

5.14: The Lindemann-Hinshelwood Mechanism for First-order Decay

First-order kinetics for a unimolecular reaction corresponds to a constant probability that a given molecule reacts in unit time. In [Section 5.7](#), we outline a simple mechanism that rationalizes this fact. This mechanism assumes that the probability of reaction is zero unless the molecule has some minimum energy. For molecules whose energy exceeds the threshold value, we assume that the probability of reaction is constant. However, when collisions are frequent, a molecule can have excess energy only for brief intervals.

The **Lindemann-Hinshelwood mechanism** for gas-phase unimolecular reactions provides a mathematical model of these ideas. Since molecules exchange energy via collisions, any given molecule acquires excess energy by collisions with other molecules, and loses it within a short time through other collisions. If it retains its excess energy long enough, it will react. If collisions are very infrequent, every molecule that acquires excess energy reacts before it undergoes a deactivating collision. In this case the reaction rate is proportional to the rate at which molecules acquire excess energy, which is proportional to the number of collisions. In a collection of A molecules, the total number of $A-A$ collisions is proportional to $[A]^2$ not $[A]$ and so the reaction rate depends on $[A]^2$ not $[A]$.

We represent molecules with excess energy as A^* , and assume that all A^* molecules undergo reaction with a constant probability. A^* molecules are formed in collisions between A molecules, and they are deactivated by subsequent collisions with A molecules.



where P is the product(s) of the reaction. The rate at which the number of moles of A^* molecules changes is

$$\frac{1}{V} \frac{dn_{A^*}}{dt} = k_1[A]^2 - k_2[A^*][A] - k_3[A^*]$$

and since we suppose that $[A^*]$ is always very small, the [steady-state approximation](#) applies, so that $dn_{A^*}/dt \approx 0$, and

$$[A^*] = \frac{k_1[A]^2}{k_2[A] + k_3}$$

The reaction rate is given by

$$\begin{aligned} \frac{1}{V} \frac{d\xi}{dt} &= k_3[A^*] \\ &= \frac{k_1 k_3 [A]^2}{k_2 [A] + k_3} \end{aligned} \quad (5.14.1)$$

When $k_2[A] \gg k_3$, the rate of deactivating collisions between A^* and A is greater than the rate at which A^* molecules go on to become products, the rate law (Equation 5.14.1) for consumption of $[A]$ becomes first order:

$$\begin{aligned} \lim_{k_2[A] \gg k_3} \frac{k_1 k_3 [A]^2}{k_2 [A] + k_3} &= \frac{k_1 k_3 [A]^2}{k_2 \cancel{[A]}} \\ &= \frac{k_1 k_3}{k_2} [A] \\ &= k_{\text{high pressure}} [A] \end{aligned}$$

where the first order rate constant $k_{\text{high pressure}}$ is a function of k_1 , k_2 and k_3 . This is termed the rate law's **high-pressure limit**.

The **low-pressure limit** occurs when $k_2[A] \ll k_3$. The rate law (Equation 5.14.1) becomes second order in $[A]$:

$$\begin{aligned} \lim_{k_2[A] \ll k_3} \frac{k_1 k_3 [A]^2}{k_2 [A] + k_3} &= \frac{k_1 \cancel{k_3} [A]^2}{\cancel{k_3}} \\ &= k_{\text{low pressure}} [A]^2 \end{aligned}$$

where the second order rate constant $k_{\text{low pressure}}$ is a function of only k_1 . The rate of product formation becomes equal to the rate at which A^* molecules are formed.

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