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The collision theory of unimolecular reactions: A second possibility to Lindemann's proposal

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Lindemann's collision theory of unimolecular reactions was studied theoretically with comparative real-life assumptions. The result holds that there is a second possibility to the Lindemann's proposal by applying quantitative/mathematical models, and assuming that in a bimolecular collision, both molecules are equally energized. This represents the second possibility of Lindemann's proposal and is hereby presented to enhance the study of chemical kinetics.

Keywords: Lindeman's proposal, reaction kinetics, unimolecular systems, collision theory.

1. Introduction

Determination or modelling of systems with varying rates of chemical interactions have remain an important subject of inquiry in various disciplines of endeavors such as chemistry, physics, biology, and engineering (Yin 2015; Mortiner 2008; Roselar 1975). Various modifications and treatments of models help us improve on the existing theories of unimolecular reactions (Turanyi and Tomlin 2014). The aim is to enhance the study of chemical kinetics of different systems. The objective of the present study is to apply some theoretical and quantitative treatment to the Lindemann's proposal regarding unimolecular reactions.

Let us consider a case of a typical football match. When two players collide head-on, it is most likely that one of them will receive the pain more than the other. The less affected has no alternative than to say to the affected "I'm sorry". When this is said, energy is taken away from the angry or more pained player and both of them will resort to normal players. On the other hand, the pain of head-on collision may affect both of them and they are both angry and lie down both for a while groaning with none to appease the other. After a while, both of them will rise up as normal players and continue to play. The second scenario is the case in consideration in this paper. Perhaps, it is better to present Lindemann's unimolecular reaction mechanism proposal before the second scenario, in order to appreciate that there is a second possibility.

2. Lindemann's postulate of mechanism of unimolecular reactions

Lindemann (1922) made use of collision theory to explain the mechanism of unimolecular reactions, say reactant (A) would undergo the following process:



In unimolecular processes, only one molecule participates in the reaction, and consequently we need to ask how the single molecule acquire the energy of activation to start reacting. Lindemann provided the answer to this puzzle in 1922 (Saha and Dua 2013). He suggested the behavior of unimolecular reactions could be explained on the basis of bimolecular collisions provided we postulate that a time lag exists between activation and reaction during which activated molecules may either react or be deactivated to ordinary molecules (Maron and Lando 1974). Consequently, the rate of reaction will not be proportional to all the molecules activated, but to those which remain active.

The Lindemann hypothesis can be formulated by the following scheme:





where A represents inactive and A* activated molecules, and the various K's the rate constants for the respective processes.

Further, the rate of reaction will be proportional to the concentration of A* (i.e., Eqn. (3) and is the rate-determining step).

Hence,

$$\frac{-d[A^*]}{dt} = K_3 [A^*] \quad (4)$$

Since [A*] is not known, it is necessary to obtain its concentration in terms of other concentrations. To do this, we resort to a postulate known as steady state approximation (principle) or stationary state approximation (principle). The principle states that: "when short-lived reaction intermediates exist at low concentration in a system, the rate of formation of the intermediates is equal to their rate of disappearance" (Maron and Lando 1974). Applying this principle to A*, we see that it is formed in Eqn. 2 with rate $K_1[A]^2$ and it disappears with rate $K_2[A][A^*]$, and also disappears with rate $K_3[A^*]$ in Eqn. 3.

Consequently,

$$K_1[A]^2 = K_2[A][A^*] + K_3[A^*] \quad (5)$$

$$[A^*] = \frac{K_1[A]^2}{K_3 + K_2[A]} \quad (6)$$

Substitute Eqn. (6) in Eqn. (4), we have:

$$\frac{-d[A^*]}{dt} = \frac{K_1 K_3 [A]^2}{K_3 + K_2 [A]} \quad (7)$$

Equation 7 predicts two limiting possibilities:

1. When $K_2[A] \gg K_3$, the equation reduces to:

$$\frac{-d[A]}{dt} = \frac{K_1 K_3 [A]^2}{K_2 [A]} \quad (8)$$

$$= \frac{K_1 K_3}{K_2} [A]$$

$$\frac{-d[A]}{dt} = K [A] \quad (9)$$

where $K = \frac{K_1 K_3}{K_2}$.

This case corresponds to a situation in the reaction where the concentration of A is high enough to produce appreciable deactivation of A* by collision with inactive molecules. Deactivation or reverse rate $K_2[A][A^*]$ is fast. Product formation rate $K_3[A]$ is slow. Under such condition, Eqn. (9) predicts a first order reaction at high pressure.

2. On the other hand, when $K_3 \gg K_2[A]$, Eqn. (7) reduces to:

$$\frac{-d[A^*]}{dt} = \frac{K_1 K_3}{K_3} [A]^2$$

$$\frac{-d[A^*]}{dt} = K_1 [A]^2 \quad (10)$$

That is, the reaction should be second order. This situation is obtained at low concentration of A where the rate of deactivation becomes so slow as to be rate-determining ($K_2[A][A^*]$ is slow and $K_3[A^*]$ is fast and deactivation becomes rate-determining).

Such changes from first order in gaseous reaction at high pressure to second order at low pressure have been observed in many gaseous reactions (Keszei 2021). Depending on the reaction and the temperature, the transition from first to second order generally starts at pressures between 10 and 200 mmHg and it is usually not completed until the pressure gets fairly low. A hypothetical representation is presented in Figure 1, which depicts the decomposition of azomethane:

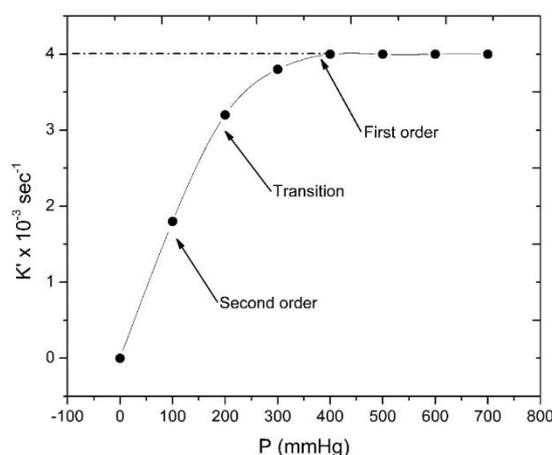
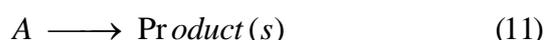
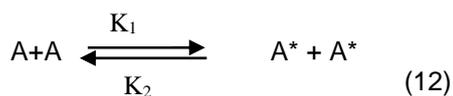


Figure 1. The plot of K' versus P_i for decomposition of azomethane $(\text{CH}_3)_2\text{N}_2$ at 330 °C

3. The second possibility to Lindemann's proposal

Here, we consider a situation where there is a bimolecular collision and both molecules are equally energized with none to withdraw the energy from the other. This can be represented with the scheme:





where A represents inactive, and A* represent energized or activated molecules, and all K's are rate constants for the respective processes. Further, the rate of reaction will be proportional to the concentration of the energized molecules available (i.e., A*)

The differential rate law is given as:

$$\frac{-d[A]}{dt} = K_3 [A^*]^2 \quad (14)$$

Since [A*] is not known, it is necessary to obtain its concentration in terms of other concentrations. To do this, we make use of steady state approximation where the rate of formation of the short-lived intermediates or energized molecules is equal to the rate of disappearance. Applying the principle to A*, we see that it is formed in Eqn. (12) with a rate $k_1[A]^2$ and it disappears with a rate $k_2[A^*]^2$ and also disappears with a rate $k_3[A^*]^2$ in Eqn. (13). Consequently,

$$k_1[A]^2 = k_2[A^*]^2 + k_3[A^*]^2 \quad (15)$$

or

$$k_1[A]^2 = [A^*]^2 (k_2 + k_3)$$

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

$$\Rightarrow [A^*] = \sqrt{\frac{k_1}{k_2 + k_3}} [A] \quad (16)$$

Substituting Eqn. 16 into Eqn. 14

$$\frac{-d[A]}{dt} = k_3 \left(\sqrt{\frac{k_1}{k_2 + k_3}} [A] \right)^2$$

or

$$\frac{-d[A]}{dt} = \frac{k_1 k_3}{k_2 + k_3} [A]^2 \quad (17)$$

$$\therefore \frac{-d[A]}{dt} = K [A]^2 \quad (18)$$

$$\text{where } K = \frac{k_1 k_3}{k_2 + k_3}$$

This corresponds to a situation in the reaction where the concentration of A is very high enough to produce appreciable deactivation of A* by collision with inactive molecules. Deactivation or reverse rate $k_2[A][A^*]$ is fast while product formation rate $k_3[A^*]$ is slow. Under such condition, Eqn. (18) predicts a second order reaction at high pressure.

4. Conclusion

By applying quantitative models, and assuming that in a bimolecular collision, both molecules are equally energized to achieve *activation energy*. This second possibility of Lindemann's theory of unimolecular reactions reveal that unimolecular reactions are mainly second order reactions. Few cases may occur mostly in gaseous reactions where a transition occurs from first order to second order reaction at high and low pressure respectively.

Conflict of Interest

The author declares that there is no conflict of interest.

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