

5.15: Why Unimolecular Reactions are First Order

In the discussion above, we assume that a molecule with energy in excess of the minimum activation energy undergoes reaction with some fixed probability, represented by the rate constant k_3 . A complete answer to the question of why unimolecular processes are characteristically first-order (in the high pressure limit) requires that we rationalize this assumption. Another way of phrasing this question is to ask why the activated molecule does not react immediately: Why isn't $k_3 \approx \infty$?

The total energy of a molecule is distributed among numerous degrees of freedom. The molecule has translational kinetic energy, rotational kinetic energy, and vibrational energy. When it acquires excess energy through a collision with another molecule, the additional energy could go directly into any of these modes. However, before the molecule can react, enough energy must find its way into some rather particular mode. If, for example, the reaction involves the breaking of a chemical bond, and the collision puts excess kinetic energy into the molecule's translational modes, the reaction can occur only after some part of the excess translational energy has been converted to excess vibrational energy in the breaking bond. This intramolecular transfer of energy among the molecule's various internal modes is time-dependent.

From this perspective, the probability that an excited molecule will react in unit time is the probability that the necessary energy will reach the critical locus in unit time. The reshuffling of energy among the molecule's internal modes is a stochastic process, and the probability that the reshuffling will put the necessary energy where it is needed is a constant characteristic of the molecule.

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