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# CONNECTION BETWEEN
# CHEMICAL RATE COEFFICIENTS
# AND TWO-PARTICLE CORRELATION FUNCTIONS
# IN AGGREGATED SYSTEMS

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# BUDAPEST

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## ABSTRACT

The forward direction rate coefficient $\lambda$ of irreversible bimolecular reaction $A+B \overset{\lambda}{\rightarrow} C$ is expressed in terms of the average velocities and of the spatial correlation of reactants. The anisotropic conditions supposed in microaggregates result in a formula differing from that in isotropic liquids. This difference ensures a conceptual possibility to explain the deviation of rate coefficients observed in microaggregates from those observed in conventional solutions.

## АННОТАЦИЯ

Постоянная скорости $\lambda$ необратимой бимолекулярной химической реакции типа $A+B \overset{\lambda}{\rightarrow} C$ выражена с помощью терминов средней скорости и пространственной корреляции реагентов. Анизотропные условия, предположенные в микроагрегате, приводят к формуле, отличающейся от выражения, полученного для изотропных жидкостей. Это отличие дает принципиальную возможность интерпретации разности постоянных скорости, наблюдаемых в микроагрегате и конвенциональных растворах.

## KIVONAT

Az $A+B \overset{\lambda}{\rightarrow} C$ tipusu irreverzibilis bimolekuláris kémiai reakció $\lambda$ sebességi együtthatóját a reagensek átlagos sebességével és térbeli korrelációjával hoztuk kapcsolatba. A mikroaggregátumban feltételezett anizotróp körülmények olyan formulát eredményeznek, amely különbözik az izotróp folyadékokra kapott kifejezéstől. Ez az eltérés elvi lehetőséget ad arra, hogy segítségével a mikroaggregátumokban, illetve a konvencionális oldatokban megfigyelt sebességi együtthatók különbségét értelmezzük.

## 1. INTRODUCTION

The present paper deals with some aspects of chemical rate coefficients in the liquid phase in the case when reactants are incorporated into more or less stable and closed aggregates of surface active molecules. The term aggregate covers here a wide range of theoretically different formations from micelles to microemulsions.

An ever increasing attention has been paid in the last decade to investigations of rate coefficients and reaction mechanisms in the presence of microaggregates [1-21]. The exact treatment of these reactions is very difficult for two reasons. First, the processes involved in aggregate formation [22-35] and in particle incorporation [36-39] are extremly complicated. Second, the systems under consideration are so small [24,29-32] that the use of concepts of classical statistical physics elaborated for large systems (e.g. diffusion [15,18,19]) can be questioned. Thus, it seems that in the case of microaggregates the classical concepts need a careful reformulation [40-41].

Experimental evidence [13,14] suggests that random collision models [3, 13,20,21,42] are adequate to describe chemical kinetics in these systems. Our aim is to express the coefficients of random collision models using the concepts of liquid physics and to discuss some features of the coefficients.

## 2. GENERAL CONSIDERATIONS

In order to describe observable phenomena due to chemical reactions in microaggregates, the first step is to determine the processes occuring in individual microaggregates. The chemical reaction is taken to be a result of reactive collisions between chaotically moving particles and the rate coefficients correspond to collision densities [42,43] which are calculated from the average number of reactive collisions per unit time.

In order to simplify the very complicated calculations [44] the following assumptions are made:

a) The processes are restricted to irreversible bimolecular reactions of type $A + B \overset{\lambda}{\rightarrow} C$.

b) Reactant molecules of type A and B are taken to be hard-core spheres with radii $r_A$ and $r_B$, respectively. The interaction between two reactant molecules depends only on their distance from each other, described e.g. either by hard-core or by Lennard-Jones potentials and the spatial distribution of molecules is not affected by their internal degrees of freedom.

c) Colliding molecules combine a reaction product molecule with probability $p_r$ which is supposed to be independent of the collision probability.

d) The system is in equilibrium; this state is not perturbed by chemical reactions.

The Hamiltonian has the form:

$$H(q_1 \ldots q_M, p_1 \ldots p_M, Q_1 \ldots Q_N, P_1 \ldots P_N) = \sum_i^M \frac{p_i^2}{2m_i} + \sum_j^N \frac{P_j^2}{2m_j'} +$$

$$+ V(q_1 \ldots q_M, Q_1 \ldots Q_N) \tag{2.1}$$

where $(q,p)$ are space coordinates and momenta of the reactants, $(Q,P)$ are generalized space coordinates and momenta of all other molecules. The interaction potential is divided into three parts as

$$V(q_1 \ldots q_M, Q_1 \ldots Q_N) = \sum_{1 \leq i < j \leq M} \Phi_1(|q_i - q_j|) + \sum_i^M \sum_j^N \Phi_2(q_i, Q_j) + \sum_{1 \leq i < j \leq N} \Phi_3(Q_i, Q_j) \tag{2.2}$$

The first term of the potential function describes the interaction between reactants (see condition b.), the second term stands for the interaction between the reactants and the other (among them the aggregate) molecules. The last term takes into account the effect of the structure of the liquid.

Note that M and N are the numbers of reactant and of other molecules, respectively, the quantities $q,p,Q,P$ are vectors and the integration with respect to $dq,dp,dQ,dP$ denotes a threefold integration.

## 3. AVERAGE NUMBER OF COLLISIONS PER UNIT TIME

In order to evaluate the average number of collisions per unit time, one has first to determine the geometrical condition of collision for a chosen pair of reactants. Let us introduce the concept of collision boundary $S_{ij}$ for particles with convex boundaries $i,j$ as follows: let the particle $j$ of type B move around the fixed particle $i$ of type A in such a way that their relative orientation remains unchanged and that their surfaces remain in contact. The collision boundary $S_{ij}$ is defined as the set of points repre-

senting all possible geometrical positions which can be taken by the centre of mass point of particle j.

In the simple case of hard-core spheres of radii $r_A$ and $r_B$ the collision boundary is a spherical surface of radius $r = r_A + r_B$ (which is well known from the textbooks of statistical physics and physical chemistry; see *Fig.1/a*).
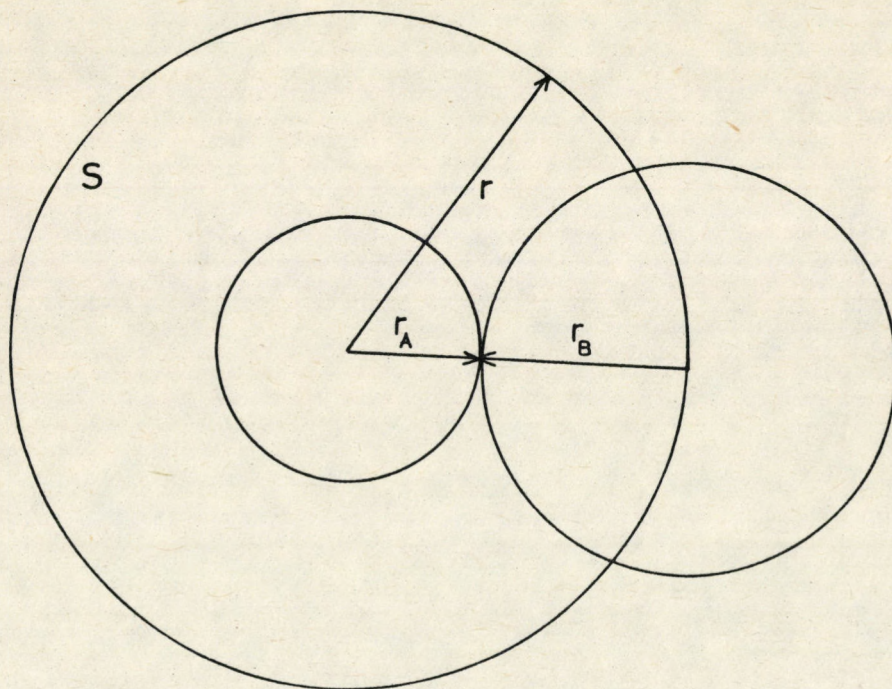


*Fig. 1/a. Definition of the collision boundary for hard-core spheres*

Let $\Delta q_{ij} = (p_j - p_i)\Delta t$ be the relative displacement vector of particles i,j during $\Delta t$ and let us define the volume element $\Delta\omega_{ij}$ by the integral:

$$\Delta\omega_{ij} = - \int_{\tilde{S}_{ij}} (n\Delta q_{ij})\, dS = -\Delta t \int_{\tilde{S}_{ij}} (p_j - p_i)\, \frac{\text{grad } S_{ij}}{|\text{grad } S_{ij}|}\, dS \qquad (3.1)$$

where $\underline{n}$ is the unit normal vector of $S_{ij}$ in the surface element dS and the integration has to be carried out over that region of the collision boundary where we have for the inner product the inequality $(n\Delta q_{ij}) < 0$.

If and only if the centre of mass point of particle j falls into the volume element $\Delta\omega_{ij}$, will particle j impinge on particle i during $\Delta t$, see *Fig. 1/b*. This event is represented by the characteristic function

$$f_{ij} = f_{ij}(\Delta t, q_i, q_j, p_i, p_j) = \begin{cases} 1, & \text{if } q_j \in \Delta\omega_{ij} \\ \\ 0, & \text{otherwise} \end{cases} \qquad (3.2)$$
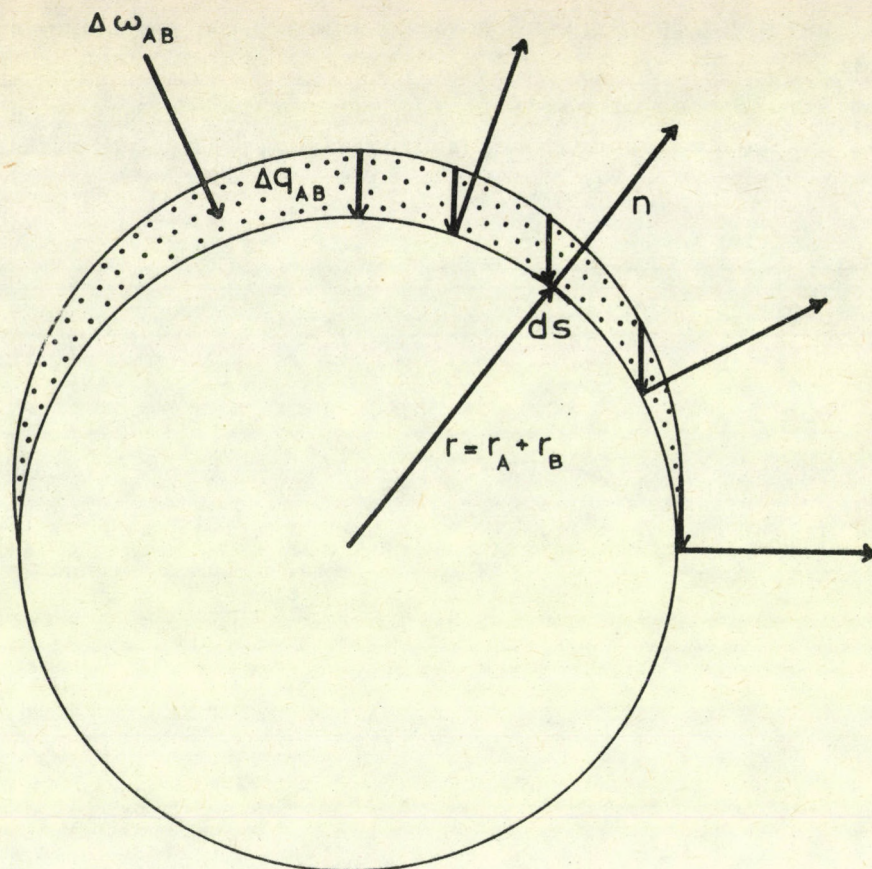
*Fig. 1/b. Determination of the volume element $\Delta\omega_{ij}$ by the collision boundary and by the relative displacement of moving hard-core spheres*

Since a collision of two particles is a mutual event, the characteristic function of their collision $\Psi_{ij}$ has to be a symmetric function in the indices; this condition is satisfied if it is expressed as the arithmetic mean of $f_{ij}$ and $f_{ji}$ in the form

$$\Psi_{ij} = \frac{1}{2} (f_{ij} + f_{ji}) = \begin{cases} 1, & \text{if } q_j \in \Delta\omega_{ij} \text{ and } q_i \in \Delta\omega_{ji} \\ 0, & \text{otherwise} \end{cases} \tag{3.3}$$

The total number of collisions between reactants of type A and B observed in $\Delta t$ is a random function of the reactant coordinates and momenta and it is given by the summation of the characteristic functions of two-particle collisions as

$$\Psi(\Delta t) = \Psi(\Delta t, q_1 \ldots q_M, p_1 \ldots p_M)$$

$$= \sum_{i}^{N_A} \sum_{j}^{N_B} \Psi_{ij}(\Delta t, q_i, q_j, p_i, p_j) + o(\Delta t) \tag{3.4}$$

$N_A$ and $N_B$ are the numbers of the A and B type reactants involved, $N_A + N_B = M$, $o(\Delta t)$ describes the number of ternary, quarternary etc. collisions. The average number of collisions $\mu(\Delta t)$ is given as

$$\mu(\Delta t) = \int \Psi(\Delta t, q_1 \ldots q_M, p_1 \ldots p_M) \, dW(q_1 \ldots q_M, p_1 \ldots p_M, Q_1 \ldots Q_M, P_1 \ldots P_M) \quad (3.5)$$

where dW is the statistical weight of finding the reactants around coordinates and momenta $q_1 \ldots q_M, p_1 \ldots p_M$ and the other particles around generalized coordinates and generalized momenta $Q_1 \ldots Q_N, P_1 \ldots P_N$. For equilibrium systems the statistical weight dW is given by the Gibbs distribution function

$$dW = Z^{-1} \exp\left[ - \frac{1}{kT}\left( \sum_i^M \frac{p_i^2}{2m_i} + \sum_j^N \frac{P_j^2}{2m_j} + V(q_1 \ldots q_M, Q_1 \ldots Q_N) \right) \right] d\Gamma \quad (3.6)$$

In Eq. (3.6) Z is the system integral, k is the Boltzmann-constant, T is the absolute temperature and $d\Gamma$ is the volume element of the phase space. Substituting this formula into Eq. (3.5) and integrating with respect the variables $Q_1 \ldots Q_N$, $P_1 \ldots P_N$ which have no direct effect on the integrand, Eq. (3.5) transforms to

$$\mu(\Delta t) = CV^{-M} \int \Psi(\Delta t, q_1 \ldots q_M, p_1 \ldots p_M) \exp\left[ - \frac{1}{kT} \sum_i^M \frac{p_i^2}{2m_i} \right] \times$$

$$\times F_M(q_1 \ldots q_M) \, dp_1 \ldots dp_M dq_1 \ldots dq_M \quad (3.7)$$

where C is a constant, V is the volume of the system, $F_M(q_1 \ldots q_M)$ is the M-particle correlation function derived from the interaction part of the Hamiltonian in Eq. (2.2) (for details see Refs. [45-47]) in the form

$$F_M(q_1 \ldots q_M) =$$

$$= V^M \exp\left[ - \frac{1}{kT} \sum_{1 \leqslant i < j \leqslant M} \Phi_1(|q_i - q_j|) \right] \cdot \int \exp\left[ - \frac{1}{kT}\left( \sum_i^M \sum_j^N \Phi_2(q_i, Q_j) + \sum_{1 \leqslant i < j \leqslant N} \Phi_3(Q_i, Q_j) \right) \right] dQ_1 \ldots dQ_N \quad (3.8)$$

$$= V^M \Phi_0(q_1 \ldots q_M) \cdot \exp\left[ - \frac{1}{kT} \sum_{1 \leqslant i < j \leqslant M} \Phi_1(|q_i - q_j|) \right]$$

Since $\Psi(\Delta t)$ is a sum of characteristic functions depending on two-particle coordinates and $F_M(q_1 \ldots q_M)$ is a symmetrical function of its arguments, $\mu(\Delta t)$ can be expressed by an integral of the two-particle correlation function $F_2(q_1, q_2)$, (see Refs. [45-47]) as

$$\mu(\Delta t) = CV^{-M} \int \sum_i^{N_A} \sum_j^{N_B} \Psi_{ij}(\Delta t, q_i, q_j, p_i, p_j) F_M(q_1 \ldots q_M) \exp\left[-\frac{1}{kT}\sum_\ell^M \frac{p_\ell^2}{2m_\ell}\right] \times$$

$$\times \, dp_1 \ldots dp_M dq_1 \ldots dq_M$$

$$= CV^{-M} \sum_i^{N_A} \sum_j^{N_B} \int \Psi_{ij}(\Delta t, q_i, q_j, p_i, p_j) F_M(q_1 \ldots q_M) \exp\left[-\frac{1}{kT}\sum_\ell^M \frac{p_\ell^2}{2m_\ell}\right] \times \quad (3.9)$$

$$\times \, dp_1 \ldots dp_M dq_1 \ldots dq_M$$

$$= CV^{-2} \, N_A \, N_B \int \Psi_{AB}(\Delta t, q_A, q_B, p_A, p_B) F_2(q_A, q_B) \exp\left[-\frac{1}{2kT}\left(\frac{p_A^2}{m_A} + \frac{p_B^2}{m_B}\right)\right] \times$$

$$\times \, dp_A \, dp_B \, dq_A \, dq_B$$

In the last line of Eq. (3.9) the subscripts A and B denote coordinates of different type reactants. The two-particle correlation function $F_2(q_1, q_2)$ can be reduced to the product of a one-particle function $F_1(q_1)$ and a conditional two-particle function $F_2(q_2|q_1)$ [45-47] of the form

$$F_2(q_2, q_1) = F_1(q_1) F_2(q_2|q_1) \qquad (3.10)$$

Substituting Eq. (3.10) into Eq. (3.9) and taking into consideration that the characteristic function $\Psi_{AB}$ is nonzero only in the region $\Delta\omega_{AB}$ where it is equal to 1, the final form to be discussed in the following is obtained as

$$\mu(\Delta t) = C \frac{N_A N_B}{V} \cdot \int \frac{F_1(q_A)}{V} \, dq_A \int F_2(q_B|q_A) \, dq_B \, \exp\left[-\frac{1}{2kT}\left(\frac{p_A^2}{m_A} + \frac{p_B^2}{m_B}\right)\right] dp_A dp_B$$

$$\Delta\omega_{AB}(\Delta t, q_A, p_A, p_B) \qquad (3.11)$$

## 4. RATE COEFFICIENTS IN DIFFERENT MEDIA

Until this point, our considerations apply to arbitrary gas and condensed phase systems. In Eq. (3.8) function $\Phi_O$ contains the boundary information for reactants: in gases and liquids, where no aggregates are present, $\Phi_O$ is non-zero for the entire reaction vessel and V is equal to its volume. In this case $F_1$ is constant and in isotropic medium $F_2(q_2|q_1)$ is a function of the coordinate differences [45-47], thus

$$F_1(q_1) = 1$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad (4.1)$$
$$F_2(q_2|q_1) = g(|q_2-q_1|) = g(q)$$

where $g(q)$ is the so called pair-correlation function. The integration in Eq. (3.11) in this case reduces to a simple integration over the colli-

sion boundary, using spherical polar-coordinates on the collision boundary $S_{AB}$ the inner integral in Eq. (3.11) leads to the simple expression

$$\int_{\Delta\omega_{AB}} F_2(q_B|q_A)\,dq_B = \Delta t\,|p_{AB}| \int_0^{2\pi} \int_0^{\pi/2} v^2 g(r)\sin\vartheta\,\cos\vartheta\,d\vartheta\,d\varphi = r^2\pi g(r)\,|p_{AB}|\Delta t \qquad (4.2)$$

and $g(r)$ is the value of the pair-correlation function at the collision boundary $S_{AB}$. Hence, integrating with respect to $q_A$ and over the momentum space, and finally, taking into account that the average number of reactive collisions in $\Delta t$ corresponds to the increase $N_r = \lambda N_A N_B \Delta t$ in reaction product molecules, from comparision of this formula and of the result of the integration the rate coefficient $\lambda$ is given as

$$\lambda = \frac{r^2\pi g(r)}{V}\,p_r C \int |p_{AB}|\exp\left[-\frac{1}{2kT}\left(\frac{p_A^2}{m_A} + \frac{p_B^2}{m_B}\right)\right] dp_A\,dp_B$$

$$= \frac{r^2\pi g(r)}{V}\,p_r\,C\,\bar{P}_{AB}(T) \qquad (4.3)$$

Some features of bimolecular rate coefficients are apparent from Eq. (4.3). The rate coefficient $\lambda$ is inversely proportional to the volume of the reaction vessel and it shows Maxwellian-type temperature-dependence in $C\bar{p}_{AB}(T)$. The factor $r^2\pi g(r)$ shows the effect of reactant size and of solution structure, $p_r$ is defined in Section 2, in condition c. If the pair-correlation function is expressed in terms of particle density (i.e. as a virial series, [45]), in the case of hard-core potentials for very dilute systems Eq. (4.3) reproduces the classical expression for gas phase rate coefficients [48].

In the case of aggregate formation, the function in Eq. (3.8) is supposed to differ from zero in the finite volume of the aggregate $V_{Ag}$; the basic assumptions listed in Section 2 are completed with this condition. The evaluation of Eq. (3.11) is not a simple task and therefore we restrict ourselves to its qualitative discussion.

According to theoretical considerations and to experimental evidence [49, 50] an aggregate is characterized by rapidly varying forces in the neighbourhood of its boundary; because of its small size the boundary effect cannot be neglected and thus it cannot be considered isotropic [45-47,49,50]. As a consequence of this fact, $F_1$ is not a constant function inside the microaggregate and the conditional two-particle correlation function cannot be replaced by the pair-correlation function $g(r)$. Instead of $g(r)$ the form $F_2 = F_2(r,\vartheta,\varphi,\vartheta_o,\varphi_o|q_1)$ has to be used which generally depends on the orientation of $q_A$ and the relative momentum $p_{AB}$ (see *Fig. 2*). The inner integral in Eq. (3.11) can be written as

$$\int_{\Delta\omega_{AB}} F_2(q_B|q_A)\,dq_B = |p_{AB}|\Delta t \int_0^{2\pi} \int_0^{\pi/2} F_2(r,\vartheta,\varphi,\vartheta_o,\varphi_o|q_A)\,r^2\cdot\cos\vartheta\,\sin\vartheta\,d\vartheta\,d\varphi \qquad (4.4)$$

and, in order to express the rate coefficient $\lambda_{Ag}$ it has to be averaged over the possible orientations of $q_A$ and $p_{AB}$ as

$$\lambda_{Ag} = \frac{r^2}{V_{Ag}} p_r c \bar{p}_{AB}(T) \int \frac{F_1(q_A)}{V_{Ag}} dq_A \ \times$$

$$(4.5)$$

$$x \int_0^{2\pi} \int_0^{\pi/2} \sin\vartheta_o d\vartheta_o d\varphi_o \int_0^{2\pi} \int_0^{\pi/2} F_2(r,\vartheta,\varphi,\vartheta_o,\varphi_o | q_A \ \cos\vartheta \cdot \sin\vartheta \cdot d\vartheta d\varphi$$
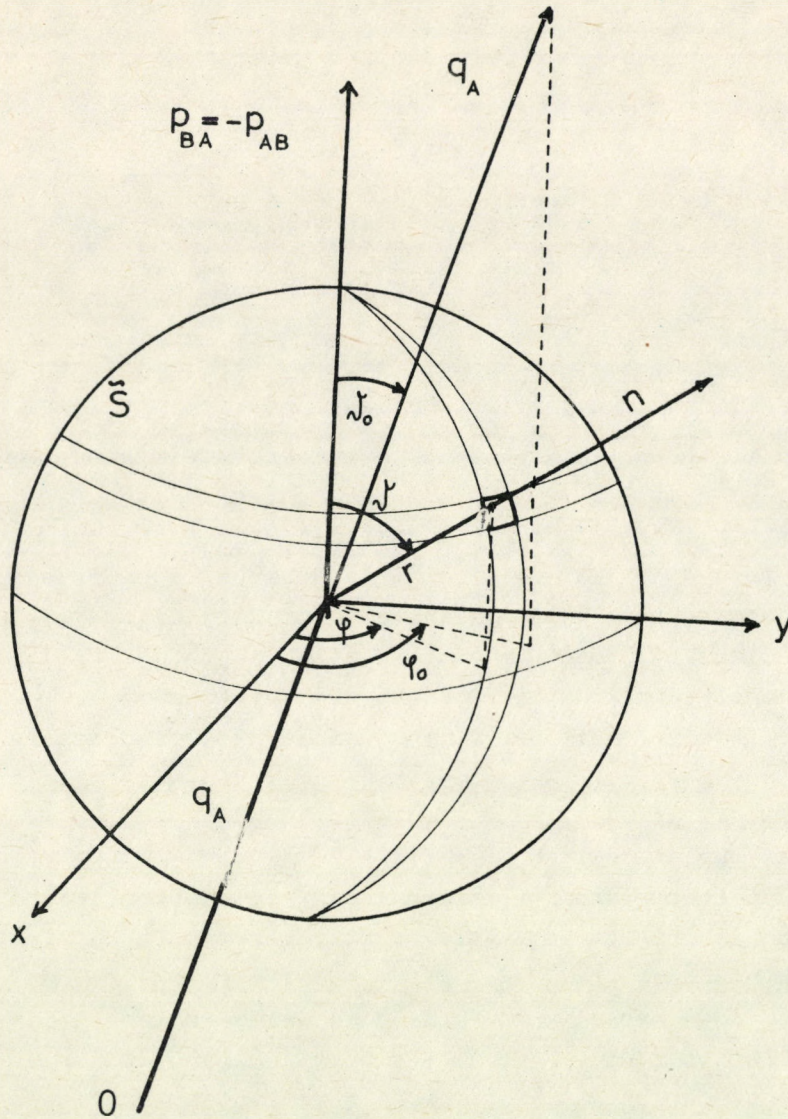


Fig. 2. *Spherical polar coordinate system connected to the relative momentum vector of the colliding hard-core spheres for the calculation of rate coefficients*

The explicit temperature dependence of the rate coefficient is of the same form, as in the case of isotropic solutions (cf. Eq. (4.3)). The rate coefficient is inversely proportional to the aggregate volume $V_{Ag}$; if the

size distribution of microaggregates is not so narrow as it is usually supposed, its effect on the reaction kinetics cannot be neglected.

The integrals in Eq. (4.5) define an average spatial correlation, which can strongly depend on the type of aggregating molecules and of reactants. If reactants are found in the boundary region of the microaggregate, the effect of the fields on the reaction probability $p_r$ has to be taken into account. These effects - which I cannot discuss in detail at the present level of my knowledge - can result in a further deviation of $\lambda_{Ag}$ from the rate coefficient determined in isotropic solutions.

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