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Polychronous Kinetics with Diffusion over the Reaction State Spectrum

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Abstract—The unsteady- and steady-state kinetics of a polychronous first-order reaction with discrete and continuous state distributions under spectral diffusion conditions are considered. An analysis of the model has demonstrated that a quasi-steady-state regime is established in the course of the reaction. In this regime, the shape of the distribution function stops changing and the reaction kinetics obeys an exponential law and can be characterized by a single, average rate constant. Equations are set up for the reaction state distribution and average rate constant in the quasi-steady-state regime. The limits of the kinetic and quasi-steady-state regimes are determined as a function of the spectral diffusion coefficient. The unsteady-state kinetics and the quasi-steady state time depend strongly on the initial state distribution.

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Polychronous kinetics is a property of a wide variety of elementary chemical and physical solid-phase processes characterized by a rate constant spectrum (distribution) [1, 2]. This kind of single-reactant processes includes first order reactions (bimolecular reactions in an excess of one reactant and monomolecular reactions) whose kinetics deviates from the first-order law. These include the reactions of radicals with alcohol glass matrices [1], the geminal recombination of radical pairs in polymers [2] and electron–ion pairs in organic glasses [3], heterogeneous reactions [4], and fluorescence and phosphorescence in solids [5].

The existence of a rate constant distribution for a given $A \longrightarrow B$ reaction is explained by the existence of a broad spectrum of activation barriers of different heights and widths in the solid phase [1]. Since the reactivity of the reactant in this case cannot be characterized by a single rate constant, attempts are made to find some universal form of kinetic curves for polychromous reactions and to develop methods for determining the rate constant distributions characterizing the reaction kinetics [1–8]. Many ways of representing polychromous kinetics have been suggested. These include fitting some portions of kinetic curves to a linear relationship between the concentration c and $\ln t$, where t is the reaction time [1, 2]; to the square-root time dependence of the rate constant, $k \sim t^{-1/2}$ [1]; to the Kohlrausch function [6]; and to the sum of two or three exponentials, as in the case of a reaction consisting of two or three independent processes [5]. The most universal representation of polychromous kinetics found to date is a series containing a sufficiently large number of terms [8, 9].

This arbitrariness in describing the reaction kinetics leads to ambiguity concerning the distributions derived from experimental data [8]. Earlier, we suggested a high-accuracy method for determining the rate constant distributions in polychronous reactions. It was demonstrated that, even if the accuracy of the experimental data is very high, the distribution derived from these data will be one of the multiple, often diametrically opposite, solutions of the inverse problem and that the invariants of these solutions can be used to obtain an unambiguous estimate of reactivity [9]. We assumed that kinetically inequivalent states of the reacting particle do not mix. However, in systems in which molecular motion changes the spatial distribution of the particles, their conformational states and structure, and the molecular mobility of their environment, random transitions from one state into another in the rate constant spectrum (spectral diffusion) are significant. These transitions must exert an effect on the reaction kinetics.

There was an attempt to evaluate the effect of spectral diffusion on polychromous kinetics [10], but the resulting approximate solution, which was obtained as the sum of two exponentials, is inadequate for describing the reaction kinetics. Here, we consider a model of a polychromous reaction under spectral diffusion conditions and make at attempt to obtain an exact solution for this model.

GENERAL SCHEME OF THE REACTION

In the most general case, a first-order reaction passes through N kinetically inequivalent states and transitions between these states take place according to the following scheme [10–12]:

$$C_i \xrightarrow{k_i} \text{products}, \quad C_i \xrightarrow{\omega_{ji}} C_j, \quad i, j = 1, 2, \ldots, N, \quad \text{(I)}$$

where k_i is the rate constant of the reaction of the ith state (C_i) and ω_{ji} is the rate constant of the transition of molecules from the ith state into the jth state (or the transition frequency, which is the reciprocal of the time interval between transition events). Hereafter, the rate constants are numbered in increasing order.

The system of reactions (I) is described by the following set of differential equations for the change of the state concentrations c_i:

$$-\frac{\mathrm{d}c_i}{\mathrm{d}t} = \left(k_i + \sum_{j \neq i}^{N} \omega_{ji}\right) c_i - \sum_{j \neq i}^{N} \omega_{ij} c_j. \quad (1)$$

In matrix notation, this set of equations takes the simple form of

$$\frac{\mathrm{d}c}{\mathrm{d}t} = -\mathbf{A}c, \quad (2)$$

where the elements of the matrix **A** are defined as

$$\mathbf{A}_{ij} = k_i + \sum_{n \neq i}^{N} \omega_{ni}, \quad i = j \text{ и } \mathbf{A}_{ij} = -\omega_{ij}, \quad i \neq j. \quad (3)$$

The way of solving the set of equations (2) is well known: introduce a symmetrical matrix **A**' whose diagonal elements are the same as in the matrix **A** and whose nondiagonal elements are defined as $\mathbf{A}'_{ij} = -(\omega_{ij}\omega_{ji})^{1/2}$. The solution will then appear as

$$c_i = f_i^{1/2} \sum_{n=1}^{N} q_n \mathbf{B}_{in} \mathrm{e}^{-r_n t}, \quad (4)$$

where f_i is the fraction of the ith state in the equilibrium distribution of states, r_n are the eigenvalues of the matrix **A**' (numbered in increasing order), **B** is the matrix of the eigenvectors (normalized) corresponding to the eigenvalues of the matrix **A**', and the coefficients q_n are determined from the following initial condition: at $t = 0$, $c_i(0) = a_i$ (the initial distribution of states).

The total concentration c as a function of time is found by summation of Eq. (4) over all states:

$$c = \sum_{i=1}^{N} f_i^{1/2} \sum_{n=1}^{N} q_n \mathbf{B}_{in} \mathrm{e}^{-r_n t}. \quad (5)$$

The equation for the average rate constant $\langle k(t) \rangle$ is obtained by simple summation of Eq. (1):

$$\langle k(t) \rangle = \sum_{i=1}^{N} k_i c_i / c. \quad (6)$$

Note that, in the general case of more complex reactions, there can be eigenvalues with an imaginary part and, accordingly, chemical oscillations [13]. However, a polychronous reaction is described by the symmetrical matrix **A**', whose eigenvalues are all real, like the eigenvalues of any symmetrical matrix with real elements.

Equation (5) shows that the kinetic curve of a polychromous reaction with or without spectral diffusion can be represented as the sum of exponentials. Thus, the case of a reaction with spectral diffusion and with a set of rate constants k_i, can be reduced to the familiar case of a reaction without diffusion and with a set of rate constants r_n [9]. Therefore, the results obtained for a reaction without state mixing [9] are applicable to polychromous reactions with state mixing.

Another specific feature of polychromous reactions with spectral diffusion is the possibility of a quasi-steady-state regime. It follows from Eqs. (4) and (5) that, at sufficiently long reaction times, only the term with the smallest eigenvalue r_1 will be significant in the sum of exponentials. The state concentration ratio c_i/c in Eq. (6) will stop changing, and the reaction kinetics will obey an exponential law.

In a reaction without state mixing, the reaction kinetics also becomes exponential at long times, but for another reason: only the state with the smallest rate constant k_1 remains at the latest stages of the reaction because of the successive "burnout" of more reactive states. Rate constants in real systems typically vary over a wide range of several orders of magnitude. Therefore, the fraction of the least active state is small and the kinetics of a reaction without spectral diffusion remains nonexponential until very high conversions.

CONTINUOUS REACTION STATE DISTRIBUTION MODEL

If the reactivity-determining state of the reacting particle includes a large number of molecules from its cage environment, then small displacements or rotations of one of them will cause insignificant changes in this state and in the corresponding rate constant. A small hop of the particle into an adjacent cage will also change the rate constant only slightly. We will assume that the molecule hops mainly from the state C_i into the nearest states C_{i-1} and C_{i+1} with equal probabilities of $\omega_i/2$. The kinetics equation (1) will then appear as

$$\frac{\mathrm{d}c_i}{\mathrm{d}t} = -k_i c_i + \frac{1}{2}(\omega_{i-1} c_{i-1} - 2\omega_i c_i + \omega_{i+1} c_{i+1}), \quad i = 2, 3, \ldots, N-1, \quad (7)$$

$$\frac{\mathrm{d}c_1}{\mathrm{d}t} = -k_1 c_1 + \frac{1}{2}(\omega_2 c_2 - \omega_1 c_1), \quad (8)$$

$$\frac{\mathrm{d}c_N}{\mathrm{d}t} = -k_N c_N + \frac{1}{2}(\omega_{N-1} c_{N-1} - \omega_N c_N). \quad (9)$$

Now let us consider the case of $\omega_i = \omega = \text{const}$. When the distance between the adjacent states, $\Delta = k_{i+1} - k_i$,

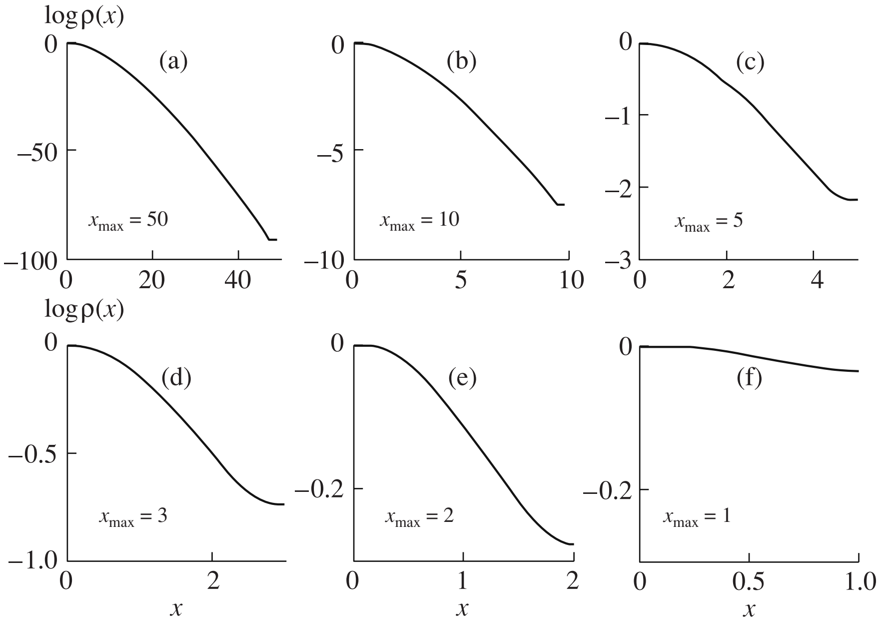

Fig. 1. State distribution ρ(x) in the (a–e) quasi-steady-state and (f) kinetic regimes at maximum dimensionless rate constant values of x_{max} = (a) 50, (b) 10, (c) 5, (d) 3, (e) 2, and (f) 1.

is sufficiently short, we can pass to a continuous distribution density $\rho(k)$ such that $c_i = \rho(k_i)\Delta$. By the Taylor expansion of $\rho(k_i - \Delta)$ and $\rho(k_i + \Delta)$ in the vicinity of k_i up to the terms of the second order of smallness (Δ^2), we obtain, from Eqs. (7)–(9), the basic kinetic equation

$$\frac{\partial\rho(k)}{\partial t} = -k\rho(k) + D\frac{\partial^2\rho(k)}{\partial k^2}, \quad D = \frac{\omega\Delta^2}{2} \tag{10}$$

subject to the boundary conditions

$$\left.\frac{\partial\rho}{\partial k}\right|_{k = k_{min}} = \left.\frac{\partial\rho}{\partial k}\right|_{k = k_{max}} = 0, \tag{11}$$

where D is the spectral diffusion coefficient and k_{min} and k_{max} are the minimum and maximum rate constants, respectively. It can readily be seen that Eq. (10) is the Einstein–Smoluchowski diffusion equation, which is widely used in the description of reactive diffusion [14]. In the case considered here, this equation describes reactive diffusion not in the physical space, but in the rate-constant space, and differs from the conventional diffusion equation in that its spatial variable is in explicit form. It is very difficult to solve this equation in a way suitable for analysis [10]. For this reason, the problem was solved in two steps. The first step is an analysis of the steady-state solution, which can be obtained in comparatively simple form, and the second step is numerical search for unsteady-state solutions.

Let us first consider fairly long reaction times, when, as follows from Eq. (5), all states begin to disappear with the same quasi-steady-state rate constant k_q, which is equal to the smallest eigenvalue r_1:

$$\frac{\partial\rho(k)}{\partial t} = -k_q\rho(k). \tag{12}$$

Thus, in the quasi-steady-state regime,

$$D\frac{\partial^2\rho}{\partial k^2} = (k - k_q)\rho. \tag{13}$$

Let us introduce the dimensionless variable x:

$$x = \frac{k - k_{min}}{D^{1/3}}, \quad x_q = \frac{k_q - k_{min}}{D^{1/3}}.$$

This will transform Eq. (13) into the familiar Airy equation [15, 16]:

$$\frac{\partial^2\rho}{\partial x^2} = (x - x_q)\rho. \tag{14}$$

Its general solution appears as

$$\rho(x) = \alpha_1[\mathrm{Ai}(x - x_q) + \alpha_2\mathrm{Bi}(x - x_q)], \tag{15}$$

where Ai(x) and Bi(x) are the Airy functions of the first and second kinds. α_1 and α_2 are constants, α_1 is determined by $\rho(x)$ normalization, and α_2 and x_q are determined from the boundary conditions (11).

The quasi-equilibrium distributions calculated using Eq. (15) for several x_{max} values are plotted in Fig. 1. In the case of a narrow distribution ($x_{max} < 1$), when D is large, there is no concentration gradient in the k-space, all states mix rapidly, and the distribution is equilibrium. However, starting at $x_{max} = 2$, an appreciable gra-

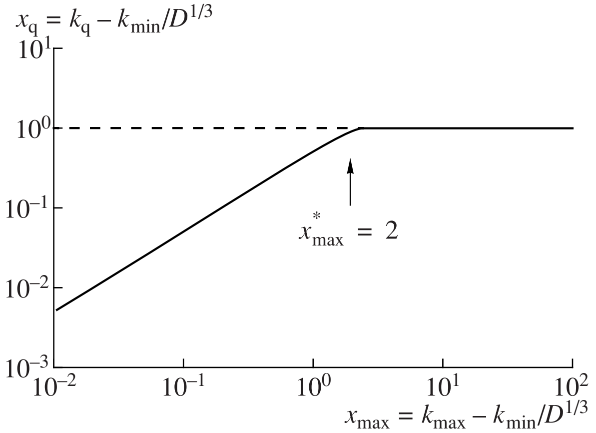

Fig. 2. Relationship between the quasi-steady-state rate constant k_q and the spectral diffusion coefficient D.

dient appears and the reaction passes to the quasi-steady-state regime. Physically, this regime is simply a diffusion regime in the rate constant k-space. In this regime, a boundary layer appears near the left edge of the rate constant spectrum and its shape remains almost invariable as x_{max} is further increased.

The dependence of quasi-steady-state rate constant x_q on x_{max} is plotted in Fig. 2. At equilibrium (at $x_{max} < 1$), x_q is proportional to x_{max} ($x_q = x_{max}/2$), so k_q is equal to the equilibrium rate constant. At quasi-equilibrium ($x_{max} > 2$) $x_q = 1.019$ (the first zero of the first derivative of $\mathrm{Ai}(x)$) and is independent of the distribution width x_{max}. Hence, the averaged rate constant and the spectral diffusion coefficient are related as follows:

$$k_q = \begin{cases} \dfrac{k_{max} + k_{min}}{2}, & \sqrt[3]{D} > \dfrac{k_{max} - k_{min}}{2} \qquad (16) \\[2ex] k_{min} + \sqrt[3]{D}, & \sqrt[3]{D} \le \dfrac{k_{max} - k_{min}}{2}. \qquad (17) \end{cases}$$

As D decreases, the quasi-steady state regime terminates once k_q has decreased to a value of the order of k_{min}, when spectral diffusion does not exert any significant effect on the reaction. Thus, the quasi-steady-state regime has the following limits:

$$k_{min}^3 \le D \le \left(\frac{k_{max} - k_{min}}{2}\right)^3. \qquad (18)$$

It follows from (18) that, at $k_{max} \gg k_{min}$, the quasi-steady-state regime exists in a wide range of diffusion coefficients.

It is clear from Eq. (17) that, in the case of a broad distribution, when k_{min} is very small, the quasi-steady-state rate constant of the polychronous reaction is almost completely determined by spectral diffusion:

$$k_q = D^{1/3}. \qquad (19)$$

When in the boundary layer, the particle travels, during the reaction time (which is equal to $1/k_q$), the distance $(2D/k_q)^{1/2} = 2^{1/2}k_q$, which is comparable with the thickness of this layer. Therefore, in the time interval between the reaction events, the molecule can visit any point of the boundary layer. This ensures mixing necessary for exponential-law kinetics to take place and for the independence of the reaction of its history.

For numerical calculation of the unsteady-state kinetics using Eq. (10), we will introduce the dimensionless time $t^* = tD^{1/3}$ and the reduced function $\rho^*(x, t) = \rho(x, t)\exp(k_{min}t)$. Equation (10) will then appear as

$$\frac{\partial \rho^*(x, t^*)}{\partial t^*} = -x\rho^*(x, t^*) + \frac{\partial^2 \rho^*(x, t^*)}{\partial x^2}.$$

Its general solution, which can be obtained by separation of variables, is as follows:

$$\rho^*(x, t^*) = \sum_{n=1}^{\infty} G_n \exp(-r_n t^*)$$
$$\times \left[\mathrm{Ai}(x - r_n)\frac{\partial \mathrm{Bi}(-r_n)}{\partial x} - \mathrm{Bi}(x - r_n)\frac{\partial \mathrm{Ai}(-r_n)}{\partial x}\right],$$

where the constant coefficients G_n are derived from the initial conditions and the eigenvalues r_n are derived from the boundary conditions (11). As follows from the general properties of the Sturm–Liouville problem [16], all r_n are positive real numbers.

Figure 3a shows the distribution $\rho(x)$ calculated using Eq. (10) for a monodisperse initial state distribution (curve *1*). At the initial stages of the reaction ($t^* = 1$), spectral diffusion disorders the initial distribution (curve *2*), generating states with both smaller and larger rate constants. At long reaction times of $t^* > 3$, a quasi-steady-state distribution forms (curve *3*), whose shape does not depend on time any longer and is determined by the equilibrium between the diffusion and reaction processes in the boundary layer.

Using the distributions calculated by Eq. (10), it is possible to calculate the current concentration $c(t)$ and the average rate constant $\langle x(t)\rangle$:

$$c(t) = \int_{x_{min}}^{x_{max}} \rho(x, t)\mathrm{d}x, \qquad (20)$$

$$\langle x(t)\rangle = \int_{x_{min}}^{x_{max}} x\rho(x, t)\mathrm{d}x. \qquad (21)$$

The current concentration data (c) calculated using Eq. (20) for different initial distributions are plotted in Fig. 3b. Curve *1* represents the case in which the initial rate constant is $\langle x(0)\rangle = 0.1$ and is below the quasi-steady-state value $x_q = 1$. In this case, spectral diffusion has the most pronounced effect on the reaction kinetics, causing an increase in the rate constant during the process, a phenomenon unnatural for first-order reactions.

If the reaction starts from any distribution with an initial rate constant of $\langle x(0)\rangle = x_q = 1$, the relaxation of the system to the quasi-steady-state distribution will not be accompanied by noticeable changes of the rate constant and the kinetics will obey the exponential law (Fig. 3b, curve *2*). If the initial rate constant is larger than x_q, the kinetic curve will take a shape typical of polychronous reactions (Fig. 3b, curve *3*).

The current rate constant data ($\langle x(t)\rangle$) data calculated using Eq. (21) for different initial distributions are plotted in Fig. 3c. Clearly, the reaction kinetics depends strongly on the initial conditions. However, after some period of time, the system comes to a quasi-steady state independent of the initial conditions. This period of time also depends strongly on the initial distribution and lies in the range of $t^* = 0$–2. For this reason, the quasi-equilibrium time in this system characterizes the initial state distribution rather than spectral diffusion.

DISCUSSION

The above results demonstrate that a polychronous reaction can show much diversified kinetics at its early stages: the average rate constant can either decrease or increase, depending on the initial state distribution. Of interest is the case in which the rate constant is almost invariable throughout the reaction. This will be observed when the initial rate constant is equal to k_q. This intuitively understandable inference was not verified analytically. It was obtained by numerical integration of Eq. (10) for different initial distributions with $\langle x(0)\rangle = 1$. According to these calculations, the current rate constant varies slightly (within a few percent) with reaction time; however, these variations are undetectable at conventional degrees of experimental accuracy.

The strong dependence of the quasi-equilibrium time on the initial state distribution is a nontrivial finding. For more general systems, the relaxation times are estimated as a function of the reaction constants [13].

An important feature of polychronous reactions controlled by spectral diffusion is the establishment of a quasi-steady state regime characterized by exponential-law kinetics and by a quasi-steady-state rate constant independent of the initial reaction conditions. The physical essence of this phenomenon is as follows. If the states of the reacting particles are initially distributed in a wide rate constant range such that the diffusion time is much shorter than the reaction time, then, due to the reaction taking place, the distribution will begin to "burn out" from the side of large rate constants, as if there were no diffusion at all. As a consequence, the distribution will narrow, and, accordingly, the time of diffusion over the remaining states will shorten. This process will continue until the diffusion time is equal to the reaction time. As a result, the reaction and spectral diffusion processes will be equilibrated in the narrow rate constant range of the final distribution.

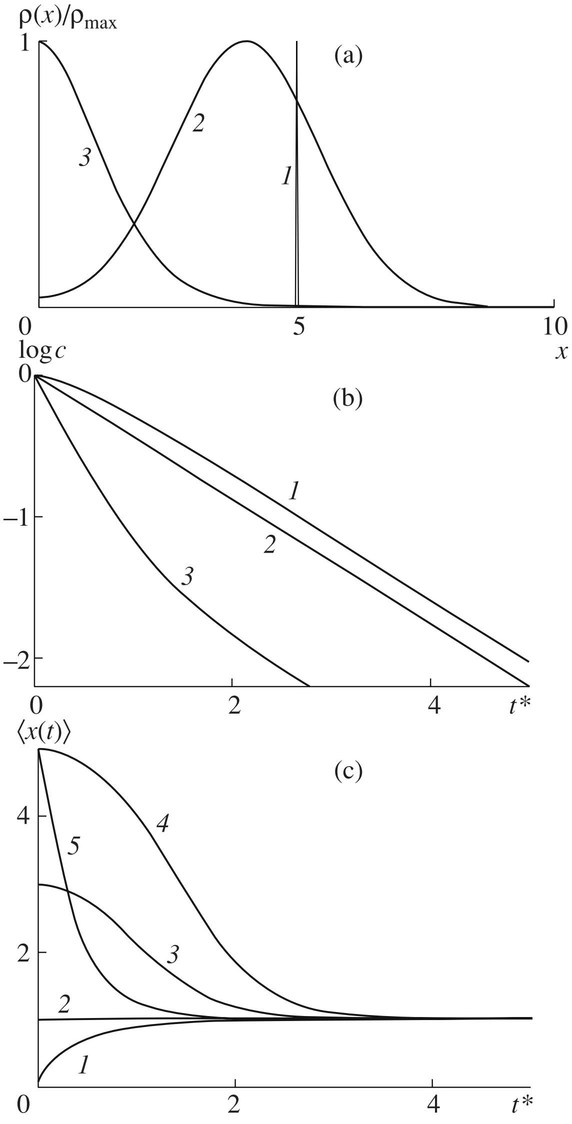

Fig. 3. Unsteady-state kinetics at a maximum dimensionless rate constant of $x_{max} = 10$. (a) State distributions $\rho(x)$ at $t^* =$ (*1*) 0, (*2*) 1, and (*3*) >4. (b) Kinetic curves for a monodisperse initial state distribution with $\langle x\rangle =$ (*1*) 0.1, (*2*) 1, and (*3*) 3. (c) Time dependence of the averaged dimensionless rate constant for (*1–4*) monodisperse initial state distributions with $\langle x\rangle =$ (*1*) 0.1, (*2*) 1, (*3*) 3, and (*4*) 5 and (*5*) a rectangular initial state distribution with $\langle x\rangle = 5$.

An inherent property of polychronous reactions, particularly those occurring at low temperatures, is strong unsteadiness, such that the process occurs in an unsteady-state regime over a reactant concentration range as wide as two orders of magnitude [1]. Therefore, the determination of the quasi-steady-state rate constant can be a complicated problem at low concentrations, when the measurement error is much larger. In this case, changing the initial conditions (for example, by enriching the state distribution with less reactive states) can modify the kinetic curves so as to increase the reactant concentrations in the quasi-steady-state regime.

As was demonstrated above, the kinetic curves of polychronous reactions with and without spectral diffusion may have the same shape, so it is difficult to judge the role of spectral diffusion from the reaction kinetics. Additional information from independent experiments is necessary here. Spectral diffusion must be manifested most clearly in kinetic curves in which the rate constant increases with time. This is the case when, at the initial point in time, all particles are in low-reactivity states with rate constants smaller than k_q. In this case, the establishment of an equilibrium generates more active states, thus raising the average rate constant.

The corresponding kinetic curve will be described by a sum of exponentials containing terms with both positive and negative coefficients. It is interesting that this kind of kinetics was observed in naproxen fluorescence decay [17]. The negative values of the distribution function derived from kinetic data cannot be accounted for in the framework of the existing understanding of polychronous reactions, but they can readily be explained by the effect of spectral diffusion. Initially, the probability of the naproxen singlet being deactivated is below its steady-state value. In the course of the reaction, it increases up to the steady-state value as a result of spectral diffusion.

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REFERENCES

1. Gol’danskii, V.I., Trakhtenberg, L.I., and Flerov, V.N., *Tunnel’nye yavleniya v khimicheskoi fizike* (Tunneling Phenomena in Chemical Physics), Moscow: Nauka, 1986.
2. Emanuel, N.M. and Buchachenko, A.L., *Khimicheskaya fizika molekulyarnogo razrusheniya i stabilizatsii polimerov* (Chemical Physics of the Molecular Destruction and Stabilization of Polymers), Moscow: Nauka, 1988.
3. Bagdasar’yan, Kh.S., *Kinetika rekombinatsii v zhidkoi srede* (Recombination Kinetics in Liquid Media), Moscow: Nauka, 1989.
4. Roginskii, S.Z., *Geterogennyi kataliz* (Heterogeneous Catalysis), Moscow: Nauka, 1979.
5. Ghiggino, K.P., Roberts, A.J., and Phillips, D., *Adv. Polym. Sci.*, 1981, vol. 40, p. 69.
6. Plonka, A. and Paszkiewicz, A., *Chem. Phys.*, 1996, vol. 212, no. 11, p. 1.
7. Barashev, P.P., *Khim. Fiz.*, 2001, vol. 20, no. 2, p. 34.
8. Liu, Y.S. and Ware, W.R., *J. Phys. Chem.*, 1993, vol. 97, no. 22, p. 5980.
9. Margolin, A.L., *Kinet. Katal.*, 2003, vol. 44, no. 4, p. 495 [*Kinet. Catal.* (Engl. Transl.), vol. 44, no. 4, p. 450].
10. Goldanskii, V.I., Kozhushner, M.A., and Trakhtenberg, L.I., *J. Phys. Chem. B*, 1997, vol. 101, p. 10 024.
11. Eyring, H., Lin, S.H., and Lin, S.M., *Basic Chemical Kinetics*, New York: Wiley, 1980.
12. Lin, S.H., *J. Chem. Phys.*, 1972, vol. 56, no. 8, p. 4165.
13. Cheresiz, V.M. and Yablonskii, G.S., *React. Kinet. Catal. Lett.*, 1983, vol. 22, nos. 1–2, p. 69.
14. Frank-Kamenetskii, D.A., *Diffuziya i teploperedacha v khimicheskoi kinetike* (Diffusion and Heat Transfer in Chemical Kinetics), Moscow: Nauka, 1967.
15. Landau, L.D. and Lifshits, E.M., *Kvantovaya mekhanika* (Quantum Mechanics), Moscow: Fizmatlit, 1962.
16. Zaitsev, V.F. and Polyanin, A.D., *Spravochnik po obyknovennym differentsial’nym uravneniyam* (Handbook of Ordinary Differential Equations), Moscow: Fizmatlit, 2001.
17. Sadlej-Sosnowska, N. and Siemiarczuk, A., *J. Photochem. Photobiol. A: Chem.*, 2001, vol. 138, no. 1, p. 35.