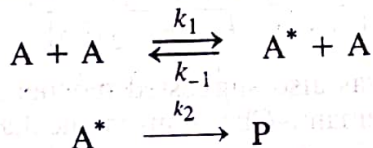


The Lindemann Theory of Unimolecular Reactions

It is easy to understand a bimolecular reaction on the basis of collision theory. Thus, when two molecules A and B collide, their relative kinetic energy exceeds the *threshold energy* with the result that the collision results in the breaking of bonds and the formation of new bonds. But how can one account for a unimolecular reaction? If we assume that in such a reaction ($A \longrightarrow P$), the molecule A acquires the necessary activation energy by colliding with another molecule, then the reaction should obey second-order kinetics and not the first-order kinetics which is actually observed in several unimolecular gaseous reactions. A satisfactory theory of these reactions was proposed by F.A. Lindemann (1886-1957) in 1922. According to him, a unimolecular reaction $A \longrightarrow P$ proceeds via the following mechanism:



Here A^* is the energized A molecule which has acquired sufficient vibrational energy to enable it to isomerize or decompose. In other words, the vibrational energy of A exceeds the threshold energy for the overall reaction $A \longrightarrow$ Products. It must be borne in mind that A^* is simply a molecule in a high vibrational energy level and not an activated complex. In the first step, the energized molecule A^* is produced by collision with another molecule A. What actually happens is that the kinetic energy of the second molecule is transferred into the vibrational energy of the first. In fact, the second molecule need not be of the same species; it could be a product molecule or a foreign molecule present in the system which, however, does not appear in the overall stoichiometric reaction $A \longrightarrow P$. The rate constant for the energization step is k_1 . After the production of A^* , it can either be de-energized back to A (in the reverse step, with rate constant k_{-1}) by collision in which case its vibrational energy is transferred to the kinetic energy of an A molecule or be decomposed or isomerized to products (in the step with rate constant k_2) in which case the excess vibrational energy is used to break the appropriate chemical bonds.

In the Lindemann mechanism, a *time lag* exists between the energization of A to A^* and the decomposition (or isomerization) of A^* to products. During this time lag, A^* can be de-energized back to A. According to the steady state approximation (s.s.a), whenever a reactive (*i.e.*, short-lived) species is produced as an intermediate in a chemical reaction, its rate of formation is equal to its rate of decomposition. Here, the energized species A^* is short-lived. Its rate of formation = $k_1[A]^2$ and its rate of decomposition = $k_{-1}[A][A^*] + k_2[A^*]$. Thus,

$$d[A^*]/dt = k_1[A]^2 - k_{-1}[A][A^*] - k_2[A^*] = 0 \quad \dots(71)$$

so that $[A^*] = \frac{k_1[A]^2}{k_{-1}[A] + k_2} \quad \dots(72)$

The rate of the reaction is given by

$$r = -d[A]/dt = k_2[A^*] \quad \dots(73)$$

Substituting Eq. 72 in Eq. 73,

$$r = \frac{k_1 k_2 [A]^2}{k_{-1} [A] + k_2} \quad \dots(74)$$

The rate law given by Eq. 74 has no definite order. We can, however, consider two limiting cases, depending upon which of the two terms in the denominator of Eq. 74 is greater. If $k_{-1} [A] \gg k_2$, then the k_2 term in the denominator can be neglected giving

$$r = (k_1 k_2 / k_{-1}) [A] \quad \dots(75)$$

which is the rate equation for a first-order reaction. In a gaseous reaction, this is the high-pressure limit because at very high pressures, $[A]$ is very large so that $k_1 [A] \gg k_2$.

If $k_2 \gg k_{-1} [A]$, then the $k_{-1} [A]$ term in the denominator can be neglected giving

$$r = k_1 [A]^2 \quad \dots(76)$$

which is the rate equation for a second-order reaction. This is the low pressure limit. The experimental rate is defined as

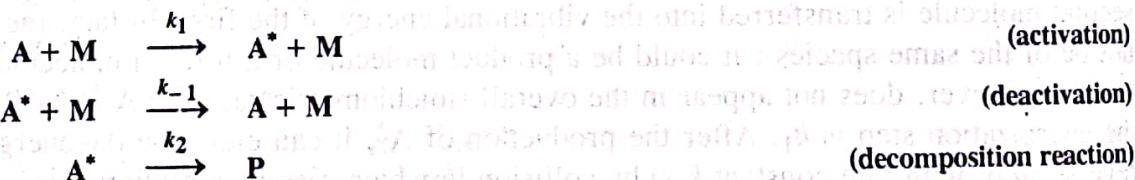
$$r = k_{\text{uni}} [A] \quad \dots(77)$$

where k_{uni} is the unimolecular rate constant. Comparing Eqs. 74 and 77 we have

$$k_{\text{uni}} = \frac{k_1 k_2 [A]}{k_{-1} [A] + k_2} = \frac{k_1 k_2}{k_{-1} + k_2 / [A]} \quad \dots(78)$$

Note : The Lindemann mechanism was also suggested independently by Christiansen. Hence, it is also sometimes referred to as the Lindemann-Christiansen mechanism. The theory of unimolecular reactions was further developed by Hinshelwood and refined by Rice, Rampsberger, Kassel and Marcus. The advanced theory of unimolecular reactions, known as the RRKM theory (*i.e.*, the Rice-Rampsberger-Kassel-Marcus theory) takes into consideration, the details of the intermolecular vibrational energy transfer. This has been discussed under **Further Information 1**.

Example 46. Consider the following Lindemann mechanism for the unimolecular decomposition of a molecule A in the presence of a species M (which may be any molecule such as an inert gas like helium or even A itself) :



Using the steady state approximation (s.s.a.), derive the rate law for the formation of the product.

Solution : $r = -d[A]/dt = +d[P]/dt = k_2 [A^*] \quad \dots(i)$

Applying s.s.a. to the transient species A^* ,

$$k_1 [A][M] - k_{-1} [A^*][M] - k_2 [A^*] = 0 \quad \text{or} \quad k_1 [A][M] = (k_{-1} [M] + k_2) [A^*]$$

$$[A^*] = \frac{k_1 [A][M]}{k_{-1} [M] + k_2}$$

Substituting this expression in Eq. (i), we obtain

$$r = k_1 k_2 \frac{[M][A]}{k_{-1} [M] + k_2}$$

Example 47. Consider the following Lindemann mechanism for the unimolecular decomposition of a molecule A in the presence of an inert gas molecule M :

