# THE EFFECT OF CHEMICAL REACTION ON DIFFUSION

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The perturbation of the velocity distribution of a reactant by a chemical reaction and the subsequent alteration of the diffusion rate are analyzed within the framework of a modified BGK equation. An intuitive explanation of the process giving rise to non-equilibrium corrections to the diffusion coefficient is presented. The effects of perturbed internal-state populations, which are more important than velocity perturbations for most chemical reactions, are also qualitatively discussed.

## 1. Introduction

It has been known for some time now (refs. [1–8]) that, in fast chemical reactions, the perturbation of the maxwellian velocity distribution, which is caused by the reaction, can give rise to non-equilibrium corrections to the theoretical rate coefficient. When these corrections are non-negligible, we can no longer interpret measured rate coefficients as equilibrium averages of the relative energy multiplied by the cross section for reaction.

It is the purpose of this paper to demonstrate how the competition between velocity relaxation and selective depletion of high-speed reactants[†] can yield corrections to transport coefficients other than the chemical rate coefficient. Our analytical result [eq. (15)] for the diffusion coefficient of one of the reactants is obtained from a *model* kinetic equation (a modified BGK [9] equation), and is not intended to provide a general formula for the estimation of non-equilibrium corrections. The essential point is that the chemical reaction *can* have effects on other transport coefficients, and these effects are significant under

the same conditions for which non-equilibrium corrections to the chemical rate coefficient are important.

## 2. The model kinetic equation

Let us consider an irreversible, bimolecular gas-phase reaction in which each species possesses a single internal quantum state

$$A + B \rightarrow C + D . \tag{1}$$
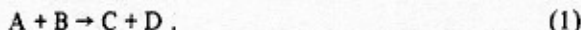
The concentration of species B is taken to be so large that we need only consider A–B and B–B collisions. It is consistent to assume that the initial phase-space distribution function of species B, which we take to be uniform in space and maxwellian in velocity, persists throughout the course of the reaction[††]:

$$f_B(r,v,t) = \left(n_B/V\right)\left(\frac{M_B}{2\pi kT}\right)^{3/2} \exp\left[-\frac{M_B v^2}{2kT}\right] . \tag{2}$$

The distribution function of species A is now assumed to be governed by the following modified BGK equation[†††]

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[†] The argument presented here is valid for any type of selective depletion. We choose to discuss the depletion of high-speed particles because this is probably the most common case.

[††] $V$ is the volume of the reaction vessel, $T$ is the temperature of the B particles, and $M_B$ is the molecular mass of a particle of type B.

[†††] The number density $n_A$ is obtained from $f_A$ by integrating over velocity.

$$\delta f_A(r,v,t)\delta t + v\nabla f_A(r,v,t)$$

$$= -(\kappa + T(v))f_A(r,v,t) + \kappa\Phi_A(v)n_A(r,t) , \qquad (3)$$

where $\Phi_A(v)$ is a maxwellian velocity distribution for species A. The velocity-dependent reactive collision frequency is $T(v)$, and the non-reactive collision frequency is denoted by $\kappa$. Because the local number density $n_A(r,t)$ contains information regarding the rates of chemical reaction and of diffusion, its calculation is our primary objective.

Eq. (3) is readily solved by introducing the Fourier—Laplace transforms of $f_A(r,v,t)$ and $n_A(r,t)$:

$$\bar{f}(k,v,z) = \int dr \int_0^\infty dt f_A(r,v,t) \exp[-ik\cdot r - zt] , \quad (4)$$

$$\bar{n}(k,z) = \int dv \bar{f}(k,v,z) . \qquad (5)$$

The resulting solution for $\bar{n}(k,z)$ is compactly written as

$$n(k,z) = [1 - \kappa\int\Lambda\Phi_A(v)dv]^{-1} \int\Lambda\bar{f}(k,v,t=0)dv , \qquad (6)$$

where $\bar{f}(k,v,t=0)$ is the Fourier transform of the (arbitrary) initial distribution function and $\Lambda$ is defined by

$$\Lambda(k,v,z,\kappa) = [z+\kappa+T(v)+ik\cdot v]^{-1} . \qquad (7)$$

To invert the Laplace-transformed number density $\bar{n}(k,z)$, we must find the poles of $\bar{n}$ in the complex $z$ plane. The long-time behavior of $n_A(r,t)$, which is of primary interest to us, is determined by the pole $z_0(k)$ of $\bar{n}(k,z)$ whose real part is least negative. Asymptotically expanding[†] the denominator of eq. (6) in inverse powers of $\kappa$, we find the following long-time pole

$$Z_0(k) = -\langle T\rangle + \kappa^{-1}\langle\delta T^2\rangle - \kappa^{-2}\langle\delta T^3\rangle$$

$$- k^2[\tfrac{1}{3}\kappa^{-1}\langle v^2\rangle - \kappa^{-2}\langle v^2\delta T\rangle] , \qquad (8)$$

[†] This expansion is meaningful if the velocity relaxation time $\kappa^{-1}$ is smaller than the inverse of the pseudo-first order rate constant $(n_B/V) k_{rate}$. Later, we show that the most interesting situation arises when $\kappa^{-1} < [(n_B/V) k_{rate}]^{-1}$, but not $\kappa^{-1} \ll [(n_B/V) k_{rate}]^{-1}$.

which is correct to second order in $\kappa^{-1}$. The *fluctuation* in the reactive collision frequency is $\delta T(v) =$

$$T(v) - \langle T\rangle \qquad (9)$$

and the bracket means an average over $\Phi_A(v)$, e.g.,

$$\langle T\rangle = \int\Phi_A(v)T(v)dv . \qquad (10)$$

Thus, for long times, i.e., after the effects of the other poles of $\bar{n}(k,z)$ have become negligible, the Fourier transform of $n_A(r,t)$ is given by

$$n_A(k,t) = R_0(k) \exp[Z_0(k)t] , \qquad (11)$$

which implies

$$dn_A/dt = Z_0(k)n_A(k,t) , \qquad (12)$$

where $R_0(k)$ is the residue of $\bar{n}(k,z)$ at $Z_0(k)$.

The *phenomenological equation* for $n_A(r,t)$

$$dn_A(r,t)/dt - D_A\nabla^2 n_A(r,t)$$

$$= -(n_B/V) k_{rate} n_A(r,t) \qquad (13)$$

involves the chemical rate coefficient $k_{rate}$ for the reaction and the diffusion coefficient $D_A$ of species A. Comparing the Fourier transform of eq. (13) to the kinetic-equation result given in eq. (12), we can immediately extract expressions for $k_{rate}$ and $D_A$ as power series in $\kappa^{-1}$:

$$k_{rate} = (V/n_B)[\langle T\rangle - \kappa^{-1}\langle\delta T^2\rangle + \kappa^{-2}\langle\delta T^3\rangle] \qquad (14)$$

and

$$D_A = \tfrac{1}{3}\kappa^{-1}\langle v^2\rangle - \kappa^{-2}\langle v^2\delta T\rangle . \qquad (15)$$

## 3. Physical interpretation

The terms in eqs. (14) and (15) involving the fluctuation $\delta T(v)$ arise because of the coupling between velocity relaxation and the chemical reaction. To illustrate these effects, assume that in a short period of time the chemical reaction selectively consumes high-speed particles of type A. The velocity distribution of the particles which remain after this period is no longer maxwellian; the high-speed tail of the maxwellian has been reduced in magnitude. Immediately following this time period, collisions with molecules of type B will cause the velocity distribution to relax

towards its equilibrium maxwellian form. However, as this relaxation proceeds, both diffusion and further chemical reaction can occur. Thus, during the time $(\kappa^{-1})$ it takes the velocity distribution to relax, chemical reaction and diffusion proceed under the influence of a velocity distribution which is deficient in high-speed particles. This temporary deficiency causes both the diffusion and reaction rates to be reduced from the values which would result if the velocity distribution were maxwellian for all time. Of course, if the velocity relaxation is very much faster than the rate of depletion of high-speed particles by the reaction, then the non-equilibrium effects in $k_{rate}$ and $D_A$ will be negligible. However, for reactions whose bimolecular rate coefficient is of the order of $10^8$ to $10^{10}$ sec$^{-1}$ mole$^{-1}$ liter, these corrections to $D_A$ and $k_{rate}$ can be important [†].

We have examined the first non-equilibrium corrections to $k_{rate}$ and $D_A$ for the line-of-centers cross-section [††]. We find that the corrections to $D_A$ are significant if both the threshold energy of the reaction is small with respect to $kT$ *and* the amplitude of the reactive cross section is of the same order of magnitude as the velocity-relaxation cross section. These conditions are identical to the conditions [1–8] under which non-equilibrium corrections to $k_{rate}$ become non-negligible.

Although the non-equilibrium effects discussed above are insignificant for all but very fast chemical reactions, analogous perturbations of vibrational-state (or other internal-state) populations [†††], caused by the non-uniform reactivity of various vibrational levels, may lead to significant non-equilibrium corrections to $D_A$. That is, if the *size* of the molecule depends relatively strongly on the vibrational state, then

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[†] We cannot discuss a reaction whose rate constant is so large as to violate the condition discussed in footnote, p. 000.

[††] See ref. [6] for the definition of this model cross section.

[†††] The effects of perturbed internal-state populations on the chemical rate coefficient have previously been discussed. For example, see refs. [1–8] and ref. [10].

molecules in different states will diffuse at different rates [*]. Thus, the selective depletion of certain vibrational levels leads to a non-equilibrium internal-state distribution which then decays toward equilibrium. During this decay, diffusion occurs at a rate which differs from the equilibrium rate obtained in the absence of chemical reaction. The importance of such non-equilibrium contributions to $D_A$ is, of course, determined by the ratio of the rate of the chemical reaction to the rate of internal-state relaxation. Because internal-state relaxation can be relatively slow, the possibility does exist for observing the corrections to $D_A$ discussed above. We defer a more complete treatment of this interesting problem to a future publication.

## Acknowledgements

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[*] Even in a non-reactive case, if strong electromagnetic radiation is used to pump higher vibrational states of a molecule, one can perturb the diffusion coefficient from its equilibrium value.

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