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ON THE INFLUENCE OF SPATIAL CORRELATIONS ON THE RATE OF CHEMICAL REACTIONS IN DENSE SYSTEMS. II. NUMERICAL RESULTS

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The explicit expressions for the rate constants k_f and k_b of a dense reactive system obtained in the preceding paper are investigated numerically. The pair correlation functions representing the spatial correlations are calculated from an associate nonreactive hard sphere system by means of the multicomponent Percus–Yevick equation. The rate constants are found to differ in their dependence on density and time up to an order of magnitude from the corresponding dilute gas values. The time behaviour of k_f and k_b was found to depend sensitively on a relation between the total volumes of the reactant and product molecules.

1. Introduction

In the preceding paper [1] (hereafter referred to as I), starting from a general quantum statistical theory of chemical reactions, for the bimolecular reaction

$$A + B \rightleftharpoons C + D \tag{1}$$

the well known rate equation

$$\dot{c}_A(t) = -k_f(t)\, c_A(t)\, c_B(t) + k_b(t)\, c_C(t)\, c_D(t) \tag{2}$$

was derived, which contains, besides the dynamics of binary collisions, the influence of the spatial correlations in the system. In this paper, the explicit expressions for the rate constants k_f and k_b are investigated numerically. The rate constants are obtained as a product of the dilute gas rate constants $k_f^{(0)}$ and $k_b^{(0)}$ with quantities $y_{I,K}$, where I, K = A, B or C, D. The $y_{I,K}$ account for spatial correlations between the molecules of any reactive pair of species I, K; they depend on the actual concentrations $c_X(t)$ of the species X = A, B, C, D and thus on time. In extremely dense systems the $y_{I,K}$ may well reach values of about 10. Thus the chemical relaxation in such systems is expected to differ largely from that in its dilute counterparts as well as the resulting equilibrium constants $K = k_f/k_b$.

The present paper is devoted to a numerical investigation of these effects. We are interested in the deviations of the values in dense systems compared to those in dilute systems only. Thus it is sufficient to evaluate the $y_{I,K}$ as a function of the concentrations of the different species (compare equations (35) in I).

To calculate $y_{I,K}$ we suppose again – as in I – that in the system considered, the number of the elastic collisions is always much larger than the number of reactive collisions. From the interpretation of the $y(r)$-function given in I it follows, that in this case $y(r)$ may be calculated from the non-reactive part of the hamiltonian. As is well known [2], the $y(r)$-function can be calculated for such systems in a very good approximation from a corresponding hard sphere system with appropriately chosen hard sphere diameters. Usually these diameters lie inside a shell

$R^0_{I,K} < r < R^1_{I,K}$. The region $r < R^0_{I,K}$ is classically not accessible for particles having the average thermal momentum. $R^1_{I,K}$ is the point where the potential changes its sign. In any case the effective hard sphere diameters lie in the strongly interacting region. It is just in this region, where the transition from a clearly identifiable species to a highly complicated complex state is expected to occur. Thus the transition shell should lie inside the shell defined above. Provided both shells are sufficiently thin so that the $y(r)$-functions in this range scarcely change we may take the $y_{I,K}$ to be equal to $y_{I,K}(R_{I,K})$, where $R_{I,K} = \frac{1}{2}(R_I + R_K)$ and R_I, R_K are the effective hard sphere radii of the molecules I and K.

2. Density dependence of rate and equilibrium constants

2.1. General remarks

According to the conditions formulated in section 1 we use the relation

$$y_{I,K}(R_{I,K}) = g_{I,K}(R_{I,K}) \tag{3}$$

for hard sphere systems, which simplifies the calculation of the $y_{I,K}$ considerably. $g_{I,K}(r)$ is the pair distribution function (PDF) for which many investigations exist [2]. In spite of its simplicity in particular the multicomponent Percus–Yevick equation is known to describe the hard sphere system remarkably well [2,3]. It can be solved exactly; the explicit expressions for the function $g_{I,K}(R_{I,K})$ are:

$$g_{I,K}(R_{I,K}) = a_I + b_I/R_{I,K} , \tag{4}$$

where

$$a_I = (1 - \xi_3 + 3R_I\xi_2)/(1 - \xi_3)^2 , \tag{5}$$

$$b_I = -3R_I^2\xi_2/2(1 - \xi_3)^2 , \tag{6}$$

$$\xi_j = \tfrac{1}{6}\pi \sum_{X=A,B,C,D} \rho_X R_X^j \tag{7}$$

and

$$\rho_X = \rho c_X, \tag{8}$$

with the concentrations c_X and the particle number density $\rho = N/V$ [4]. Sometimes it is convenient to choose the reduced density,

$$\eta = \tfrac{1}{6}\pi\rho \sum_X c_X R_X^3 , \tag{9}$$

as a parameter instead of ρ.

Expressions (3)–(9) show that the $y_{I,K}$ depend on the four radii R_X and ξ_2, ξ_3 (and thus on c_X) as free parameters. To illustrate most clearly the expected

Table 1
Variations of parameters which seem to be suitable to investigate the different kinds of corrections

Group of parameters	(2.2) evaluation of $[k_f(t)/k_f^{(0)}]$ as a function of $\eta, \rho, c_X, \lvert R_A - R_B\rvert$	(2.3) evaluation of $K/K^{(0)}$ as a function of $\rho, c_X, \lvert R_A - R_B\rvert$	(3.1) evaluation of $k_f/k_f^{(0)}(t)$	(3.2) evaluation of the corrections of $\dot{c}_A(t)$ as a function of ρ
η	$0.3 \leq \eta \leq 0.7$			
$V_X = \frac{4}{3}\pi R_X^3$ X = A, B, C, D max. radius R_X normalized to 1.0	$V_A + V_B = V_C + V_D$ $R_C = R_D$	R_C, R_D arbitrary	$V_A + V_B \gtrsim V_C + V_D$ $R_C = R_D$; R_A, R_B arbitrary or $R_C = R_A$, $R_D = R_B$	$V_A + V_B \lesssim V_C + V_D$ $R_C = R_D$ R_A, R_B arbitrary
c_X X = A, B, C, D $\Sigma_X c_X = 1$	(1) $c_A \gg c_B, c_C, c_D$ (2) $c_B \gg c_A, c_C, c_D$	$c_A + c_B \gg c_C + c_D$ $c_A c_B > c_C c_D$	$c_A(0) = c_B(0) = 0.5$ $c_C(0) = c_D(0) = 0.0$ $k_f^{(0)}/k_b^{(0)}$ have to be assumed such, that $c_A(\infty) = c_B(\infty) \to 0$	
$\rho^{(0)}, \rho$	evaluable from η, c_X			

effects, we have selected suitable parameter combinations out of the parameters R_X and c_X which are given in table 1. It should be noted, however, that we have not intended to scan the whole possible parameter space so that there might well exist other combinations leading to additional conclusions.

The criterion whether or not the equation

$$V_A + V_B = V_C + V_D \,, \tag{10}$$

(where $V_X = \frac{4}{3}\pi R_X^3$ is the effective volume of a molecule of species X) is valid plays an important role in choosing the relevant parameter combinations. This relation could be approximately valid in many cases because one might expect that there are only minor changes in the total volumes of reactants A and B and products C and D for many bimolecular reaction types. As far as we know, contrary to the one-component case, the η-values for close packing as well as for the phase transition are not known for mixtures of hard spheres. For that reason the range of the η-values was chosen according to the one-component data.
In this section the correction of the rate and equilibrium constants as a function of the density and the choice of radii and concentrations of different components will be treated.

2.2. Density dependence of the reaction rates

In fig. 1 the ratio $k_f/k_f^{(0)}$ is plotted against the reduced density η for two different sets of radii. We can see that the reaction rate constant may increase by at most one order of magnitude due to the increasing reduced density η. In fig. 2 $k_f/k_f^{(0)}$ is plotted as a function of $|R_A - R_B|$ with $R_C = R_D$ for two different densities ρ [4] and concentration sets. The maximum change of the reaction rate was observed under the following conditions: at high density the molecules with largest diameters exist in the highest possible concentration and the diameter difference of molecules of sorts A and B is at minimum.

A physical explanation of the results of fig. 2 is obtained from the screening model for correlations [3]. According to this model we select a pair of molecules, say A, B, which screen each other depending on their relative diameters. The spatial correlation between A and B originates from the collisions between the molecules, surrounding A and B, and A and B respectively. It is maximal if the mutually screened solid angle between A and B is as large as possible. This reasoning immediately explains the observed increase of the correlations with decreasing difference $|R_A - R_B|$, since the mutual screening is at a maximum if $R_A = R_B$. On the other hand, the reduced density and thus the collision cross section of the surrounding molecules in the unscreened region of A and B respectively increases, if the concentration of species having the greatest diameter increases. This fact leads again to an enhancement of the correlations. It should be noted that this simple screening model is also capable of explaining the density dependent corrections discussed below.

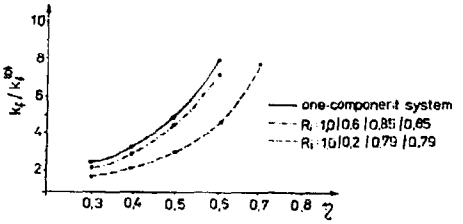

Fig. 1. Plot of the PDF $g_{A,B}(R_{A,B}) = k_f/k_f^{(0)}$ against the reduced density η for a one-component system (solid line) and four-component systems for two different sets of radii and $c_A = c_B = c_C = c_D = 0.25$ (dashed line).

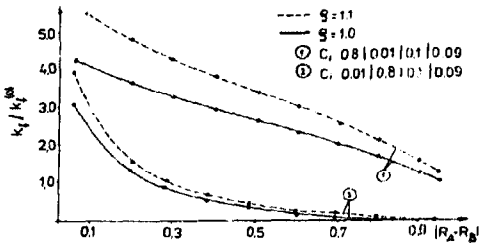

Fig. 2. Representation of the ratio $k_f/k_f^{(0)}$ as a function of the difference of radii, $|R_A - R_B|$, where $R_C = R_D$, for two densities and two sets of concentration.

[4] In describing chemical reactions of type (1) the choice of the particle number density instead of the reduced density as a parameter seems to be more suitable, because constant particle number also means constant ρ.

2.3. Density dependence of the equilibrium constants

To estimate the deviation of the K-value of a dense system from its dilute system value $K^{(0)}$ one needs the concentrations of the species at times near the relaxation time. Thus, the rate equation (2) with the density dependent constants has to be solved for given initial values $c_X(0)$, X = A, B, C, D. Because of the nonlinearity of this differential equation this could only be done numerically. To avoid this, we have used an iterative procedure:

Using (35) from I and (3) K is written as

$$K = k_f^{(0)} g_{A,B}(R_{A,B}) / k_b^{(0)} g_{C,D}(R_{C,D}) \,. \tag{11}$$

As a first approximation we evaluate the PDF's and thus K from the equilibrium concentrations of the corresponding dilute system. With the help of K_0,

$$\sum_{X=A,B,C,D} c_X = 1 \,, \tag{12}$$

and assuming that the two concentrations with the smallest absolute value are constant, new equilibrium concentrations are calculated which we use to evaluate new PDF's and thus K_1 in a second step. This procedure converges very fast. Knowing the behaviour of the density dependent corrections of the rate constants from previous discussions (see section 2.2), we may conclude: the ratio $K^{(0)}/K$ will be maximal, if both $|R_A - R_B|$ as well as the component with the largest molecular diameter and $R_C \approx R_D$ are as large as possible for high densities. As an example, fig. 3 represents the quantitative behaviour of $K^{(0)}/K$ as a function of the particle number density ρ for different sets of radii.

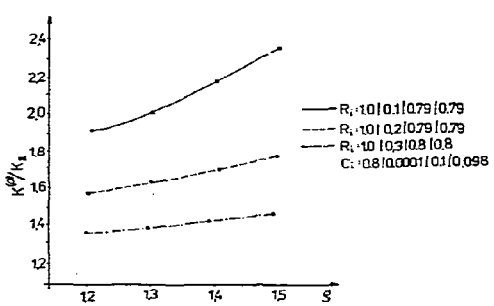

Fig. 3. Ratio of the equilibrium constants in the dense and dilute media $K/K^{(0)}$ plotted against the particle number density ρ for different sets of radii and $K^{(0)} = 100$.

3. Time dependent corrections in dense systems

In realistic dense systems the rate constants are time dependent mainly for two reasons: (1) as previously discussed, the spatial correlations depend on the concentrations of the different species and these change with time during the relaxational process; (2) due to the influence of the surrounding molecules on the reactive binary collision, the cross section or even the reaction mechanism itself can change. Formally this leads to the replacement of $k_f^{(0)}$ and $k_b^{(0)}$, according to time dependent equations for them. In a dilute system important conclusions about the reaction mechanism can be drawn from studying the time dependence of the rate constants in the rate equation (2); the rate constants are time independent only if the reaction is an elementary one [5]. However, in a dense system these conclusions are possible only if the time dependence introduced by the spatial correlations is known. For this reason we investigate the time dependence of the rate constants due to the spatial correlations.

Fig. 4 shows, that the ratio $k_f(t)/k_f^{(0)}$ or $k_b(t)/k_b^{(0)}$

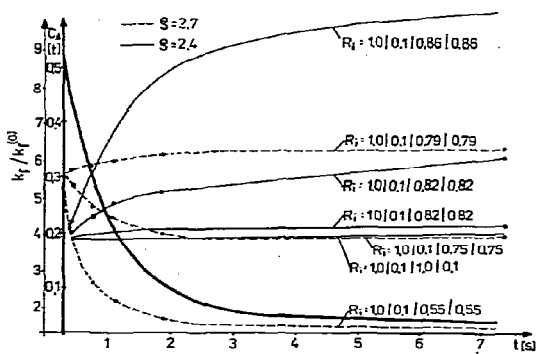

Fig. 4. Plot of the ratio $k_f/k_f^{(0)}$ against time t for two densities and different sets of radii. The heavy line represents the concentration C_A as a function of time t, evaluated from the gas phase relations: $k_f^{(0)} = 1$s, $k_b^{(0)} = 0.01$ s, $c_A(0) = c_B(0) = 0.5$, $c_C(0) = c_D(0) = 0.0$.

depends weakly on concentration and thus on time provided (10) is valid. In fact, for $R_C = R_D$ and for highly different radii R_A and R_B the maximum change of $k_f(t)$ or $k_b(t)$ related to the initial value at time $t = 0$ is 8–12%. If (10) is not valid, the ratio $k_f(t)/k_f^{(0)}$ (or $k_b(t)/k_b^{(0)}$) changes appreciably with time (see fig. 4); it decreases with $c_A(t)$ for $V_A + V_B > V_C + V_D$ and increases for $V_A + V_B < V_C + V_D$. This behaviour may be explained with the help of the screening model, as has been done in section 2.2. One may summarize, that a maximal dependence of the rate constants on concentration and thus on time occurs, if the total volume of two reactants A and B differs strongly from that of the products C and D for a reaction where the concentrations change considerably. The results obtained allow us to draw some conclusions on the rate of change of the concentrations itself.

For the parameter considered in fig. 4, the rate equation (2) may be approximately written in the form

$$-(k_f^{(0)})^{-1}\, dc_A/dt = g_{A,B}(R_{A,B} c_X(t)) \times [c_A(t) c_B(t) - K^{-1} c_C(t)\, c_D(t)]\,, \qquad (13)$$

where $k_f^{(0)}/k_b^{(0)}$ and $c_C(0)$, $c_D(0)$ where chosen in such a manner, that the second term in the rate equation (1) contributes only at times, when the concentrations are already very close to their equilibrium values ($k_f/k_b = 10^{-2}$, $c_C^{(0)} = c_D^{(0)} = 0$). From the corresponding curves, shown in fig. 5, it is immediately obvious, that in a dense system the chemical relaxation is much faster than in the dilute gas case. Comparing curves (2) and (3) in fig. 5 with the corresponding curves in fig. 4 we conclude that the time dependence of the rate constants is only weakly reflected in the time dependence of $c_A(t)$, at least in the cases considered. The same is true for $\dot{c}_A(t)$, obtained by integrating $c_A(t)$. The results demonstrate that the correction to the $c_A(t)$-function arises mainly from the correction to the equilibrium constant from $K^{(0)}$ to K. This means, that a careful analysis of any empirically obtained curve $c_A(t)$ is necessary to detect the correct time behaviour of the rate constants.

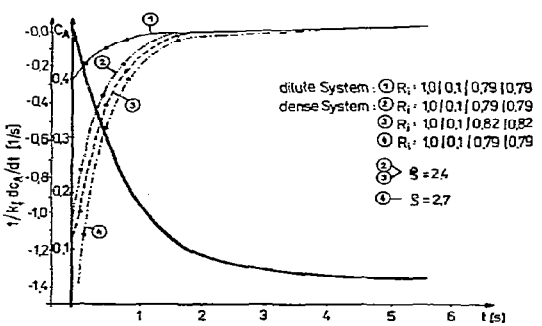

Fig. 5. Plot of the reaction rate $(1/k_f)\, dc_A/dt$ as a function of time t for the dilute system ① and dense systems with different particle-number-densities ρ (dashed lines ③ and ④). The heavy line represents $c_A(t)$ in the dilute gas case.

4. Concluding remarks

In the present paper we studied the dependence of the rate constants k_f and k_b and the equilibrium constant K on density and time for the parameter combinations shown in table 1. The rate constants of a dense system were found to differ by up to an order of magnitude from their dilute gas values due to the influence of the spatial correlations. To decide whether the time dependence of rate constants is

(a) due to time dependent spatial correlations or,

(b) due to concentration dependent changes in the binary collision cross section and the reaction mechanism respectively, relation (10) plays a decisive role.

If relation (10) is fulfilled, the time dependence of the rate constant originates from (b). If relation (10) is violated, the time dependence of the spatial correlations has to be properly taken into account in drawing any conclusions about the reaction mechanism from the time dependent rate constants. In this sense the present paper might contribute to investigation of the reaction mechanism in dense systems.

Acknowledgement

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