Role of reaction products in unimolecular gas reactions: A few remarks in light of the Lindemann theory

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The Role of Reaction Products in Unimolecular Gas Reactions

A few remarks in light of the Lindemann theory

Some of the misconceptions used in many physical chemistry textbooks with respect to the so-called unimolecular reactions were pointed out in *this Journal* some years ago.[2] In that work, however, the importance of the role played by non-reacting molecules, especially product molecules, as active colliders is not sufficiently emphasized, nor is explicit attention paid to the abusive use of $|A|$, time t concentration (or pressure) of reacting species, instead of $|A|_0$, initial concentration of A.

Therefore, it seemed interesting to us to complete the Lindemann theory bearing in mind the above remarks. In spite of its 50 year old formulation, the Lindemann theory still maintains a great interest, and not only from the pedagogic point of view. In fact, "most modern theories of unimolecular reaction rates are based on the fundamental Lindemann mechanism."[3]

Problems found by newcomers to unimolecular reaction theories begin with a frequent textbook confusion between purely experimental facts, on the one hand, and their theoretical explanation (model, theory) on the other hand. This distinction must be clearly made in experimental sciences, and emphasized in teaching. On the other hand, in respect to the connection between experiment and theory in chemical kinetics, it is good to recall that "a kinetic problem, like a crime, calls for a proof beyond "reasonable doubt" and not a mathematical proof."[4]

We shall first consider the experimental facts of an isomerization reaction. The overall reaction is

$$A \rightarrow B \qquad (1)$$

In a given run (given $|A|_0$), the observation is made that the overall reaction rate is first-order in A throughout the course of the experiment; i.e.
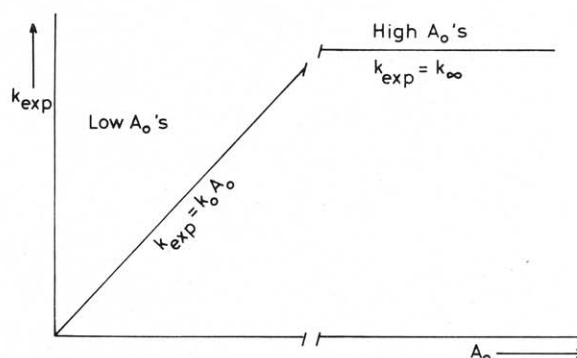
$$v = -\frac{dA}{dt} = k_{exp}A \qquad (2)$$

where A stands for $|A|$ and k_{exp} is the first-order rate constant *for this run*. Another experiment at the same temperature with a different A_0 (for $|A|_0$) also satisfies eqn. (2), but it yields a different k_{exp}. That means k_{exp} is a pseudo-constant, since it depends not only on the temperature but also on the A_0 value.

The function

$$k_{exp} = k_{exp}(A_0)$$

has the general form shown in the figure. The plot is purely experimental. It is the result of several experiments performed
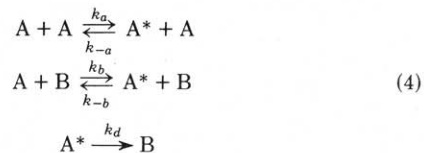
[1] To whom correspondence should be addressed.
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The function $k_{exp}(A_0)$ at the high and low pressure limits.

at different values of A_0. It does *not* refer to only one run; i.e., it must *not* be inferred from the figure that the reaction order changes as a given experiment proceeds.[2]

Let us now consider the theory. At any moment according to eqn. (1)

$$A + B = A_0 \qquad (3)$$

The modified Lindemann mechanism would be

$$A + A \underset{k_{-a}}{\overset{k_a}{\rightleftharpoons}} A^* + A$$

$$A + B \underset{k_{-b}}{\overset{k_b}{\rightleftharpoons}} A^* + B \qquad (4)$$

$$A^* \overset{k_d}{\longrightarrow} B$$

where the constants have the obvious, usual meanings. A^* symbolizes, as usual, an energized A molecule.

Definition of a theoretical first-order rate constant as

$$k_{theor} = -\frac{1}{A}\frac{dA}{dt}$$

and straightforward application of the steady-state hypothesis for A^* leads to

$$k_{theor} = k_d \frac{k_a A + k_b B}{k_{-a}A + k_{-b}B + k_d} =$$

$$k_d \frac{(k_a - k_b)A + k_b A_0}{(k_{-a} - k_{-b})A + k_{-b}A_0 + k_d}$$

where B is eliminated, using eqn. (3). The last expression reduces to

$$k_{theor} = k_d \frac{k_b A_0}{k_{-b}A_0 + k_d} \qquad (5)$$

if one assumes

$$k_a \simeq k_b$$
$$k_{-a} \simeq k_{-b} \qquad (6)$$

This assumption may be justified. For example, it has been found[5] that $\beta_p \equiv k_a/k_b \simeq 1.0$ for the isomerization of cyclopropane to propylene. Another example could be the extensively studied reaction $CH_3NC \rightarrow CH_3CN$. Chan, et al.[6] studied the relative efficiency of CD_3CN and found $\beta_p = 0.92$, close to 1. They also report that "isotopic substitution of H

by D does not have an appreciable effect on efficiency." Thus, eqn. (6) could as well hold in this case.

Let us now consider the high ($A_0 \to \infty$) and low ($A_0 \to 0$) pressure limits. In the former case

$$k_{-b}A_0 \gg k_d$$

and eqn. (5) reduces to

$$k_{theor} = k_d \frac{k_b}{k_{-b}} \simeq k_d \frac{k_a}{k_{-a}}$$

in accordance with the experimental facts ($k_{exp} = k_\infty$). In the low pressure limit

$$k_{-b}A_0 \ll k_d$$

and

$$k_{theor} = k_b A_0 \simeq k_a A_0$$

also in accordance with the experience ($k_{exp} = k_0 A_0$, see the fig).

In conclusion, the role of the product, B, is fundamental in explaining the experimental facts. Otherwise, if one makes $k_b = k_{-b} = 0$, one arrives at

$$k_{theor} = k_d \frac{k_a A}{k_{-a}A + k_d}$$

which depends on A, leading to a variable reaction order as the reaction proceeds, except if $k_{-a}A \gg k_d$. That requires A to be sufficiently high, which is not the case in low pressure (A_0) runs, and would, in fact, only hold at the beginning of the reaction in high pressure experiments.

It may be added that the role of B is not decisive in the first moments of a run, when $A \gg B$. If one explicitly refers to the *initial* rate (what is *not either* usually made in textbooks), then one can obviously suppress step 2 in eqn. (4) and arrive at eqn. (5), because under these conditions $A = A_0$. On the other hand, B is necessary at any other time, and so the present treatment is valid under any conditions and proves the flexibility and capacity of the Lindemann theory.

A final comment regarding terminology may be illuminating to students. The definition of molecularity applies to elemental reactions, i.e. one-step reactions. The Lindemann mechanism is universally accepted as qualitatively correct and its appearance is of a multi-step type. So, would it not be more appropriate to speak of first-order reactions instead of unimolecular reactions? If one looks at eqn. (4) it is at first-sight apparent that only in step 3 is the left-hand side *chemically* different from the right-hand side, while the first and second steps only imply energy transfer processes and not chemical changes. So the Lindemann mechanism is in accordance with the idea of unimolecularity if only chemical and not physical steps are counted. This discussion may be thought-provoking.