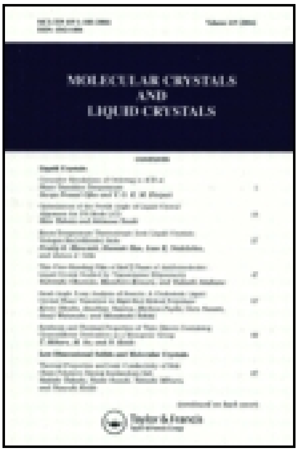

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Dispersive Transport and Reactivity of Charge Carriers in Disordered Solids

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DISPERSIVE TRANSPORT AND REACTIVITY OF CHARGE CARRIERS IN DISORDERED SOLIDS

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Abstract The percolation approach to the diffusion of charge carriers in disordered systems is applied to the analysis of their reactivity in the case, when the reaction rate is controlled by the dispersive transport of reactants. Expressions for quantities, which govern kinetics of both bulk and geminate elementary processes, have been derived. Our theoretical results are found to be in agreement with experimental observations and show that the nonregularity of the disposition of traps (so-called bond disorder) as well as their distribution in the energy depth (so-called site disorder) affect kinetics of elementary processes mentioned above.

INTRODUCTION

The reactivity of charge carriers in disordered solids are usually treated on the basis of a formally borrowed method[1,2] employed in describing the electron transfer in liquids, where the hop frequency for the motion of reactants is believed to be time independent giving rise to the ordinary Gaussian mode of their transport. Since in the framework of such a method the diffusion coefficient, D, is usually considered as the phenomenological parameter, the apparent rate constant, k_a, for bulk reactions can easily be calculated by solving the Smoluchowski-type equation for the distribution of reacting species in space and in time, t. As has been shown[3-8], for any possible reaction mechanisms the Gaussian diffusion approach yields

$$k_a(t) = 4\pi DR[1+R/(\pi Dt)^{1/2}]. \tag{1}$$

Here R is the reaction radius of reactants which depends on the "genuine" rate constant, k, on physical interaction between active species, on the sum of the radii, R_0, and on D if we are dealing with semiclassical or quantum mechanisms of the reaction.

Eq.(1) seems to be consistent with experimental data on time evolution of electron transfer processes in liquids, but is not adequate to describe the reaction kinetics in disordered solids[9]. Numerous observations indicate that in the latter case $k_a(t)$ should decrease with increasing t following the empirical law[9]

$$k_a = Bt^{-1+\alpha}, \tag{2}$$

where B and α constants ($0<\alpha\leq 1$).

The physical origin of the discrepancy results from neglecting the non-Gaussian (dispersive) mode of the diffusion motion of reactants in condensed media[10-12] implied in the derivation of Eq.(1). For such a mode the dispersion of the spatial distribution of charge carriers is not proportional to t [12]. Because of this fact such a motion of particles through the disordered medium is often called dispersive transport.

The important physical factors which account for the anomalous dispersion of carriers diffusion in disordered solids are the lack of regularity in positions of traps visited by these particles in the course of their random walks (so called bond disorder) and the distribution of trapping sites on their energy depth E (so called site disorder)[10,11]. Here we present some theoretical results, which show that these types of disorder can also be responsible for unusual kinetic regularities of charge carriers reactions in solids.

DIFFUSION OF CHARGE CARRIERS AND THEIR REACTION KINETICS

Following our previous analysis[14,15] we consider the "trap-to-trap" motion of carriers in disordered media in the framework of the percolation theory[13]. Such an approach permits us to separate all traps into two groups. The first group forms the so-called diffusion cluster (DC) responsible for the macroscopic transport of reactants and hence for the frequency of their random collisions. The second group, i.e. isolated centers (IC), plays the role of the sources and/or sinks for species moving along DC and therefore makes no direct contribution to the diffusion flow. Thus, from a microscopic point of view there are some preferential trajectories for the diffusion motion of charge carriers in disordered solids. The existence of such trajectories seems to be the principle distinction between diffusion in disordered and ordered media since in the latter case the mobility of any particle is always independent of the path.

To describe the behavior of reactants in the long-time limit within the framework of the model considered above we introduce the local concentration, $n(r,t)$, of "mobile" carriers (that is, belonging to DC) around their partner B and the concentration, $N(t)$, of charge carriers located on IC. The introduced quantities are related by

$$N(t) = \int_0^t \Phi(t-\tau)n(\tau)d\tau + N_0Q(t), \qquad (3)$$

where N_0 is the initial concentration of species at IC, $\Phi(t)$ and $Q(t)$ denote functions describing the rate of charge exchange between IC and DC, calculated in Refs.[14] and [15].

With a trivial modification of our previous results[14,15] we find that in the present case $n(r,t)$ satisfies the equation

$$\frac{\partial n}{\partial t} + \frac{\partial}{\partial t}\int_0^t \Phi(t-\tau)n(\tau)d\tau - \frac{D}{r^2}\frac{\partial}{\partial r}\left[r^2\left(\frac{\partial n}{\partial r} + \frac{r_c}{r^2}n\right)\right] + N_0\frac{\partial Q}{\partial t} = 0. \qquad (4)$$

Here $r_c = e^2/(\epsilon k_B T)$ is the Onsager distance, k_B is the Boltzmann constant, T is a temperature, e is the electron charge and ϵ is the dielectric constant.

The solution of Eq.(4) with different boundary and initial conditions allows to find quantities which characterize the kinetics of various elementary chemical reactions involving charge carriers. Typical examples will be considered in the next section.

RESULTS AND DISCUSSION

Geminate recombination

In this case the initial spatial distribution of carriers is given by

$$N_{tot}(0) = \frac{N_0 + n_0}{4\pi r_0^2}\delta(r - r_0), \qquad (5)$$

where $N_{tot}(0)$ and n_0 are the total concentration of carriers at t=0 and their initial concentration at DC, respectively. Furthermore, since the probability of finding reactant at long distances from its partner must tend to zero, one can write

$$n(\infty,t) = 0. \qquad (6)$$

Besides, n(r,t) should satisfy the following condition at $r = R_0$

$$4\pi R_0^2 D \left[\frac{\partial n}{\partial r} \bigg|_{R_0} + r_c n(R_0,t)/R_0^2 \right] = kn(R_0,t). \qquad (7)$$

The boundary value problem (4-7) can be solved by the Laplace transform method. This makes it possible to calculate the quantities which are of physical interest, in particular the rate of geminate recombination $R(t) = 4\pi R_0^2 kn(R_0,t)$ and the survival probability

$$\Omega(t) \square (4\pi/N_{tot}(0)) \int_0^\infty r^2[n(t) + N(t)]dr. \qquad (8)$$

For example, denoting the average frequency of charge transfer along DC by W_R and putting $U(x) = \exp(-r_c/x) + [Dr_c/(kR^2) - 1] \exp(-r_c/r_0)$, one gets

$$\Omega(t) = U(r_0)\, U(\infty)^{-1} \left[1 + \left(W_R/D\right)^{1/2} r_c U(\infty)^{-1} \left(W_R t\right)^{-\alpha/2}\right]. \qquad (9)$$

Here α is the dispersion parameter specified for different types of disorder in table I in terms of time $\tilde{t}$ appropriate for treating the given reaction as the essentially non-stationary process. Note that for geminate recombination $\tilde{t} \simeq r_c^2/D$ (see e.g.[16]) while, for instance, in the case of homogeneous reactions $\tilde{t} \simeq R_0^2/D$.

Thus, the survival probability decreases vs. time as a linear function of $t^{-\alpha/2}$. For $t \to \infty$ this quantity tends to the nonzero and finite limit which coincides with the well-known expression for the ultimate escape probability[16]. Besides, it has been shown that $R(t) \sim t^{-1+\alpha/2}$. These analytical findings agree with the decay law for the recombination luminescence in irradiated organic glasses (see e.g.[17,18]) and with results of a computer simulation study of geminate recombination[19,20].

TABLE I Expressions for dispersion parameter, α, in cases of side-disordered media (SDM) with exponential (EXP-D) and normal (NOR-D) energy distributions of traps.

Type of disorder	α
SDM with EXP-D	T/T_0
SDM with NOR-D	$\frac{1}{2}(k_BT/\sigma_E)^2 \ln[W_R\tilde{t}\sigma_E^2/(k_BT)]$
BDM with RAN-D	$(a/\xi_c)^3 \ln^2(W_R\tilde{t})$

Homogeneous recombination and scavenging

It is obvious that at t=0 electrons involved in processes of this type may be found at any distance from their partners (a cation, a hole, a neutral or a charged scavenger) with equal probability. Therefore instead of Eq.(5) we have

$$n(r,0) = n_0 \quad \text{and} \quad N(r,0) = N_0. \tag{10}$$

In addition, n(r,t) must satisfy the radiation boundary condition (7) and the total concentration of carriers should tend to the constant value $N_{tot} = n_0 + N_0$ as $r \longrightarrow \infty$.

The solution of Eq.(4) with these initial and boundary conditions allows to find k_a using the relation

$$k_a = kn(R_0,t)/N_{tot} \tag{11}$$

It can be shown[11] that in the long-time Eq.(11) reduces to Eq.(2) with α given in table I and $B = 4\pi D_0kR_0W_R^{-1+\alpha}/(k + 4\pi D_0R_0)$ for homogeneous reactions between charge carriers and neutrals or $B = 4\pi D_0kr_cW_R^{-1+\alpha}/\{k[1-\exp(-r_c/R_0)] + 4\pi D_0r_c\exp(-r_c/R_0)\}$ for processes involving oppositely charged species. This means that parameter B depends on the physical nature of reactive species, on the specific mechanism of their transport (retrapping or hopping) and on the type of disorder. The latter physical factor also completely define the value of exponent α (see table I).

Summing up, we conclude that in the long-time limit the approach proposed adequately describes the evolution of both geminate and homogeneous reactions of charge carriers in disordered solids. It explains the polychromatic kinetics of such processes by the dispersive mode of reactants transport which partially controls the rate of the elementary reaction in disordered systems. Moreover, results of the present study can be applicable to reactions of other active species proceeding by the quantum mechanism, in particular to some physico-chemical processes in low-temperature solids[1,21].

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