

Many reactions in solids and liquids are diffusion-controlled. The reactants are usually either defects of two different types A and B (in a solid, for example, a pair of radiation-created Frenkel defects, i.e., vacancies, and interstitial atoms recombining in a reaction $A + B \rightarrow C$), or electronic excitations (excitons) and energy acceptors that play the role of sinks (reaction $A + B \rightarrow B$). The reactants A and B are often significantly correlated in space (for example, as a consequence of the mechanism of creation of a Frenkel pair by radiation), and this influences the kinetics of the reaction between them.

Currently, there are two different approaches to the theory of diffusion-controlled reactions: the so-called symmetric and nonsymmetric approaches. The symmetric approach was first proposed in the work of Antonov-Romanovskii [1] (see also [2]), and the nonsymmetric approach was first proposed in the work of Waite [3] (see [4-6]). Both theories are limited to the two-particle level of kinetic description, i.e., they use one-particle distribution functions (concentration of reactants c_A and c_B) and two-particle distribution functions (pair densities of number of particles) of reactants of the same type (X_1 and X_2) and a different type (Y). The breaking of the chain of equations in both theories is based on the use of the superposition approximation of Kirkwood for three-particle correlations. Both theories also ignore correlations of reactants of the same type, and it is assumed that $X_{1,2} = c^2$ ($c_A = c_B = c$).

The difference between these two approaches is that the symmetric approach uses a single function of the distribution of reactants differing in type (Y), and the nonsymmetrical approach uses two such functions, separately for the so-called initially correlated pairs (Y_C) and the uncorrelated pairs (Y_U). In contrast to the concept of correlated distribution, in which the degree of correlation is unambiguously characterized by the deviation of the distribution function from its asymptotic value c^2 (positive space correlation $Y > c^2$, negative $Y < c^2$), the concept of initially correlated or uncorrelated pairs is extremely indeterminate as to content. Actually, it is not clear what principle may be used in considering an arbitrary pair of defects as correlated; i.e., what is the quantitative criterion? Since space correlations of reactants are determined largely by the mechanism of their formation, each genetic Frenkel pair is considered as correlated, i.e., as being formed in a single act of generation.

The distribution of defects in genetic pairs is described by the function $f(r)$ ($4\pi \int_0^\infty fr^2 dr = 1$).

On the assumption of a random distribution of genetic pairs in space, it is stated that with $t = 0$, $Y = c_0 f + c_0^2$, where c_0 is the initial concentration. The term $Y_C = c_0 f$ is termed the distribution function of the correlated pairs, and $Y_U = c_0^2$ the distribution function of the uncorrelated pairs [3, 5, 6].

The existence of two theories to describe a single reaction is obviously unsatisfactory. Currently, in interpreting experiments, both theories are used, often simultaneously [7]. The present work has been aimed at demonstrating the correctness of a refined symmetric approach in the example of the reaction $A + B \rightarrow C$ ($c_A = c_B = c$).

SYMMETRIC APPROACH

Recently we proposed a generalized theory that takes into account (within the framework of the two-particle approximation) the correlation of partners of the same type (A-A and B-B) and also of different types (A-B) [8-10]. In the approximation of instantaneous annihilation with an explicit radius of reaction R_a , the kinetic equations have the form

$$\partial c / \partial t = -4\pi R_a^2 D Y' (R_a) = -\Phi, \quad (1)$$

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$$\frac{\partial X_v}{\partial t} = 2D_v \nabla^2 X_v - \frac{\Phi X_v}{r R_a c^3} \int_{|r-R_a|}^{r+R_a} Y(r') r' dr', \quad (v = 1, 2), \quad (2)$$

$$\frac{\partial Y}{\partial t} = D \nabla^2 Y - \frac{\Phi Y}{r R_a c^3} \int_{r-R_a}^{r+R_a} X(r') r' dr', \quad (r > R_a), \quad (3)$$

where $Y(r \leq R_a) = 0$; $Y'(r) = \partial Y / \partial r$; Φ is the flux of reactants through the sphere of annihilation; $X = 1/2(X_1 + X_2)$; D_v are the partial diffusion coefficients; $D = D_A + D_B$. The characteristic feature of the system of equations (1)-(3) is interdependence of the space correlation of like and unlike partners, i.e., the correlation of some partners gives rise to a "compensating" correlation of the others [9, 10]. Strong initial space correlation of unlike partners corresponds to values of the distribution function $Y \gg c^2$ with small values of r . This correlation leads to the appearance of a negative correlation of like defects ($X_v < c^2$) in the same region of coordinates. The existence of a region $0 < r < R_a$, where $Y \equiv 0$, in contrast, is responsible for positive correlation $X_v > c^2$ with large values of t .

For the many-body problem, the only reliable evaluation of the character of the assumptions that have been made is a comparison with certain problems that can be solved exactly (test problems). As a test in this particular case, we can use a known solution for monomolecular recombination [2]. We will examine the correlated distribution of reactants in pairs with a characteristic distance in the pairs R_0 and a minimal distance between pairs $R \gg R_0$. Such a distribution can be established with low concentrations of reactants. For times $t \ll R^2/D$, the recombination kinetics are completely determined by the process in the pairs (stage of correlated annealing), and when $R_0 \rightarrow R_a$, the recombination is completely monomolecular. With $t \ll R^2/D$, the terms of the equations describing three-particle correlations must vanish for $r < R$. This requirement is fulfilled in Eq. (3), since in the model distribution, $X_v \equiv 0$ for $r < R$ (the distance between like defects on the order of the distance between pairs) with $t = 0$, and nonzero values of X_v are provided only by the diffusion mechanism. Dropping the last term in Eq. (3) and taking (1) into account, we obtain the known kinetics of monomolecular recombination. The test problem, on the one hand, confirms the reliability of Eqs. (1)-(3), and on the other hand, indicates the urgent need to account for correlations of monotypical reactants as well.

In the approximation $X_v = c^2$, Eqs. (1) and (3) reduce to the equations of Antonov-Romanovskii [1]: Eq. (1) remains the same as before, but in place of (3) we have

$$\partial Y / \partial t = D \nabla^2 Y - 2\Phi Y / c. \quad (4)$$

As already known [2, 5], for the test problem with $R_0 \rightarrow R_a$, these equations do not give complete monomolecular recombination. The reason is understandable; the last term in (4) for $t \ll R^2/D$ does not vanish, and it gives fictitious three-particle correlations. Consequently, the source of error in Eq. (4) is the approximation $X_v = c^2$, which is clearly unfortunate in the present case. In [5], however, an incorrect conclusion was drawn, that the errors of the system of equations (1) and (4) are related to the symmetry of the approach. It is stated that a correct solution of the problem is possible only by introducing the concepts of correlated and uncorrelated pairs, i.e., by accounting for "our" and "their" reactants in the kinetic equations.

NONSYMMETRIC APPROACH

Waite's system of equations [3] consists of three equations

$$\partial c / \partial t = -(\Phi_c + \Phi_u), \quad (5)$$

$$\frac{\partial Y_c}{\partial t} = D \nabla^2 Y_c - \Phi_u \frac{2Y_c}{c}, \quad (6)$$

$$\frac{\partial Y_u}{\partial t} = D \nabla^2 Y_u - (\Phi_c + \Phi_u) \frac{2Y_u}{c}. \quad (7)$$

The first term in (5) describes a monomolecular stage and the second term a bimolecular stage of recombination; here,

$$\Phi_c = 4\pi R_a^2 D Y'_c(R_a), \quad \Phi_u = 4\pi R_a^2 D Y'_u(R_a). \quad (8)$$

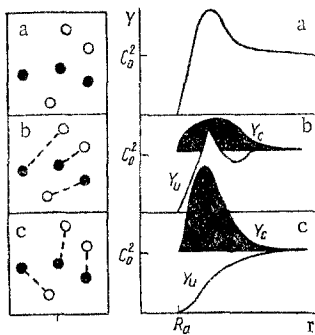


Fig. 1. Ambiguity of assignment of initial conditions in nonsymmetric theory. On the left: a) is a certain spatial distribution of reactants, the assignment of which is more than sufficient for a description of the recombination kinetics at the two-particle level; b, c) two possible methods for breaking up the reactants into genetic pairs. On the right: pair functions of unlike reactants Y corresponding to this distribution, with Y in cases b and c being broken up into components Y_c and Y_u .

Traditionally, the system (5)-(7) is solved with the simplest initial conditions

$$Y_c = c_0 f, \quad Y_u = c_0^2. \quad (9)$$

In the limit $c_0 \rightarrow 0$, the solution of Waite's equations corresponds to monomolecular recombination [5], such that Waite's theory is entirely satisfactory and is more correct than the theory based on the system of equations (1) and (4). Thus, by varying the form of the function $f(r)$ in (9), it is possible in principle to match theoretical curves to experimental curves [1]. However, the possibility of such an approximation of results still does not mean that the theory is true. We are alerted by the insensitivity of the results of Waite's theory to the approximation $X_v = c^2$.

The nonsymmetric theory [3] stands out sharply among the known theories of physical kinetics. The following rules are generally accepted in the known theories: The distribution functions describe the probability of finding particles in volume elements of the phase space close to selected points in this space; the method of assigning these points is not dependent on the processes taking place in the system; the physical processes determine only the specific form of the kinetic equations describing the evolution of the system. The pair formation of Frenkel defects in a single act of generation characterizes only the process of accumulation of defects, and it cannot serve as a basis for changing the definition of the distribution functions. Violation of these rules leads to a number of paradoxes that have not been noted previously in the literature.

Paradox of Incompleteness of Information. We doubt the possibility of assigning initial conditions of the type of (9) for Eqs. (5)-(7). Waite's theory, the same as theories based on Eqs. (1)-(3) or (1) and (4), pretends to describe the influence of the initial spatial distribution of defects on the overall picture of annealing. In order to refute this, we will examine the following problem. In a model level, let the spatial distribution of defects be completely assigned, i.e., let the coordinates of all defects be known (see Fig. 1, left-hand side). Such information can be obtained by computer-modeling of the defect accumulation process. We can also examine an ordered distribution of reactants (for example, with a lattice of the NaCl type). For theories based on Eqs. (1)-(3) or (1) and (4), a knowledge of the coordinates of all defects is more than sufficient for calculation of the distribution functions for c , Y , and X_v by statistical treatment of the information, but this knowledge is not completely necessary, since a two-particle level of description uses only part of the total information (which is also a source of error in these theories). The correct probability description assumes the existence of an unambiguous link between the distribution of defects and the distribution functions.

For Waite's theory, complete information on the initial defect structure (Fig. 1a) is insufficient to formulate the initial conditions. Waite's distribution functions Y_c and Y_u

cannot be calculated separately, as for Y in (3), since these distribution functions carry additional information on the prehistory of the creation of the given structure. The mathematical nature of the insufficiency of information is understandable. At the two-particle level of description, the complete set of distribution functions is c , Y , and X_V . The approximation $X_V = c^2$ reduces the number of independent functions and hence the number of independent kinetic equations, down to two. Since correlated pairs of reactants are indistinguishable from uncorrelated pairs in their physical properties, the possibility of an unambiguous breakup of Y into parts Y_C and Y_U simply does not exist. Consequently in the system (5)-(7), the number of equations (three) is greater than the true number of independent distribution functions (two). The noted insufficiency of information in Waite's theory is masked by the completely unjustified postulate (9).

Paradox of Labels. The process of accumulation and annealing of defects is a random Markov process. For a Markov process, the probability of a transition from an initial state to a final state (from one defect structure to another) is completely determined by these states and is independent of what path was taken in creating the initial state, i.e., it is independent of the prehistory. From a physical point of view, the initial state of the system is completely and unambiguously defined by the distribution (coordinates) of the reactants (Fig. 1). In Waite's approach, a difference between the pairs of reactants (defects) is introduced, based not on their physical properties, which naturally cannot be distinguished, but on "kinship relations" depending on whether the partners of a given pair were created in a single act of generation or in two different acts. Thus, what has actually been introduced into the theory is a "demon" that follows the history of creation of the reactant distribution and applies labels to the genetic pairs.

In Waite's approach, as can be seen from Fig. 1, the assignments of the initial states without labels (Fig. 1a) is insufficient; sufficient information is obtained by means of the "demon" (Fig. 1b), and on the basis of this information, the distribution functions Y_C and Y_U are calculated, assigning the initial conditions for Eqs. (5)-(7). Let us now represent the labels in an arbitrary manner (Fig. 1c) and again calculate the initial conditions of Y_C and Y_U . Even though, from the physical point of view, the spatial distribution of reactants (see Figs. 1b and 1c) is unchanged, Eqs. (5)-(7) give different solutions in these two cases, and this contradicts the concept of a Markovian character of the recombination process.

Thus, in Waite's theory, the breakup of Y into two parts $Y = Y_C + Y_U$ not only fails to offer the possibility of calculating each of the quantities Y_C and Y_U separately, but it also makes it impossible to obtain correct kinetic equations. It should be emphasized that these shortcomings of the theory are not a consequence of any sort of mathematical approximation in splitting up the hierarchy of kinetic equations in [3]. The reason for these shortcomings is hidden in the physical assumption that a genetic pair, even though identity is ascribed to particles of monotypical reactants, can still be distinguished among all possible pairs. It is specifically this internal contradictory assumption that replaces mathematical apparatus suitable for a description of a system of identical particles (symmetric theory) by another apparatus in which identity is "preserved," but pairs of unlike types of particles are given individual characteristics. Violation of the physical principle of identity of particles in statistical physics leads to the well-known Gibbs paradox, and the above-noted paradoxes are essentially kinetic analogs of this paradox.

CONCLUSIONS

Equations (1)-(3), as more general equations, offer the possibility of establishing the region of applicability of the simplified equations (1) and (4). These simplified equations are inapplicable in the case of strong correlation of reactants, since the assumption $X_V = c^2$ is violated. On the other hand, even with the initial condition $X_V = c^2$, Eqs. (1) and (4) are incorrect for long periods of elapsed time. In this case, the recombination-generated spatial correlations of reactants $X_V \gg c^2$ and $Y \ll c^2$, reflecting the timewise formation of dynamic accumulations of monotypical reactants, do not correspond to the more quasi-stationary reaction constant $K_0 = 4\pi DR_\alpha$. General relationships for the long-time asymptotic of the reaction $A + B \rightarrow C$ were established in [11, 12], in particular, $c \sim t^{-3/4}$ when $t \rightarrow \infty$. The asymptotic solution Eqs. (1)-(3) that we obtained in [13] supports the results of [11, 12] and gives us grounds for applying these equations in the absence of explicit limitations on them. On the other hand, the nonsymmetric approach [3-6] has shortcomings that cannot be eliminated.

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