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Textbook Errors, 79

Unimolecular Gas Reactions At Low Pressures

The rate of a unimolecular reaction in the gas phase is equal to the concentration of activated molecules times the specific rate at which activated molecules react to form the product (where the term "activated molecule" designates a molecule whose available internal energy lies above a certain minimum value). At sufficiently high pressures, the rate of both activation and deactivation is fast in comparison with the rate of product formation, so that the equilibrium concentration of activated molecules is maintained throughout the course of the reaction. At lower pressures this is no longer the case, and the high-energy population becomes depleted as a consequence of the chemical reaction.

In the simplest theory, that of Lindemann, application of these ideas leads to the rate equation

$$v = kk_d[A]^2/(k'[A] + k_d) \qquad (1)$$

where [A] symbolizes the concentration of the reactant A, k and k' are the second-order rate constants for activation and deactivation, respectively, and k_d is the specific rate of decomposition (or isomerization) of an activated molecule.

Most textbooks[1] now proceed to show that as the pressure decreases, the observed first-order rate constant which may be defined by the expression

$$k_{obs} = kk_d[A]/(k'[A] + k_d) \qquad (2)$$

starts decreasing from its high-pressure value of kk_d/k' until at very low pressures the rate equation becomes

$$v = k[A]^2 \qquad (3)$$

The reaction is then stated to follow second order kinetics.

All this must be very puzzling to the student. Inspection of eqn. (1) leads to the conclusion that, in the intermediate pressure range, the order of the reaction changes continuously as the reaction proceeds; in the same range, the quantity defined by eqn. (2) is clearly not a "constant" at all. Moreover, eqn. (1) seems to imply that a reaction which starts well within the high-pressure range may enter the intermediate

range and change its order at sufficiently high conversion where [A] has become small. Furthermore, from what he has been taught, the student must conclude from eqn. (3) that at very low pressure a plot of 1/[A] against time should yield a straight line. All these conclusions would be erroneous.

The student may understand the situation a little better when it is explained to him in a somewhat more advanced textbook that a molecule of A can be activated and deactivated through collisions, not only with another molecule of A, but also with a molecule of any other gas M (including the product), different gases differing however in their efficiency in maintaining the equilibrium concentration of activated molecules.

Such a consideration leads to the expression

$$k_{obs} = \sum_M k_M[M]/(\sum_M k'_M[M] + k_d) \qquad (4)$$

where the sum is to be taken over all the gases present, including A. If $\sum_M k_M[M]$ (and hence, from the principle of microscopic reversibility, $\sum_M k'_M[M]$) is "approximately constant during a run, as when the product compensates for the disappearing reactant as activator and deactivator" (1), the reaction will be first order during any given run, whatever the intial pressure. Although this is an over-simplification (2, 3), it seems to be a very satisfactory approximation in many cases (4). The observed first-order rate constant thus indeed deserves to be called a "constant," although it is only a pseudo first-order constant and may change from one run to another.

At this point, the student's attention should be drawn explicitly to the fact that the term "reaction order" may have different meanings depending on whether the order is determined from a single run, or by comparing different runs carried out at different initial pressures (using, for example, the method of half-lives). In the case under discussion, the reaction is first order in the former sense, but may be of higher order in the latter. This fact is duly emphasized only in very few textbooks (5). In particular, the expression "second order kinetics," universally used to describe the situation at low pressures, is easily misinterpreted, and it may not be realized that, even under these conditions, the reaction can still be pseudo first-order.

Apart from thus being ambiguous, the statement that unimolecular reactions follow second-order kinetics at low pressures is somewhat misleading in another

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[1] Since the purpose of this column is to prevent the spread and the continuation of errors and not the evaluation of individual texts, the sources of errors discussed will not be cited. In order to be presented an error must occur in at least two independent recent standard books.

sense. It leaves the student with the impression that such a behavior is not only a mathematical consequence of eqn. (1), but is quite universally observed. Whereas this is true with respect to the fall-off of k_{obs} with decreasing pressure, the actual low-pressure limit is only sometimes (2, 3, 6), and by no means always, experimentally attained. This is connected with the fact that eqn. (1) follows from an oversimplified theory which predicts a steeper fall-off of k_{obs} than is actually observed. The pressure at which a reaction becomes second order is thus lower than that calculated from the Lindemann theory.

It might be added that a situation similar to that discussed here for monomolecular reactions arises in the gas-phase conversion of para-hydrogen to ortho-hydrogen. The observed rate is equal to the rate of the reaction

$$H_2(p) + H \rightarrow H + H_2(o)$$
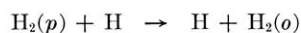
Now, [H] may be assumed (7) to be proportional to the total hydrogen pressure, irrespective of the ratio between para- and ortho-hydrogen present. Since the total pressure is constant during any given run, [H] is thus also constant, and the run follows first-order kinetics. On the other hand, the observed first-order rate constant is not a true constant; being proportional to [H], it is proportional to the square-root of the hydrogen pressure (7). The reaction is therefore sometimes stated to be of the order 3/2. Although this statement is formally correct, it easily leads to the misconception that a three-halves-order kinetic law should be followed during a given run.

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Literature Cited

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(4) See, e.g., Rampsberger, H., J. Am. Chem. Soc., 49, 1495 (1927); Howlett, K. E., J. Chem. Soc. 1952, 3695; Pritchard, H. O., Sowden, R. G., and Trotman-Dickenson, A. F., Proc. Roy. Soc. (London) A217, 563 (1953).
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(7) Farkas, A., Z. physik. Chem., B10, 419 (1930).