

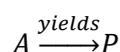
Lindemann Theory of Unimolecular Reactions

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It is easy to understand a bimolecular reaction on the basis of collision theory.

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 comes and the formation of new bonds.

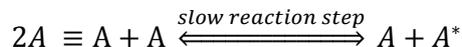
But how can one account for a unimolecular reaction? If we assume that in a reaction of type



the molecule A acquires the necessary activation energy for 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** in 1922.

According to him, a unimolecular reaction $A \xrightarrow{\text{yields}} P$ proceeds via the following mechanism:

In first step the molecule reacts with itself to produce a conjugate pair.



Here, let, the rate constant being k_f for forward reaction & k_b for backward.

And for $A^* \longrightarrow P$ assume the rate constant k_{f_2} .

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 $A \xrightarrow{\text{yields}} P$. 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 to 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 $A \xrightarrow{\text{yields}} P$. The rate constant for the energization step is k_f . After the production of A^* , it can either be de-energized back to A (in the reverse step) by collision in which case its vibrational energy is transferred and added to the kinetic energy of molecule A or be decomposed or isomerized to products (in the second step, $A^* \longrightarrow P$) 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 $A \rightarrow A^*$ and the decomposition (or isomerization) of A^* to products. During the time lag, A^* can be de-energized back to A .

Mathematical Treatment

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 = $k_f \times [A]^2$ and its rate of decomposition = $k_b \times [A][A^*] + k_{f_2} \times [A^*]$.

Thus

$$\frac{d[A^*]}{dt} = k_f \times [A]^2 - k_b \times [A][A^*] + k_{f_2} \times [A^*] = 0 \dots(1)$$

So that

$$[A^*] = \frac{k_f \times [A]^2}{(k_b \times [A] + k_{f_2})} \dots\dots(2)$$

The rate of the reaction is given by

$$r = -\frac{d[A]}{dt} = k_{f_2} \times [A^*] \dots(3)$$

Substituting Eq.2 in Eq.3,

$$r = k_{f_2} \frac{k_f \times [A]^2}{(k_b \times [A] + k_{f_2})}$$

$$\text{Or, } r = \frac{k_f k_{f_2} \times [A]^2}{(k_b \times [A] + k_{f_2})} \dots(4)$$

The rate law given by Equation (4) has no definite order. We can, however consider two limiting cases, depending upon which of the two terms in the denominator of Equation (4) is greater.

Case 1: If $k_b[A] \gg k_{f_2}$, then the k_{f_2} term in the denominator can be neglected giving:

$$r = \left(\frac{k_f k_{f_2}}{k_b}\right) [A] \dots\dots(5)$$

which is the rate reaction 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 $k_f[A] \gg k_{f_2}$.

Case 2: If $k_{f_2} \gg k_b[A]$, then the $k_b[A]$ term in the denominator of Equation (4) can be neglected giving

$$r = k_f[A]^2 \dots\dots(6)$$

which is the rate equation of a second order reaction. This is the low pressure limit.

The experimental rate is defined as

$$r = k_{uni} [A] \dots(7)$$

where k_{uni} is unimolecular rate constant.

Comparing Eqs.4 & 7 we have

the rate constant of Unimolecular reaction:

$$k_{uni} = \frac{k_f k_{f_2} [A]}{\{k_b [A] + k_{f_2}\}}$$

$$\text{or } k_{uni} = \frac{k_f k_{f_2}}{k_b + \frac{k_{f_2}}{[A]}}$$

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