Equilibrium Molecular-pair Treatment of Fast Bimolecular Reactions in Solution

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In the equation $k(t) = k_A[1 - \int_0^t h(t')dt']$ for the time-dependent second-order rate constant for a bimolecular association A + B = P in solution, $h(t)$ is the probability per unit time of recombination of a geminate AB pair at time t following its creation from P at time zero.

Without assuming any particular equations for molecular transport or any particular molecular shapes, sizes, spins, or conformations, *etc.*, it is shown below that the time dependence of the second-order rate coefficient $k(t)$ of a fast bimolecular reaction $A + B \rightarrow P$ in solution is determined entirely by the behaviour of AB pairs formed from products (geminate pairs). This clarifies the molecular-pair analyses of Noyes and generalizes similar conclusions derived by Berg from a diffusion-equation analysis with spherical molecules.[1—3]

When reactants initially have equilibrium spatial distributions, $k(t)$ can be expressed by equation (1).[1—6] For equilibrium spatial distributions, the activation-control rate constant k_A applies. As time passes in a product-free system, AB pairs with small initial separations react, radial concentration gradients develop around reactant molecules, diffusion begins to limit the reaction rate, and the rate coefficient decreases.

$$k(t) = k_A[1 - \textstyle\int_0^t h(t')dt'] \qquad (1)$$

Noyes used artificial devices to maintain equilibrium spatial distributions in product-free systems.[1,2] The present analysis avoids artificialities by applying Noyes' method to a system that is at equilibrium.

Consider an equilibrium system. Let time zero be chosen arbitrarily. Denote as 'old' those reactant molecules that are present at time zero. At a later time, some old A and B molecules will have reacted and some 'new' ones will have been formed from products. A corresponding product-free system will contain only old A and B at all times.

At time zero, the distributions of A and B are identical in equilibrium and corresponding product-free systems. In the equilibrium system, in contrast to the product-free system, the concentration gradients that develop for old A and B molecules are exactly compensated (ignoring or averaging fluctuations) by new A and B. All $A + B \rightarrow P$ events are balanced in time, space, and other aspects by their microscopic reverses, $P \rightarrow A + B$.

A 'geminate' pair consists of particular A and B molecules that were created together from the same particular product molecules.[7] 'Geminate reaction' is the formation of P from a geminate pair. Let $h'(t)$ be the probability per unit time of geminate reaction at time t of a geminate pair created at time zero. Then equation (2) describes the time development of the equilibrium system. Here [ ] and $[\ ]_n$ denote, respectively, bulk concentrations of all molecules and of new ones.

$$\begin{aligned} k_A[A][B] = {} & k(t)([A] - [A]_n)([B] - [B]_n) \\ & + k(t)([A] - [A]_n)[B]_n + k(t)[A]_n([B] - [B]_n) + k(t)[A]_n[B]_n \\ & + k_A[A][B]\textstyle\int_0^t h'(t')dt' \qquad (2) \end{aligned}$$

Equation (2), which is analogous to one given by Noyes,[8] expresses the rate of all AB reactions (left side) as the sum (right side) of the rates of five AB reaction types: old A–old B, old A–new B, new A–old B, nongeminate new A–new B, and geminate new A–new B. In the fifth term of the right side, the rate of geminate pair production is $k_A[A][B]$, the rate of product formation, because at equilibrium geminate pairs are formed from products at the same rate that products are formed from A and B.

Equation (2) rearranges to equation (3). Comparison of equations (3) and (1) identifies $h(t)$ as $h'(t)$.

$$k(t) = k_A[1 - \textstyle\int_0^t h'(t')dt'] \qquad (3)$$

The interpretation of the behaviour of a product-free system in terms of $h'(t)$ is necessarily indirect, since neither products nor geminate pairs are present. However, certain AB pairs in product-free systems must behave exactly as do geminate pairs, since A and B initially have identical, equilibrium distributions in corresponding product-free and equilibrium systems. The disappearance of these 'geminate-cognate' pairs results in the time dependence of $k(t)$ in a product-free system.

The long-time limit of equation (1) or (3) is equation (4), where k is the 'long-time' rate constant and $\bar{a}$ is the probability of geminate recombination $[\int_0^\infty h'(t)dt]$. The rate constant k describes bimolecular association to a close approximation after about 10^{-9} s, according to Noyes.[1] Equation (4) has been derived previously through a thermochemical kinetic argument.[9]

$$k(\infty) = k = k_A(1 - \bar{a}). \qquad (4)$$

That $h(t)$ is the geminate-reaction probability $h'(t)$ cannot be extracted from considerations of product-free systems only. Nevertheless, correct treatments of equilibrium and product-free systems must be equivalent.

In Noyes' 1961 treatment, a hypothetical system is considered in which no actual reactions occur but each A and B that 'get into a situation where they would react if the system were a real one' are marked as having 'reacted'.[2] Then $h(t)dt$ is defined as the probability 'that a pair of molecules in infinite volume that have previously 'reacted' with each other will undergo their first subsequent 'reaction' with each other between t and $t + dt$ later.' Equations (2) and (1) follow.

The artificiality of the system in terms of which the 1961 $h(t)$ is defined obscures its fundamental physical meaning. In the light of the present analysis, the 1961 $h(t)$ can be given the following interpretation. The only situation that an A and B can 'get into' that would guarantee reaction in a real system is the transition state for P formation. An A and B that reach the transition state and are marked (but don't react) must behave after marking as if they were formed from P by the microscopic reverse of their 'reaction', since they are emerging towards reactants from the transition state that separates P from A and B and since their behaviour must preserve equilibrium over marked and unmarked A and B molecules. Consequently, emergent pairs must behave as geminate pairs and Noyes' 1961 $h(t)$ is properly interpreted as the probability $h'(t)$ of geminate reaction.

Noyes' 1954 molecular-pair treatment does not lead to equation (4) and the '$h(t)$' defined therein is not equivalent to $h'(t)$. The 1954 '$h(t)$' is the reaction probability per unit time of an A and a B that *separated* at time zero from adjacent positions in solution.[1] That the 1954 treatment does not lead properly to equation (1) may account for some of the confusion in the literature over the equivalence (or lack thereof) of molecular-pair and diffusion-equation treatments.[2,4,10—13]

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References

1 R. M. Noyes, *J. Chem. Phys.*, 1954, **22**, 1349.

2 R. M. Noyes, *Prog. React. Kinetics*, 1961, **1**, 129.

3 O. G. Berg, *Chem. Phys.*, 1978, **31**, 47.

4 S. A. Rice, 'Diffusion-Limited Reactions,' in 'Comprehensive Chemical Kinetics,' vol. 25, eds. C. H. Bamford, C. F. H. Tipper, and R. G. Compton, Elsevier, Amsterdam, 1985. See especially pp. 220, 242—249, 377—379.

5 M. Smoluchowski, *Z. Phys. Chem.*, 1917, **92**, 129.

6 F. C. Collins and G. E. Kimball, *J. Colloid Sci.*, 1949, **4**, 425.

7 R. M. Noyes, *J. Am. Chem. Soc.*, 1955, **77**, 2042.

8 Ref. 2, p. 139, equation 3.2.

9 J. F. Garst, *J. Chem. Soc., Chem. Commun.*, 1987, 589.

10 K. R. Naqvi, K. J. Mork, and S. Waldenstrom, *J. Phys. Chem.*, 1980, **84**, 1315.

11 K. R. Naqvi, S. Waldenstrom, and K. J. Mork, *J. Phys. Chem.*, 1982, **86**, 4750.

12 B. Stevens, *J. Phys. Chem.*, 1981, **85**, 3552.

13 S. H. Northrup and J. T. Hynes, *J. Chem. Phys.*, 1979, **71**, 871, 884.