Magnetic-field dependence of chemical reaction rates at high temperatures

B. Spivak and F. Zhou
Physics Department, University of Washington, Seattle, Washington 98195
(Received 1 July 1993)

The theory of magnetic-field dependence of chemical reaction rates at high temperatures is discussed. It is shown that in the zero-order approximation in the parameter $(\mu H/kT)^2$ this dependence can be significant. It depends crucially on the nature of the reaction and the way particles are created.

PACS number(s): 05.20.−y, 82.20.−w

I. INTRODUCTION

In this paper we shall consider the magnetic-field dependence of monomolecular $A+A\rightarrow C$ and bimolecular $A+B\rightarrow C$ reactions at high temperature. Suppose the reacting particles have spins. We would like to address the following question: is it possible to have significant magnetic-field dependence of the recombination rate in the zero-order approximation of parameter $(\mu H/kT)^2 \ll 1$, when the spin polarization of reagents is negligible and does not affect the rate of the reaction? Here H is the magnetic field, μ is the Bohr magneton, and T is the temperature. We show below that correlation effects can lead to a significant magnetic-field dependence of the recombination rate.

In the following we will investigate the case where the product of recombination C does not have spin, and only pairs of particles in the singlet states can recombine in the course of elementary process. In the "mean-field" approximation, where the spatial correlation between reagents is neglected, there is no significant H dependence of the recombination rate for $(\mu H/kT)^2 \ll 1$. However, in the course of recombination spatial correlations between reacting particles are induced. That is, nearby singlet pairs recombine quickly, while distant singlet pairs survive recombination more effectively. This type of correlation leads to the deviation from the "mean-field" approximation and renormalizes the reaction rate. Evaluation of such corrections to the recombination rate is a part of the general problem of calculation of the fluctuational corrections to hydrodynamic equations Refs. [1–4]. Magnetic field can affect these corrections, resulting in a significant H dependence of recombination rate.

We consider the following model: reacting particles can diffuse in space with diffusion coefficient D and undergo the processes of spin relaxation. Recombination can occur only when the reacting particles are situated in the same point and form a singlet state. The correlation function of recombining particles and corresponding corrections to the recombination rate turn out to be strongly dependent on the decay rate of the singlet state, which in turn depends on the magnetic field. There are two sources for such a decay: (1) spin relaxation with characteristic time $\tau_s(H)$ and (2) a difference in the g factors of the A and B particles. Because of the latter, the singlet state is no longer an eigenstate in the presence of magnetic field, and will mix with the triplet state. Both mechanisms provide the H dependence of the recombination rate. The significance of the second mechanism was discussed in Refs. [5-7] where one can also find reviews of both experimental and theoretical situations for the H dependence of the chemical reaction rate.

We arrange our paper as follows. In Sec. II we discuss correlational corrections to the recombination rate of spinless particles, and then extend these calculations to find the H dependence of the recombination rate of particles with spins. We show that the magnitude of the H-dependent part of the recombination rate is crucially dependent on the way the particles are created. It is maximized when particles with different spins are created at uncorrelated locations, and is absent when singlet pairs are created at the same location (for example, due to the photodissociation of C particles). The H dependence of the recombination rate can be a nonmonotonic function.

In Sec. III, we consider the H dependence of the recombination rate in a nonstationary case. We show that at initial stages of recombination the H-dependent corrections have the same form for monomolecular and bimolecular reactions, and for both cases the corrections can be large. At long times the H-dependent corrections are very small in the case of bimolecular reactions and can be relatively large in the case of monomolecular reactions. In Sec. IV we discuss our results.

II. MAGNETIC-FIELD DEPENDENCE OF CHEMICAL REACTION RATES IN STATIONARY CASE

In this section we discuss the H dependence of the recombination rate in the stationary case.

First we start with a discussion of the irreversible bimolecular recombination of spinless particles $A+B\rightarrow C$. In the "mean-field" approximation, when the spatial correlation between A and B particles is neglected, the reaction can be described by the equation

$$\partial_t n(t)=I-\gamma_0 n(t)^2 \tag{1}$$

which, in the stationary case, gives

 ©1994 The American Physical Society

$$n=\left[\frac{I}{\gamma_0}\right]^{1/2} . \tag{2}$$

Here $n(t)=\langle n_A(\mathbf{r},t)\rangle=\langle n_B(\mathbf{r},t)\rangle$ is the average concentration of reacting particles. $I=\langle I_A(\mathbf{r},t)\rangle=\langle I_B(\mathbf{r},t)\rangle$ are average intensities for the creation of A and B particles; γ_0 is the recombination constant, which in the gas approximation can be estimated as $\gamma_0 \sim DR_0$, D is the diffusion coefficient, and R_0 is the recombination radius.

Elementary acts of reactions take place when reagents are situated at the same point, which means that in the course of recombination close pairs of reagents are eliminated and spatial correlation of distribution of reagents is produced [8–11]. This correlation changes the recombination rate and, as we shall see, leads to significant H dependence of the recombination rate in the case of particles with spins. We start with the equations

$$\partial_t n_A(\mathbf{r},t)=-\gamma_0 n_A(\mathbf{r},t)n_B(\mathbf{r},t)+D\Delta n_A(\mathbf{r},t)+I_A(\mathbf{r},t) ,$$
$$\partial_t n_B(\mathbf{r},t)=-\gamma_0 n_A(\mathbf{r},t)n_B(\mathbf{r},t)+D\Delta n_B(\mathbf{r},t)+I_B(\mathbf{r},t) , \tag{3}$$

where D is assumed to be equal for A and B particles, $I_A(\mathbf{r},t)=I+\delta I_A(\mathbf{r},t)$, $I_B(\mathbf{r},t)=I+\delta I_B(\mathbf{r},t)$, of which the second terms are random creation sources of A (B) species particles. We assume that

$$\langle \delta I_{A(B)}(\mathbf{r},t)\delta I_{A(B)}(\mathbf{r}',t')\rangle=I\delta(\mathbf{r}-\mathbf{r}')\delta(t-t') ,$$
$$\langle \delta I_A(\mathbf{r},t)\delta I_B(\mathbf{r}',t')\rangle=K_{AB}(\mathbf{r}-\mathbf{r}',t)\delta(t-t') . \tag{4}$$

Above, $K_{AB}(\mathbf{r}-\mathbf{r}')=0$ would mean that A and B particles are created at uncorrelated locations, while $K_{AB}=I\delta(\mathbf{r}-\mathbf{r}')$ would mean the creation of pairs of A and B particles at the same location. Using perturbation theory for Eqs. (3) and (4), after averaging we obtain

$$\partial_t n(t)=-\gamma_0 n(t)^2+g_{AB}(\mathbf{R},t) ,$$
$$\partial_t g_{AA}(\mathbf{R},t)-D\Delta g_{AA}(\mathbf{R},t)+2\gamma_0 n(t)[g_{AA}(\mathbf{R},t)+g_{AB}(\mathbf{R},t)]=0 ,$$
$$\partial_t g_{AB}(\mathbf{R},t)-D\Delta g_{AB}(\mathbf{R},t)+2\gamma_0 n(t)[g_{AB}(\mathbf{R},t)+g_{AA}(\mathbf{R},t)]=K_{AB}(\mathbf{R},t)-\gamma_0 n(t)^2\delta(\mathbf{r}-\mathbf{r}') \tag{5}$$

Here $g_{AA}(\mathbf{R},t)=\langle \delta n_A(\mathbf{r},t)\delta n_B(\mathbf{r}',t)\rangle$, $g_{AB}(\mathbf{R},t)=\langle \delta n_A(\mathbf{r},t)\delta n_B(\mathbf{r}',t)\rangle$, with $\mathbf{R}=\mathbf{r}-\mathbf{r}'$. Equation (5) holds as long as corrections to recombination rate are small, which means that $n(t)^2 \gg g_{A,B}(0,t)$. Thus in the case $K_{AB}=0$, we have a source for the correlation function on the right-hand side of Eq. (5), which is proportional to the unperturbed recombination rate. On the other hand, if A and B particles are created at the same location and $K_{AB}=I\delta(\mathbf{r}-\mathbf{r}')$, the source on the right-hand side of Eq. (5) is identically zero.

We would like to note the direct analogy between this source and the corresponding source term for the nonequilibrium correlation function of the distribution function. (See Refs. [13] and [14].)

The boundary conditions for Eq. (5) are that there are zero fluxes of A and B particles through the sample boundary S:

$$\mathbf{n}\cdot\nabla g_{AA}(\mathbf{r}-\mathbf{r}',t)|_s=0 ,$$
$$\mathbf{n}\cdot\nabla g_{AB}(\mathbf{r}-\mathbf{r}',t)|_s=0 . \tag{6}$$

In the stationary case, from Eq. (5) we find

$$g_{AB}(0)=-\gamma_0 n^2\sum_{\mathbf{Q}}\frac{1}{D\mathbf{Q}^2}\left[1-\frac{K_{AB}(\mathbf{Q})}{\gamma_0 n^2}\right] . \tag{7}$$

Here $K_{AB}(\mathbf{Q})$ is the Fourier transform of $K_{AB}(\mathbf{R})$. $\mathbf{n}$ is the vecto vector normal to the boundary. In the case when $K_{AB}(\mathbf{R},t)=0$, the correction to the recombination rate has the form

$$\delta\gamma_0=\frac{I}{\langle n\rangle^2}-\gamma_0 =-\gamma_0^2\sum_{\mathbf{Q}}\frac{1}{D\mathbf{Q}^2} . \tag{8}$$

This expression is similar to that for the weak-localization correction to conductivity of disordered metals at low temperatures [15,16]. It is important that there is no cutoff in the denominator of Eq. (8), which is intrinsically connected with recombination.

Similar to weak localization, in the three-dimensional case $d=3$. Equation (8) is determined by large $|\mathbf{Q}|\sim l^{-1}$, where Eqs. (5) are actually inapplicable. Here $l=\sqrt{3D\tau}$ is the mean free path, and τ is the scattering mean free time of the particles. However, we will show below that the magnetic-field dependence of $\delta\gamma_0(H)$ is completely determined by small $|\mathbf{Q}|$. In one and two dimensions Eq. (8) diverges at small $|\mathbf{Q}|$, and we introduce a cutoff length L_0 the physical origin of which will be discussed below. As a result we obtain the correction to the recombination rate due to correlation:

$$\frac{\delta\gamma_0}{\gamma_0}=-\frac{\gamma_0}{Dl}\begin{cases}\sim 1, & d=3\\ \times\dfrac{l}{L_z}\ln\dfrac{L_0}{l}, & d=2.\\ \times\dfrac{L_0 l}{L_x L_y}, & d=1\end{cases} \tag{9}$$

The definitions for the $d=1$, 2, and 3 cases are the same as in the theory of weak localization [15,16]: $d=1$ corresponds to $L_x, L_y \ll L_0, L_z \gg L_0$; $d=2$ corresponds to $L_z \ll L_0, L_y, L_x \gg L_0$; and $d=3$ corresponds to $L_x, L_y, L_z \gg L_0$.

Equations (8) and (9) are valid as long as corrections to the recombination rate are small. But the corresponding expressions for $d=1$ and 2 diverge when L_0 goes to infinity. This divergency is a direct consequence of the assumption about absence of correlation between A and B sources: $K_{AB}=0$. Furthermore, at $L_0=\infty$ in the $d=1$ and 2 cases the stationary solution of the problem

does not exist [11]. A qualitative explanation of this fact is as follows: the numbers of A and B particles created per unit time in a finite volume are different, and they can disappear from the volume due to recombination only by pairs which conserve the difference of the numbers of A and B particles. The difference between the total numbers of A and B particles created in a region with a size L_0 during a time interval t_0 is of the order of $\sqrt{It_0/(L_0)^d}$. This difference can be eliminated only by diffusion of A and B particles over a distance of the order of L_0, which takes time $t_0=(L_0)^2/D$. As a result,

$$n(t)\sim\delta n_A\sim\delta n_B\sim\sqrt{I(L_0)^{2-d}D^{-1}}\ . \tag{10}$$

Equation (10) shows that at $d\leq 2$, δn_A increases with L_0, which means that at low dimensions diffusion is not effective enough to redistribute the excess of the particles all over the sample volume. As a result, the concentrations of particles grow with time, and a stationary solution of the problem in the infinite sample is absent. The physical reason for this is that the segregation of A and B particles prevents their recombination.

In a real situation the A and B particles can be created in space as correlated pairs (correlation length L_0 has a finite value). The cutoff length L_0 in Eq. (9) is the characteristic size of a volume where the total numbers of created A and B particles are the same. In this case, at small enough L_0 Eqs. (8) and (9) are valid. At sufficiently large L_0 we have Eq. (10), which is strongly dependent on the cutoff length L_0.

As we have noticed, in the case when A and B particles are created by pairs at the same location, the corrections to the recombination rate considered above are identically zero due to the exact cancellation between correlations created by recombination and by creation of particles.

In the case of monomolecular reaction $A+A\rightarrow C$, there are no corrections to recombination constant.

Let us now turn to the magnetic-field dependence of the reaction rate. Suppose A and B particles have spins $\frac{1}{2}$, and particle C does not have spin, so only the recombination of a singlet pair of A and B particles is possible. (A generalization to larger spins is straightforward.) Let us start with the case of the monomolecular reaction $A+A\rightarrow C$. In this case we have to substitute the singlet-singlet component $\rho_{ss}(\mathbf{r}-\mathbf{r}';t)$ of two-particle density matrix $\rho_{\alpha\beta}(\mathbf{r}-\mathbf{r}';t)$ instead of g_{AB} in the first of Eqs. (5). We introduce

$$g_{\alpha\beta}(\mathbf{R},t)=\rho_{\alpha\beta}(\mathbf{R},t)-\tfrac{1}{4}n(t)^2\delta(\mathbf{R})\delta_{\alpha\beta} \tag{11}$$

as the correlational part of the density matrix $\rho_{\alpha\beta}$ arising from recombination. Here α and β are the spin indexes corresponding to the singlet state S and triplet states T_0,T_+,T_-, which corresponds to the $0,+1,-1$ projection of the total spin on the z axis. The equations for diagonal elements of the density matrix are

$$\begin{aligned}&\partial_t g_{SS}(\mathbf{R},t)-D\Delta g_{SS}(\mathbf{R},t)+\gamma_0 n(t)[g_{SS}(\mathbf{R},t)+g_{TT}(\mathbf{R},t)]-\frac{3g_{SS}(\mathbf{R},t)-g_{TT}(\mathbf{R},t)}{\tau_s}=-\gamma_0 n(t)^2\delta(\mathbf{R})\ ,\\&\partial_t g_{TT}(\mathbf{R},t)-D\delta g_{TT}+\gamma_0 n(t)3[g_{SS}(\mathbf{R},t)+g_{TT}(\mathbf{R},t)]-\frac{g_{TT}(\mathbf{R},t)-3g_{SS}(\mathbf{R},t)}{\tau_s}=0\ .\end{aligned} \tag{12}$$

In the case $\mu H\ll kT$, $g_{T_0T_0}(\mathbf{R},t)=g_{T_-T_-}(\mathbf{R},t)=g_{T_+T_+}(\mathbf{R},t)$, and we introduce $g_{TT}(\mathbf{R},t)=g_{T_-T_-}(\mathbf{R},t)+g_{T_+T_+}(\mathbf{R},t)+g_{T_0T_0}(\mathbf{R},t)$. Equation (12) differs from Eq. (5) by the term corresponding to spin relaxation. We assume the conventional magnetic-field dependence of the spin relaxation time (see, for example, Ref. [17]):

$$\tau_s(H)=\tau_s(0)[1+(\tau_0\mu H)^2]\ . \tag{13}$$

Here $\tau_s(0)$ is the spin-relaxation time in the absence of magnetic field, and τ_0 is the correlation time for the random magnetic field which causes the relaxation. Equation (12) holds as long as the correlational corrections to the recombination rate are small. In the stationary case, similar to Eq. (8), we have

$$\frac{\delta\gamma_0(H)}{\gamma_0}=\gamma_0-\tfrac{3}{4}\sum_{\mathbf{Q}}\frac{1}{D\mathbf{Q}^2+4\tau_s^{-1}(H)}\ . \tag{14}$$

For $d=3$, Eq. (14) diverges at large Q (or small distances) just like Eq. (8), which makes it inapplicable because of the violation of the diffusion approximation. It is important, however, that as in the theory of weak localization [15,16] the magnetic-field dependence of the recombination rate can be calculated in the diffusion approximation in any dimension. Indeed,

$$\frac{\delta\gamma_0(H)-\delta\gamma_0(0)}{\gamma_0}=\gamma_0\tfrac{3}{4}\sum_{\mathbf{Q}}\left\{\frac{1}{D\mathbf{Q}^2+4\tau_s^{-1}(0)}-\frac{1}{D\mathbf{Q}^2+4\tau_s^{-1}(H)}\right\} \tag{15}$$

is determined by small Q. As a result we find

$$\frac{\delta\gamma_0(H)-\delta\gamma_0(0)}{\gamma_0} = \frac{3}{4}\times\begin{cases} 2\pi^2\left[\dfrac{\gamma_0}{D\sqrt{D\tau_s(H)}}-\dfrac{\gamma_0}{D\sqrt{D\tau_s(0)}}\right], & d=3 \\ \pi\dfrac{\gamma_0}{DL_z}\ln\dfrac{\tau_s(0)}{\tau_s(H)}, & d=2 \\ \pi\dfrac{\gamma_0}{DL_xL_y}[\sqrt{D\tau_s(0)}-\sqrt{D\tau_s(H)}], & d=1 \end{cases} \tag{16}$$

In $d=3$ this correction is small but important, in that it can be much larger than the parameter $(\mu H/KT)^2$. In the one- and two-dimensional cases the corrections described by Eq. (16) diverge as τ_s goes to infinity. The reason for this is exactly the same as that which leads to the corresponding divergency in Eq. (8).

As we have mentioned already, in this case Eq. (12) cannot be applied to describe the situation. However, it is possible to estimate H dependences of the recombination rate by substituting L_0 for $\sqrt{D\tau_s}$ in Eq. (10):

$$\delta\gamma_0(H)\sim\begin{cases} \dfrac{DL_z}{\ln\dfrac{\tau_s(H)}{\tau}}, & d=2 \\ DL_xL_y\dfrac{1}{\sqrt{D\tau_s(H)}}, & d=1\ . \end{cases} \tag{17}$$

We see that in this regime the H dependence is very significant and does not depend on γ_0, which is a consequence of the fact that the segregation of particles with different spins dominates the dynamics of the system.

Let us now turn to the case of bimolecular reactions $A+B\rightarrow C$, which we will describe with the help of the equations for the density matrix:

$$\begin{aligned} &\partial_t n(t)=-\gamma_0\{n(t)^2+4g_{AB;SS}(\mathbf{R},t)\}\ , \\ &\partial_t g_{ij;T_0S}(\mathbf{R},t)-D\Delta g_{ij;T_0S}(\mathbf{R},t)+\frac{g_{ij;T_0S}(\mathbf{R},t)}{\tau_s(H)}+i\omega_H[g_{ij;SS}(\mathbf{R},t)-g_{ij;T_0T_0}(\mathbf{R},t)](1-\delta_{ij})=0\ , \\ &\partial_t g_{ij;\alpha\alpha}(\mathbf{R},t)-D\Delta g_{ij;\alpha\alpha}(\mathbf{R},t)+2i\omega_H g_{ij;T_0S}(\mathbf{R},t)(1-\delta_{ij})(\delta_{\alpha S}+\delta_{\alpha T_0}) \\ &\quad+\gamma_0 n\left\{2g_{ij;\alpha\alpha}(\mathbf{R},t)-\sum_{j'}(1-\delta_{jj'})\left[g_{ij';\alpha\alpha}(\mathbf{R},t)-\sum_{\beta}{}' g_{ij';\beta\beta}(\mathbf{R},t)\right]\right\} \\ &\qquad\qquad+\frac{4g_{ij;\alpha\alpha}(\mathbf{R},t)-\sum_\beta g_{ij;\beta\beta}}{\tau_s(H)}=-\gamma_0 n(t)^2\delta(\mathbf{R})(1-\delta_{ij})\ . \end{aligned} \tag{18}$$

Here i,j labels particles A, B; $\alpha,\beta=S$; T_0,T_-,T_+, $g_{ij;\alpha\beta}(\mathbf{R},t)$ is the density-matrix element of the reagent i,j with spin states α,β; $g_{ij;T_0S}(\mathbf{R},t)$ are the off-diagonal matrix elements, which describe the mixture of singlet and triplet states in the magnetic field, provided the A and B particles have different g factors; $\omega_H=(g_1-g_2)\mu H$ is the difference of Larmor frequencies of the spins of A and B reagents, and $\sum_\beta'$ is the summation over the spin states excluding the α state.

In the stationary case we obtain from Eq. (18) the H-dependent part of the correction to the chemical reaction rate, which differs from Eq. (17) only by the term arising from the difference of the g factor of reagent A and B:

$$\delta\gamma_H-\delta\gamma_0=\frac{\gamma_0^2}{6}\sum_{\mathbf{Q}}\left\{\frac{2}{D\mathbf{Q}^2+\tau_s^{-1}(0)}-\frac{1}{D\mathbf{Q}^2+\tau_s^{-1}(H)}-\frac{D\mathbf{Q}^2+\tau_s^{-1}(H)}{[D\mathbf{Q}^2+\tau_s^{-1}(H)][D\mathbf{Q}^2+4\tau_s^{-1}(H)]+2\omega_H^2}\right\}. \tag{19}$$

As a result we have

$$\frac{\delta\gamma_0(H)-\delta\gamma_0(0)}{\gamma_0}\sim\frac{\gamma_0}{6}\times\begin{cases} \dfrac{\gamma_0}{D\sqrt{D\tau_s(H)}}+\dfrac{\gamma_0}{D\sqrt{D\sqrt{\omega_H^{-2}+\tau_s^2(H)}}}-2\dfrac{\gamma_0}{D\sqrt{D\tau_s(0)}}, & d=3 \\ \dfrac{\gamma_0}{DL_z}\left\{\ln\left[\dfrac{\tau_s(0)^2}{\omega_H^{-2}+\tau_s(H)^2}\right]^{1/2}+\ln\dfrac{\tau_s(0)}{\tau_s(H)}\right\}, & d=2 \\ \dfrac{\gamma_0}{DL_xL_y}(2\sqrt{D\tau_s(0)}-\sqrt{D\tau_s(H)}-\{D[\omega_H^{-2}+\tau_s(H)^2]^{1/2}\}^{1/2}), & d=1 \end{cases} \tag{20}$$

An interesting feature of Eq. (20) is that, because ω_H is proportional to H while $[\tau_s(H)^{-1}]$ decreases with H, a nonmonotonic magnetic-field dependence of $\delta\gamma_0(H)$ may be possible.

As we have noted above, the origin of Eq. (20) is very similar to the corresponding equation for the weak-localization corrections to the conductivity [15,16]. The physical reason for this is the following: the first scattering of particles A and B creates spin correlation between the particles. The particles then diffuse and the recombination probability at their second scattering depends on the spin correlation. This qualitative picture of the H dependence of the recombination rate has been discussed in many papers (see, for example, Refs. [5–7]). We would like to stress, however, that Eq. (19) holds only for the case when $K_{AB}=0$, while in the $K_{AB}(\mathbf{R},t)=I\delta(\mathbf{R})$ the corrections are identically zero. This corresponds to the obvious fact that the change in the mass action law is governed by parameter $(\mu H/kT)^2$.

It is important that as long as $\tau_s \gg \tau$ and $(g_1-g_2)\mu H\tau \ll 1$, the magnetic-field-dependent part of $\delta\gamma_0$ is determined by small Q for all dimensions, which means that all results can be obtained in the diffusion approximation. The definition of dimensionality is the same as described above with the substitution L_0 for $\min(L_0,\sqrt{D\tau_s})$.

As we have discussed above, in the case of a bimolecular reaction in low dimensions $d \le 2$ and at large L_0 the key feature is the segregation of particles A and B. Therefore spin dynamics in this case does not play a significant role in reaction kinetics, and the magnetic-field dependence of the recombination rate is small even compared with perturbation result Eq. (16). Thus we see a dramatic difference between monomolecular and bimolecular reactions in this regime. We will see that the same reasoning leads to a similar conclusion in the nonstationary case.

III. THE H DEPENDENCE OF THE REACTION RATES IN THE NONSTATIONARY CASE

In this section, we discuss the nonstationary situation where one prepares uniform and uncorrelated distributions of A and B particles and then allows the recombination to start at $t=0$. Such a situation can arise, for example, when the source of dissociation of particles C into A and B is suddenly switched off at the time $t=0$.

As an introduction, we begin with the recombination of spinless particles. In this case the initial stage of recombination basically follows the "mean-field" solution Eq. (1):

$$n(t)=\frac{1}{1+\gamma_0 n(0)t}\ , \tag{21}$$

with small correlation corrections.

Zeldovich and Ovchinnicov [8] showed that for the bimolecular reaction $A+B\rightarrow C$, at $t>T_{ZO}$ (we will give the definition of T_{ZO} below) this law changes to

$$n(t)\sim t^{-d/4}\ . \tag{22}$$

The reason for this is the existence of initial spatial fluctuations of the densities of particles A and B. For large length and time scales the recombination is much quicker than the diffusion. As a result, at $t\sim T_{ZO}$, the recombination leaves "lakes" of segregated A and B particles with densities of the order of the initial fluctuations. Further on the recombination process is limited by the diffusion between such lakes, whose size depends on time. This leads to Eq. (22). The phenomenon of the segregation of particles in the course of recombination was investigated in many papers (see Refs. [8–12]), where Eq. (24) was confirmed. In this paper we restrict ourselves to a calculation of corrections to the recombination rate in the framework of the perturbation theory, which means the opposite limit, when the effects of particles' segregation are small. T_{ZO} is the time such that $n(T_{ZO})^2\sim g_{AB}(0;T_{ZO})$.

Using perturbation theory, from Eq. (5) one gets $g_{AB}(0;t)\sim n(0)/(Dt)^{d/2}$, with $n(0)$ being the initial concentration of the reagent. Together with Eq. (21), it leads to the estimate

$$T_{ZO}=\left\{\frac{D^d}{\gamma_{0d}^4 n(0)^2}\right\}^{1/(4-d)}\ , \tag{23}$$

where γ_{0d} is

$$\gamma_{0d}=\begin{cases}\gamma_0, & d=3\\ \dfrac{\gamma_0}{L_z}, & d=2\\ \dfrac{\gamma_0}{L_xL_y}, & d=1\ .\end{cases} \tag{24}$$

In the case of monomolecular reaction $A+A\rightarrow C$, Eq. (21) holds at arbitrary large time, and the Zeldovich-Ovchinnicov regime is not realized.

Let us now consider the magnetic-field dependence of concentration $n(H,t)$.

First, let us note that, at an asymptotically large time the result is different for monomolecular and bimolecular reactions. That is, the kinetics of a bimolecular reaction in this case is determined by the segregation of A and B particles, and does not depend on details of the elementary process of recombination. This means that the magnetic-field dependence of the reaction rate in this case is very small. On the other hand, we will show that a monomolecular reaction can be described at long times by a "mean-field" solution Eq. (21) with the same magnetic-field dependence of γ_0 [Eq. (16)] as in the stationary case,

At an intermediate observation time t the magnetic-field dependence of the recombination rate in the nonstationary case depends on the ratio between parameters $\tau_s(0)$, $[\tau_s^{-2}(H)+\omega_H{}^2]^{-1/2}$, T_{ZO}, and t.

It is clear from previous discussion that in the case in which all these parameters are of the same order, the segregation of the particles with different spins is also of the order of unity and $\dot{n}(H)-\dot{n}(0)\sim\dot{n}(0)$. In the case of a bimolecular reaction it is a maximally possible change of the reaction rate by the magnetic field. In the case of a

monomolecular reaction the effect of the magnetic field can be much larger. Consider, for example, the situation when $\tau_s(H) \gg T_Z \gg \tau_s(0)$. At $H=0$ and $t > \tau_s(0)$, the reaction follows the mean field Eq. (21), while in the presence of the magnetic field the Zeldovich-Ovchinnikov regime [Eq. (22)] takes place in the time interval $\tau_s(H) > t > T_{ZO}$. However, the description of this case is beyond the scope of this paper because, as we have mentioned, Eqs. (12) and (18) can be applied only to the case in which the correction to the rate is small.

Using Eq. (18), one obtains

$$\partial_t n(t;H) = -\gamma_0(t;H) n(t;H)^2 ,$$

$$\gamma_0(t;H) = \gamma_0 \left[1 + \frac{g_{AB;SS}(\mathbf{r},\mathbf{r},t;H)}{n(t;H)^2} \right] , \tag{25}$$

$$g_{AB;SS}(\mathbf{r},\mathbf{r},t;H) = -\gamma_0 \int n(t';H)^2 G(\mathbf{r},\mathbf{r};t,t';H) dt' ,$$

where

$$G(\mathbf{r},\mathbf{r}';t,t';H) \sim \exp\left\{ -\frac{t-t'}{\tau_s(H)} - \frac{(\mathbf{r}-\mathbf{r}')^2}{D(t-t')} \right\} \frac{1}{[D(t-t')]^{d/2}} \tag{26}$$

is the Green function of Eq. (18). Such a form of the Green's function is valid as far as $\tau_s(H)^{-1} \gg \omega_H$.

Equations (25) and (26) can be applied both to monomolecular and bimolecular reactions, provided $\tau_s^{-1} \ll \omega_H$. In the opposite case τ_s should be replaced by ω_H. There are two significant contributions in the integral Eq. (25). The first one is due to t', which is close to t. At long times (in the case of monomolecular reactions) this contribution dominates and we arrive at the solution Eq. (21) with the H-dependent γ_0 of the form given by Eq. (16). The second contribution, which corresponds to Zeldovich-Ovchinnikov corrections, is from $t' \sim (\gamma_{0d} n(0))^{-1}$. When $t \geq 1/\gamma_0 n(0)$, we can express this term in the following form:

$$\delta\gamma_0(H) - \delta\gamma_0(H) = -\left[\frac{t}{T_{ZO}} \right]^{(4-d)/2} \left[\exp\left[-\frac{t}{\tau_s(H)} \right] - \exp\left[-\frac{t}{\tau_s(0)} \right] \right] . \tag{27}$$

Equation (27) holds for $t \ll t_{ZO}$. The relation between Eqs. (27) and (20) depends on the parameters mentioned above.

IV. CONCLUSION

We have shown that in both stationary and nonstationary cases the magnetic-field corrections to chemical reaction rates can be much larger than those which are governed by the parameter $(\mu H/kT)^2$. Moreover, in some cases they can be of the order of, and even larger than, unity.

In the stationary case the corrections are maximal when particles with different spins are created at uncorrelated locations. In three dimensions the relative amplitude of the corrections is smaller than unity, but it is enhanced in the low-dimensional cases $d=1$ and 2, where in principle it could be larger than unity.

In cases when the particles are created in a stationary fashion by pairs at the same locations, the H dependence of the rate considered above is absent.

In the nonstationary case at $t < T_{ZO}$ corrections due to the magnetic field are of the same order for monomolecular and bimolecular reactions. Their relative amplitude depends on the parameters t/T_{ZO}, and τ_s/T_{ZO} and can be of the order of unity.

The characteristic magnetic field of the problem, where the corrections become significant, is determined by the parameters $\mu H \tau_0$ and $(g_1 - g_2)\mu H \tau_s$.

In conclusion, we would like to mention another possible mechanism for the H dependence of reaction rates: the H dependence of the diffusion coefficient $D(H)$ (or scattering mean free path l) [18–20], which enters the expression for the recombination rate through Eqs. (8) and (9). Such a dependence (which is called the Zenftleben effect) arises in the case when the mean free path l depends on the angle between the directions of particle velocity and spin, $l = l_0[1 + \Gamma(\mathbf{v}\cdot\mathbf{S}/vS)]$. The estimate [18,20] $[D(H) - D(0)]/D(0) \sim \Gamma^2[1 + (\mu H \tau)^2]$ shows that this contribution usually is small compared with that considered above, because Γ is of relativistic origin. However, we would like to stress that in cases when the recombination rate is significantly suppressed due to the segregation of A and B particles, it is this mechanism which determines the H dependence of the recombination rates. Moreover, these corrections can oscillate as a function of the magnetic field due to magnetic-field-mediated intersections of Zeeman levels in some molecules [19,20].

ACKNOWLEDGMENTS

We thank V. Gurevich, B. Shklovski, I. Yanson, P. Wyder, and I. Vagner for useful discussions.

[1] B. Adler and B. L. Wainwright, Phys. Rev. Lett. **118**, 988 (1967).
[2] M. H. Ernest and J. R. Dorfman, Physica **61**, 157 (1972).
[3] K. Kawasaki and I. Oppenheim, Phys. Rev. **139**, 1763 (1965).
[4] A. F. Andreev, Zh. Eksp. Teor. Fiz. **75**, 1132 (1987) [Sov. Phys. JETP **48**, 570 (1978)].
[5] U. E. Steiner and T. Ulrich, Chem. Rev. **89**, 51 (1989).
[6] K. M. Salikhov, Y. N. Molin, R. Z. Sagdeev, *Spin Polarization and Magnetic Effects in Radical Reactions* (Elsevier, Amsterdam, 1984).
[7] S. Boxer, Ann. Rev. Phys. Chem. **34**, 389 (1983).
[8] Ya. B. Zeldovich and A. A. Ovchinnikov, Pis'ma Zh. Eksp. Teor. Fiz. **26**, 588 (1977) [JETP Lett. **26**, 441 (1977)].
[9] D. Tossaint and F. Wilchek, J. Chem. Phys. **78**, 2642

(1983).

[10] S. F. Burlatski, A. A. Ovchinnikov, and G. S. Oshanin, Zh. Eksp. Teor. Fiz. **95**, 1993 (1989) [Sov. Phys. JETP **68**, 1153 (1989)].

[11] Katji Lindenberg, Bruce J. West, and R. Kopelman, Phys. Rev. Lett. **60**, 1777 (1988); J. Stat. Phys. **54**, 5 (1989); **54**, 6, 1989.

[12] M. Bramson and L. Leibovitz, Phys. Rev. Lett. **61**, 2397 (1988).

[13] S. M. Kogan and A. Y. Shulman, Zh. Eksp. Teor. Fiz. **56**, 862 (1969) [Sov. Phys. JETP **29**, 467 (1969)].

[14] K. V. Gantsevich, V. L. Gurevich, and R. Katilus, Vista Del Nuovo Cimento **2**, 1 (1979).

[15] B. L. Altshuler, D. Khmelnitski, A. Larkin, and P. Lee, Phys. Rev. B **22**, 5142 (1980).

[16] L. Gorkov, A. Larkin, and D. Khmelnitski, Pis'ma Zh. Eksp. Teor. Fiz. **30**, 248 (1979) [Sov. Phys JETP Lett. **30**, 228 (1979)].

[17] C. P. Slichter, *Principles of Magnetic Resonance* (Springer-Verlag, New York, 1980).

[18] Yu. Kagan and L. A. Maksimov, Zh. Eksp. Teor. Fiz. **41**, 842 (1961) [Sov. Phys. JETP. **14**, 604 (1962)]; **51**, 1893 (1966) [**24**, 1272 (1967)].

[19] L. Gorelik, Pis'ma Zh. Eksp. Teor. Fiz. **33**, 403 (1981) [JETP Lett. **33**, 387 (1981)].

[20] N. S. Averkiev and M. I. Dyakonov, Pis'ma Zh. Eksp. Teor. Fiz. **35**, 196 (1982) [JETP Lett. **35**, 242 (1982)].