

# PECULIARITIES OF DIFFUSION-CONTROLLED RECOMBINATION KINETICS AT LONG TIME AND/OR FOR GREAT INITIAL REAGENT CONCENTRATIONS

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The earlier developed generalized theory of bimolecular reactions between reagents (defects) in solids and liquids, based on a more complete than the standard one decoupling of the hierarchy of equations for many-point densities, is used for detailed calculations of the  $A + B \rightarrow AB$  reaction kinetics at long time (great reaction depth). The effects of great initial concentrations and relative diffusion coefficients upon the reaction kinetics are also studied. The earlier predicted lowering of the reaction rate due to a dynamical aggregation of similar (non-interacting) reagents is confirmed. The greater the initial reagent concentration and if one kind of reagents ( $A$ 's or  $B$ 's) are immobile, the more pronounced is the aggregation effect.

## 1. INTRODUCTION

The theory of diffusion-controlled bimolecular reactions between reagents  $A$ ,  $B$  (e.g. defects) in solids and liquids is supposed to be well developed [1–9]. As is well understood now, a rigorous phenomenological description of the reaction kinetics has to be based on the analysis of the hierarchy of equations for many-point densities (correlation functions) of reagents [1, 3, 4, 6–9]. However, there are several points that have not been clarified yet. Thus, there is a problem of rigorous description of the carrier motion at short times [10–13], no clear way of taking into account dissimilar ( $AB$ ) reagent correlated (e.g. geminate) distribution [14], and *many-particle* effects in bimolecular kinetics for great initial reagent concentrations. Numerous papers (e.g. [5, 15–19]) have dealt with the latter effect in energy transfer. Owing to different (sometime vague) approximations involved a great variety of results is obtained here.

Quite recently generalized kinetic equations have been derived describing diffusion-controlled bimolecular reactions, incorporating Frenkel defect recombination,  $A + B \rightarrow AB$ , energy transfer,  $A + B \rightarrow B$ , excitation annihilation,  $A + A \rightarrow B$  [8, 14]. Unlike earlier theories, the identity of similar reagents and spatial correlations of both dissimilar ( $A - B$ ,  $B - A$ ) and similar ( $A - A$ ,  $B - B$ ) reagents are here rigorously taken into account. This theory is based on the Kirkwood standard superposition approximation for three-particle densities and a simple diffusive description of reagent motion. Sometimes the accuracy of the former can be estimated (see [14a] and Conclusion) whereas the diffusive motion is known to occur over not a very short time  $t$  and not very low temperature  $T$  (when the carrier motion is incoherent). For instance, it is sure to take place for radiation Frenkel defects in alkali halides at  $T > 30$  K,  $t > 10^{-10}$  s.

Both our theory [8, 14] and quite a different approach [20] argue that dissimilar reagent recombination,  $A + B \rightarrow AB$ , results at long time in dynamical *aggregation* of similar reagents ( $A$ 's or  $B$ 's) even if initially reagents are randomly distributed.

Such an aggregation *lowers* the reaction rate  $K$  thus leading to its *derivation* from the standard quasi-steady reaction rate

$$(1) \quad K_0 = 4\pi D r_0,$$

well known in the formal chemical kinetics [1]. ( $D$  is the relative diffusion coefficient,  $D = D_A + D_B$ ,  $r_0$  being the instant recombination radius.)

In particular, the analytical analysis of our kinetics equations for the reaction  $A + B \rightarrow AB$  has shown [14] that at very long time the decay law also depends on the ratio of the diffusion coefficients  $D_A$  and  $D_B$ . Thus for equal reagent concentrations,  $N_A = N_B = N$ , one gets  $N \propto t^{-3/4}$  if both  $D_A, D_B \neq 0$ , but  $N \propto t^{-1/2}$  if  $D_A = 0$  and  $D_B \neq 0$  (and vice versa). (The formal chemical kinetics predicts  $N \propto t^{-1}$ .) If one of the reagents is in excess,  $N_A \ll N_B$ ,  $N_A \propto t^{-3/2}$  or  $N_A \propto t^{-1}$  (whereas  $N_A \propto \exp(-K_0 N_B t)$  is expected in the standard chemical kinetics).

The purpose of this paper is to calculate in detail the  $A + B \rightarrow AB$  reaction kinetics at arbitrary times on a computer in order to estimate the actual significance of the effects of the reduced rate and the reagent aggregation. One of the important points is whether these effects could be observed under real experimental conditions. To answer these questions the influence of the initial reagents spatial distribution, their concentrations and mobilities,  $D_A$  and  $D_B$ , upon the diffusion-controlled reaction kinetics is analysed. Note once more that in order to investigate the *reaction* effects we confine ourselves to the incoherent continuous diffusive description of reagent motion.

## 2. BASIC EQUATIONS AND RESULTS

Instead of parameters  $N_A, N_B, D_A, D_B$  it is convenient to employ the following dimensionless (dashed) parameters:  $N'_v = 4\pi r_0^3 N_v$ ,  $D'_v = 2D_v/D$ ,  $D = D_A + D_B$ ,  $v = A, B$ ,  $r' = r/r_0$ ,  $t' = Dt/r_0^2$ ,  $K' = K/K_0$ . (The dashes are omitted below.) In these parameters the basic set of kinetics equations read [14]

$$(2) \quad \frac{dN_A}{dt} = \frac{dN_B}{dt} = -KN_A N_B, \quad K = \left( \frac{\partial Y}{\partial r} \right)_{r=1},$$

$$(3) \quad \frac{\partial X_A}{\partial t} = D_A \Delta X_A - 2KN_A X_A J(Y),$$

$$(4) \quad \frac{\partial Y}{\partial t} = \Delta Y - KY \sum_{v=A,B} N_v J(X_v),$$

where

$$(5) \quad J(Z) = \frac{1}{2r} \int_{|r-1|}^{r+1} (Z(r') - 1) r' dr' ,$$

$X_v$  ( $v = A, B$ ),  $Y$  are the joint (two-point) densities (correlation functions) for similar ( $A-A, B-B$ ) and dissimilar ( $A-B, B-A$ ) reagents, describing spatial reagent correlations.

Since spatial correlations become negligible at great relative distances  $r$ , one gets the boundary condition

$$\lim_{r \rightarrow \infty} X_{v_0} Y = 1 .$$

An instant annihilation of  $A-B$  pairs at  $r \leq r_0(1)$  is taken into account by the boundary condition  $Y(r \leq 1) \equiv 0$ . Another boundary condition is  $X(r \rightarrow 0)$ -limited which assumes that reagent sizes are negligible in comparison with the annihilation sphere radius  $1(r_0)$  (which is usually the case for crystalline defects).

The many-particle effects are incorporated in our theory through the second terms on the right-hand side of eqs. (3), (4) (derived in the standard Kirkwood superposition approximation).

The set of equations (2) to (5) is reduced to the earlier theories [1-7] if *similar* noninteracting reagents are assumed to be *always* randomly distributed:  $X_v \equiv 1$ , i.e.  $J(X_v) \equiv 0$ . It immediately leads to the law of the standard chemical kinetics  $K = 1$  at  $t \rightarrow \infty$  (see eq. (4)). The assumption that  $X_v = 1$  at *all* reaction times means nothing but that the Poisson fluctuation spectrum of reagent densities invariably takes place. However, the analysis of the set of equations (2) to (4) [8, 14] has demonstrated clearly that the just mentioned, generally-accepted (but intuitively based) assumption that similar reagents remain uncorrelated in the course of reaction since they do not interact is *wrong*. Since the spatial correlations of similar and dissimilar reagents are back-coupled (see eqs. (3), (4)), the fluctuation spectrum of *similar* reagents clearly becomes the *non-Poisson* one during the reaction owing to their indirect interaction through recombination of dissimilar reagents.

Let us consider below the results of computer calculations of the set of equations (2) to (4). The initial distribution of all reagents is assumed usually to be random:  $X_v(r) = Y(r > 1) \equiv 1$ . Here the reaction kinetics can be uniquely described by the parameters  $N_A, N_B, D_A, (D_B = 2 - D_A)$ . To investigate the role of the initial distribution the so-called "quasi-steady" distribution  $X_v(r) = 1, Y(r > 1) = 1 - 1/r$  [1] is also to be considered. (This distribution occurs in the earlier theories [1-7] after the time several times exceeding the distinctive time  $t_0 = r_0^2/D$ .)

The many-particle effects under study could be detected experimentally through: (i) the deviation with time  $t$  (or reaction depth  $\tau = N(t)/N_0$ ) of the reaction rate  $K$  from the quasisteady  $K_0 = 1$  given by the standard chemical kinetics, (ii) the critical exponent  $\gamma$  of the time decay of the macroscopic concentration:  $N \propto t^{-\gamma}$ .  $\gamma$  is expected to be essentially less than unity, known in the standard kinetics for equal reagent concentrations.

2.1. Random initial distribution

Fig. 1 shows the calculated dependence of the reaction rate  $K$  (see eq. (2)) on the inverse reaction depth  $\tau^{-1} = N_0/N(t)$  ( $\tau$  is the share of reagents surviving till the moment  $t$ ). The obvious conclusion can be drawn that for equal diffusion coefficients (curves  $a$ ) the reaction rate is considerably reduced when the dimensionless initial concentration is large enough,  $N_0 \gtrsim \gtrsim 0.1$  ( $N_0 = 4\pi r_0^3 N_0$  in "usual" units). As is shown in [8], the irradiation-induced reagent concentration does not exceed  $N_0 \approx 1$ . Therefore calculations for  $N_0 > 1$  serve as an object model.

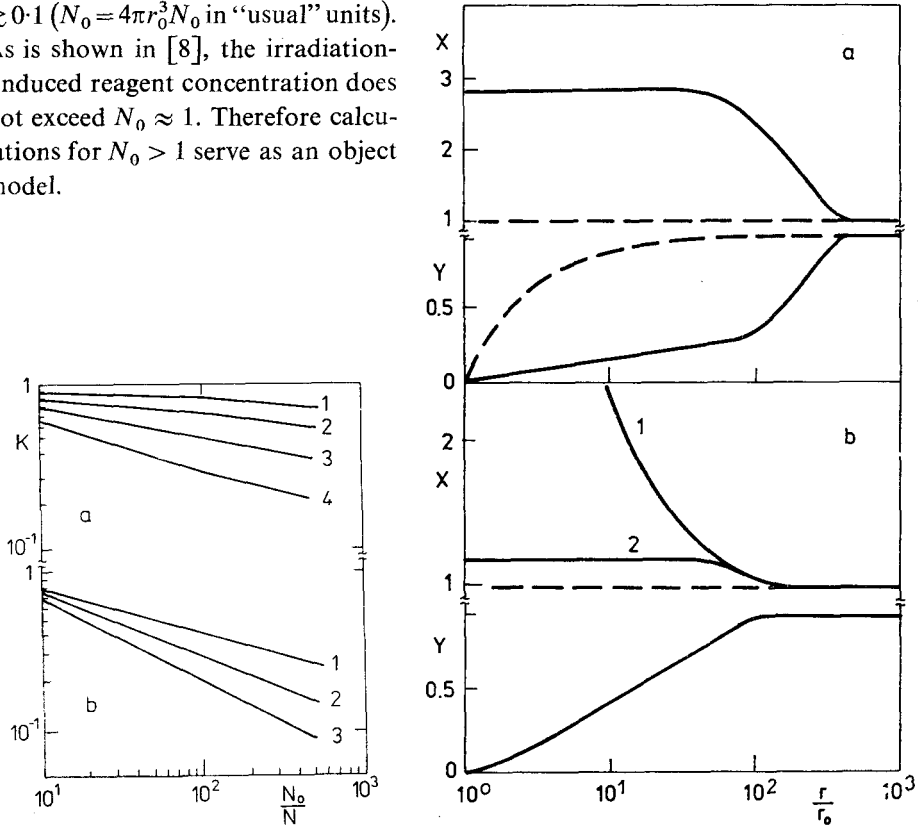


Fig. 1. The dependence of the dimensionless reaction rate  $K$  on the inverse reaction depth  $\tau^{-1}$  for a random initial distribution.  $a$  — equal diffusion coefficients;  $D_A = D_B$ . The dimensionless initial concentrations: 1 — 0.01, 2 — 0.1, 3 — 1.0, 4 — 10.

$b$  — reagents of one kind are immobile ( $D_A = 0$ ). The dimensionless initial concentrations: 1 — 0.3, 2 — 1.0, 3 — 5.0.

Fig. 2. The joint densities (correlation functions) for similar,  $X_v$ , and dissimilar,  $Y$ , reagents.  $a$  — equal diffusion coefficients ( $D_A = D_B$ ), the dimensionless initial concentration  $N_0 = 1$ ,  $N = 1.2 \times 10^{-4}$ ,  $t = 3.5 \times 10^4$  ( $r_0^2/D$ ). The reaction rate  $K = 0.19$ , the critical exponent  $\gamma = 0.82$ . The broken curve — standard neglect by similar reagent correlations [1–3].

$b$  — reagent of the kind are immobile ( $D_A = 0$ ). The similar reagent joint densities: 1 — reagents  $A$ , 2 — reagents  $B$ .  $N_0 = 5$ ,  $N = 10^{-3}$ ,  $t = 10^3$ ,  $K = 0.076$ , the critical exponent  $\gamma = 0.6$ .

Roughly, one can observe experimentally about 3–4 orders of magnitude in the decay of reagent concentration or recombination luminescence. In its turn, for the maximum concentration  $N_0 = 1$ , the decrease in the reaction rate  $K$  at  $\tau = 10^{-4}$  is by 80% ( $K = 0.2$ ). (The reaction time  $t = 10^5 r_0^2/D$ .) The corresponding critical exponent  $\gamma \simeq 0.8$  a little exceeds the magnitude  $\gamma = 0.75$  predicted in [14, 20] for  $t \rightarrow \infty$  but is considerably less than unity anyway.

If one of reagents is immobile (curves *b*), the observed reduction of the reaction rate and the effect of the initial concentration are considerably more pronounced. For instance, at reaction time  $t = 10^3$  the critical exponents are 0.77, 0.7 and 0.65 for  $N_0 = 0.3, 1$  and 5, respectively. In the latter case  $\gamma$  approaches closely the asymptotic estimate  $\gamma = 0.5$  (analytically obtained in [14] for  $t \rightarrow \infty$ ).

If reagent concentrations (unlike diffusion coefficients) are not equal, we *cannot* observe any deviation of the reaction rate. For *immobile* reagents of one kind (either  $D_A$  or  $D_B$  are zero) and great concentrations  $N_{0A} = 1, N_{0B} = 2$  the deviation in question was still detected. In accord with the asymptotic estimates [14], the exponential decay of  $N_A$  is replaced at long time by  $N_A \propto t^{-\gamma}$  with the minimum magnitude  $\gamma \simeq 3$ .

## 2.2. Correlation functions

The spatial correlations of reagents described by the joint densities are shown in fig. 2. One can conclude that in the course of the reaction the reagent distributions become *qualitatively* different from those given by the standard kinetics.

The joint density of similar reagents at small relative distances exceeds considerably the Poisson value ( $X_v = 1$ ) which means their *dynamical aggregation* (clustering) [8, 14]. (Remember that similar reagents do not interact.) Both correlation functions  $X, Y$  for the similar and dissimilar reagents approach the Poisson values  $X, Y = 1$  only at large distances  $L \propto t^{1/2}$  giving the average size of the aggregates. One can see that it exceeds greatly the distinctive spatial scale in the standard kinetics:  $L \gg 1(r_0)$ .

By means of optical absorption one can distinguish (at least in ionic crystals) macroscopic concentrations of isolated vacancies with a bound electron (the so-called *F* centres) and their dimers, trimers, etc. If the aggregation effect discussed above took place, one would detect concentrations of these complicated centres exceeding the Poisson magnitude. In fact, such observations were carried out but for the radiation-induced aggregation under KBr irradiation [21].

If one of the reagents is immobile (curves *b* in fig. 1), the behaviour of the spatial correlations considerably changes. The deviation of the joint density of mobile similar reagents becomes smaller whereas that for *immobile* reagents abruptly increases at small distances (up to  $X \simeq 10^{4-6}$  for an investigated time interval fig. 2b). In terms of physics it means that immobile reagents form very dense aggregates which do not dissolve owing to the absence of diffusion.

As one can see from fig. 1b, these peculiarities of the spatial distribution of reagents affect directly the reaction kinetics.

### 2.3. Quasi-steady initial distribution

As is well known, a prolonged irradiation of solids results in non-uniform spatial distribution of radiation (Frenkel) defects. To study how it affects the reaction kinetics we have chosen the quasi-steady distribution of dissimilar reagents,

$$(6) \quad Y(r > 1) = 1 - 1/r,$$

which occur in the standard chemical kinetics after a short transient period  $t \simeq \simeq 10^5(r_0^2/D)$ .

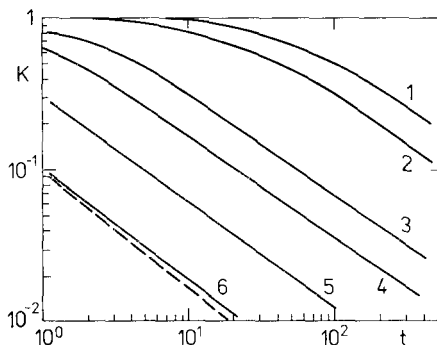


Fig. 3. The dependence of the dimensionless reaction rate  $K$  on time for the quasi-steady initial reagent distribution in the case of  $D_A = D_B$ . The dimensionless initial concentrations: 1 — 0.05, 2 — 0.1, 3 — 0.5, 4 — 1.0, 5 — 2.7, 6 — 10. The broken line — the decay kinetics for  $N_0 = 10$  and  $D_A = 0$ .

The conclusion can be drawn from fig. 3 that a variation of the initial concentrations within great bounds does not affect the decay law. The latter is characterized by a critical exponent  $\gamma \simeq 0.33$  (at  $10^5 > t > 10^2$ ). Careful calculations reveal that the curves in fig. 3 for great reaction depths approach those in fig. 1, i.e. the critical exponent  $\gamma$  reveals non-monotonous behaviour. Note that the time at which the kinetics becomes independent of the initial distribution could be experimentally unreachable.

A comparison of figs. 1 and 3 shows that for the latter initial distribution even for not long times the decreasing of the reaction rate is much greater and thus the decay of reagent concentrations is much slower than for the random distribution. Such a different behaviour of two decay kinetics is clearly due to the fact that a non-Poisson fluctuations of reagent densities  $X, Y$  come about rather slowly for their random distribution whereas the quasi-steady distribution (6) involves long-range correlations from the very beginning.

An analysis of the calculations for a random distribution and *short* times [22] reveals that the reaction rate is reduced to  $K = 1$  during a time interval *shorter* than the corresponding transient period required for this in the standard chemical kinetics.

It demonstrates once more that small non-Poisson spatial correlations of reagents being formed at the early stage of the reaction can affect considerably its kinetics in practice at *all* times.

### 3. CONCLUSION

The above presented and discussed calculations of the kinetics of the diffusion-controlled reaction  $A + B \rightarrow AB$  incorporating the many-particle effects reveal that there is a hope to observe experimentally the earlier predicted [8, 14] lowering of the bimolecular reaction rate at great initial reagent concentrations,  $4\pi r_0^3 N \gtrsim 0.1$ . This is in good agreement with the range of the applicability of the so-called "impact approximation" [23].

Perhaps the analytically predicted asymptotical decay law  $N \propto t^{-3/4}$  (for  $t \rightarrow \infty$ ,  $N_A = N_B = N$ ,  $D_A = D_B$ ) cannot be demonstrated in actual experiments but the deviation of the critical exponent  $\gamma$  ( $N \propto t^{-\gamma}$  at great  $t$ ) from the  $\gamma = 1$  known from the standard kinetics is quite sufficient for its observation.

It should be also stressed that the effect is more pronounced if the reagents are not initially distributed at random and one of two reagents is immobile. The coincidence of our decay law (in the case  $D_A = D_B$ )  $N \propto t^{-3/4}$  with that obtained in [20] in a quite different way argues greatly that the decoupling of the infinite hierarchy of equations made in eqs. (3), (4) is still rather efficient and incorporates many-particle effects in question.

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