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# Nonequilibrium effects in reactive systems; the effect of reaction products and the validity of the Chapman–Enskog method

Bernie D. Shizgal, Duncan G. Napier

*Department of Chemistry, University of British Columbia, Vancouver, BC V6T 1Z1, Canada*

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## Abstract

The rates of gas phase reactions can be calculated from the averages of the appropriate reactive cross sections with the velocity distribution functions of the reacting species. The reactive process, especially for reactions with activation energy, removes translationally energetic species and the velocity distribution functions depart from Maxwellian. The rate coefficients can differ from the equilibrium rate calculated with the Maxwell–Boltzmann distribution. The extent of the departure of the distribution function from Maxwellian can be estimated from solutions of the Boltzmann equation with appropriate choices for the elastic and reactive collision cross sections. If there is a good separation in the elastic and reactive collision time scales, a steady solution of the Boltzmann equation can be obtained with a procedure analogous to the Chapman–Enskog method for transport coefficients. In the present paper, the nonequilibrium effects for model reactive systems of the type  $A + A \rightleftharpoons B + B$ , with and without the reverse reaction, and the reaction  $A + C \rightarrow$  products are examined with both a Chapman–Enskog method along with an explicitly time-dependent solution for the irreversible reaction  $A + A \rightarrow B + B$ . The main objectives are to study the effect of the inclusion of the products with and without a reverse reaction as well as the range of validity of the Chapman–Enskog method.

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## 1. Introduction

Nonequilibrium effects associated with reactive systems have received considerable attention in the literature for a long time [1–23]. A complete bibliography can be found in the references cited in these papers. Many calculations have been carried out for model reactive systems of the type



with the complete neglect of the products. The main objective is the calculation of the extent of the departure of the translational distribution functions from Maxwellian and the fractional decrease of the nonequilibrium rate coefficient,  $k$ , from the equilibrium value,  $k^{(0)}$ , that is,

$$\eta = [k^{(0)} - k]/k^{(0)}.$$

The approach employed by most workers involve the application of the Chapman–Enskog (CE) method of solution of the Boltzmann equation [24]. This method has been shown to be valid only if there is a good separation of reactive and elastic time scales [9,10]. The reactive process must be a small perturbation on the system. The CE approach yields a very special solution of the Boltzmann equation referred to as a “normal solution” [24], for which the time dependence of the distribution function is implicit through the time dependence of the density,  $n(t)$ , and the time variation of the temperature,  $T(t)$ , that is,  $f(c, t) = f(c; n(t), T(t))$ .

The CE method is known to be invalid for strongly nonequilibrium systems for which the required separation of length and time scales is not obtained [25–29]. Several groups have considered the description of transport for such systems far from equilibrium; in particular nonlocal heat transport in plasmas [25], hypersonic flows [26], diffusive flows [27,28] as well as astrophysical applications [29]. For spatially inhomogeneous systems, the CE method is valid when the mean free path of the constituents is much less than the typical length scale [24,30]. For reactive systems, a CE method is applicable when the elastic time scale is much less than the reactive time scale [9]. Kogan [31] and Alexeev et al. [32–34] have considered extensions of the CE method to chemically reactive systems far removed from equilibrium. Alexeev has referred to this method as the generalized CE method. A study of the range of validity of the CE method is an important endeavour and one of the major objectives of the present paper. A comparison of the CE method and Grad’s moment method was reported by Eu and Li [11].

An alternate and complementary approach to the study of nonequilibrium effects in reactive systems is a Monte Carlo simulation of reaction and relaxation dynamics. This has been carried out principally by Baras and Malek-Mansour [13,18] as well as by Popielawski and co-workers [15,16,21–23]. Since direct experimental verification of these nonequilibrium effects have not been reported to date, these Monte Carlo simulations can be viewed as providing the experimental results with which direct solution methods of the Boltzmann equation can be compared [13,18,19].

Cukrowski et al. [16] recently carried out an approximate study of the nonequilibrium effects for the reaction



Cukrowski et al. assumed that the distribution functions of the two species were local Maxwellians at different temperatures and the reaction was treated as an adiabatic process. The Boltzmann equations are then approximated by the time-dependent equations for the number densities and the species temperatures. This approach is similar to the

time dependent theory of hot atom reactions [35] and temperature relaxation [36]. The results of their calculations were compared with estimates of  $\eta$  obtained with the CE analysis by Cukrowski, Fritzsche and Popielawski [15] and from computer simulations. The main objective of the work by Cukrowski et al. [16] was to compare the nonequilibrium effects of  $A + A \rightarrow B + B$  with those of  $A + C \rightarrow$  products. A second objective of the present paper is to re-examine the nonequilibrium effects of the reactions above with particular attention to the effect of the reverse reaction and the density dependence of the products. Shizgal and Karplus demonstrated long ago [7,8] that the nonequilibrium effects in reactive systems are particularly sensitive to whether the system is adiabatic ( $dT/dt \neq 0$ ) or isothermal ( $dT/dt = 0$ ). If  $dT/dt \neq 0$ , the nonequilibrium effects have an explicit dependence on the heat of reaction [2,21]. Also, in the time-dependent studies of the reaction with products,  $A + A \rightarrow B + B$ , the value of  $dT/dt$  in the limit of vanishing products requires some careful analysis [15,17].

The limit of vanishing products, studied previously by Pyun and Ross [5], and Fitzpatrick and Desloge [14], is of particular interest to the present paper. We study the difference between results obtained from a CE analysis of the model reaction  $A + C \rightarrow$  products, where the product species are completely ignored, and results obtained for the model reaction  $A + A \rightarrow B + B$  with the products taken into account. We also consider the reversible reaction  $A + A \rightleftharpoons B + B$  in comparison with the other systems. Shizgal and Karplus [8] conducted a CE analysis of the general reversible reaction  $A + B \rightleftharpoons C + D$ , which includes the effect of the reverse reaction.

Section 2.1 describes the CE method of solution of the Boltzmann equations for the distribution functions of the two species involved in the reaction  $A + C \rightarrow$  products. The extent of nonequilibrium effects in terms of the quantity  $\eta$  is determined. The usefulness of the Shizgal–Karplus temperature, introduced by Cukrowski and coworkers [15] is evaluated.

The irreversible reaction  $A + A \rightarrow B + B$  and the reversible reaction  $A + A \rightleftharpoons B + B$  are considered in like manner in Sections 2.2 and 2.3, respectively. An important aspect of the analysis is the use of microscopic reversibility in the case of the reversible reaction and the lack thereof for the irreversible reaction. Although these three reactive systems are very similar, the kinetic theory treatment of the nonequilibrium effects involves several important subtle aspects that are discussed in detail. In Section 3, we present the results of a time-dependent solution of the Boltzmann equation and determine the range of validity of the CE approach. In the appendix, we show that the CE procedure by Cukrowski et al. [15] is deficient in several ways.

## 2. The Chapman–Enskog solution of the Boltzmann equation

We consider detailed calculations for the hard sphere elastic and line-of-centers reactive model system used previously [6–8]. The differential elastic cross sections are taken to be hard spheres ( $\sigma_E = d_E^2/4$ ) and the total reactive cross section is the line-of-centers cross section given by

$$\begin{aligned}\sigma^* &= \pi\sigma_R(1 - E^*/E), & E &\geq E^*, \\ &= 0, & E &< E^*.\end{aligned}\quad (3)$$

where  $E^*$  is the threshold energy and  $\sigma_R = d_R^2/4$ . The hard sphere elastic and reactive diameters are  $d_E$  and  $d_R$ , respectively.

### 2.1. The reaction $A + C \rightarrow$ products

The distribution functions for the two species are denoted by  $\gamma$  and  $\eta$  equal to 1 for species A and 2 for species C. For this reaction, the distribution functions are assumed to be given by two coupled Boltzmann equations of the form

$$\begin{aligned}\frac{\partial f_1}{\partial t} &= \int \int [f'_1 f' - f_1 f] \sigma_{11} g d\Omega d\mathbf{c} + \int \int [f'_1 f'_2 - f_1 f_2] \sigma_{12} g d\Omega d\mathbf{c}_2 \\ &\quad - \int \int f_1 f_2 \sigma^* g d\Omega d\mathbf{c}_2,\end{aligned}\quad (4)$$

$$\begin{aligned}\frac{\partial f_2}{\partial t} &= \int \int [f'_2 f' - f_2 f] \sigma_{22} g d\Omega d\mathbf{c} + \int \int [f'_1 f'_2 - f_1 f_2] \sigma_{12} g d\Omega d\mathbf{c}_1 \\ &\quad - \int \int f_1 f_2 \sigma^* g d\Omega d\mathbf{c}_1,\end{aligned}\quad (5)$$

where  $\sigma_{\gamma\eta}$  and  $\sigma^*$  are the elastic and reactive cross sections, respectively. The first collision operators on the right-hand side of Eqs. (4) and (5) are the *self*-collision terms for A–A and C–C elastic collisions. The second collision operators take account of A–C elastic collisions and couple the two equations. The reactive terms with the reactive cross section represent the loss of both species. The other quantities have their usual definitions [6–8]. The notation employed in Eqs. (4) and (5) is standard [24], where the unlabeled distribution and velocity variable refer to the other particle in a binary collision. For all applications in this paper, we set  $\sigma_{11} = \sigma_{22} = \sigma_{12} = \sigma_E$  and vary the ratio  $\sigma_R/\sigma_E$ . The method of solution of these coupled Boltzmann equations is as described in a previous paper [7]. The distribution functions are expanded about local Maxwellians,  $f_\gamma^{(0)} = n_\gamma(t) [m_\gamma/2\pi kT(t)]^{3/2} \exp[-m_\gamma c^2/2kT(t)]$ , characterized by time-dependent number densities,  $n_\gamma(t)$ , and the single temperature,  $T(t)$ .

The Boltzmann equations are solved with the expansion about the Maxwellian, that is,

$$f_\gamma = f_\gamma^{(0)} [1 + \psi_\gamma], \quad (6)$$

where  $\psi_\gamma$  is the perturbation from Maxwellian. We review the methodology of the previous paper [7] for completeness, and to permit a clear comparison with the other models discussed in Sections 2.2 and 2.3, as well as with the time-dependent approach in Section 3.

The CE approach involves the assumption that (to lowest order) the time dependence of the distribution function is given by

$$\frac{\partial f_\gamma}{\partial t} = \frac{\partial f_\gamma^{(0)}}{\partial n_\gamma} \left( \frac{dn_\gamma}{dt} \right)^{(0)} + \frac{\partial f_\gamma^{(0)}}{\partial T} \left( \frac{dT}{dt} \right)^{(0)}, \quad (7)$$

where the time variation of the densities is determined from the Boltzmann equations, and given by

$$\left( \frac{dn_1}{dt} \right)^{(0)} = \left( \frac{dn_2}{dt} \right)^{(0)} = - \int \int \int f_1^{(0)} f_2^{(0)} \sigma^* g d\Omega d\mathbf{c}_1 d\mathbf{c}_2. \quad (8)$$

For this reaction, there is a loss of energy owing to reactive collisions and the variation of the temperature (to lowest order) is given by

$$\left( \frac{dT}{dt} \right)^{(0)} = \frac{2T}{3n} \int \int \int f_1^{(0)} f_2^{(0)} \left[ 3 - \frac{m_1 c_1^2}{2kT} - \frac{m_2 c_2^2}{2kT} \right] \sigma^* g d\Omega d\mathbf{c}_1 d\mathbf{c}_2. \quad (9)$$

With the substitution of Eq. (6) into the Boltzmann equations, Eqs. (4) and (5) and use of Eqs. (7)–(9), we find that the CE equations for the perturbations  $\psi_\gamma$  are given by

$$\begin{aligned} & \int \int f_1^{(0)} f^{(0)} [\psi'_1 + \psi' - \psi_1 - \psi] \sigma_{11} g d\Omega d\mathbf{c} \\ & + \int \int f_1^{(0)} f_2^{(0)} [\psi'_1 - \psi_1] \sigma_{12} g d\Omega d\mathbf{c}_2 + \int \int f_1^{(0)} f_2^{(0)} [\psi'_2 - \psi_2] \sigma_{12} g d\Omega d\mathbf{c}_2 \\ & = f_1^{(0)} C_1(c_1), \end{aligned} \quad (10)$$

$$\begin{aligned} & \int \int f_2^{(0)} f^{(0)} [\psi'_2 + \psi' - \psi_2 - \psi] \sigma_{22} g d\Omega d\mathbf{c} \\ & + \int \int f_1^{(0)} f_2^{(0)} [\psi'_2 - \psi_2] \sigma_{12} g d\Omega d\mathbf{c}_1 + \int \int f_1^{(0)} f_2^{(0)} [\psi'_1 - \psi_1] \sigma_{12} g d\Omega d\mathbf{c}_1 \\ & = f_2^{(0)} C_2(c_2), \end{aligned} \quad (11)$$

where the inhomogeneous terms are defined by

$$C_\gamma(c_\gamma) = \left[ -\frac{1}{n_\gamma} \left( \frac{dn_\gamma}{dt} \right)^{(0)} - \frac{1}{T} \left( \frac{3}{2} - x_\gamma^2 \right) \left( \frac{dT}{dt} \right)^{(0)} + R_\gamma^{(0)}(c_\gamma) \right], \quad (12)$$

where  $x_\gamma^2 = m_\gamma c_\gamma^2 / 2kT$  and

$$R_\gamma^{(0)}(c_\gamma) = \int \int f_\eta^{(0)} \sigma^* g d\Omega d\mathbf{c}_\eta. \quad (13)$$

The solution of these coupled linear integral equations is obtained with the expansion of the unknown functions  $\psi_\gamma$  in Sonine (Laguerre) polynomials,  $S_\gamma^{(i)}(x_\gamma^2)$  defined in the previous papers [6–8]. With the expansions

$$\psi_\gamma(x_\gamma) = \sum_{i=1}^N a_i^{(\gamma)} S_\gamma^{(i)}(x_\gamma^2),$$

we get the set of algebraic equations for the coefficients  $a_i^{(\gamma)}$  given by

$$\sum_{j=1}^N \left[ \left( n_1^2 [S_1^{(i)}, S_1^{(j)}] + n_1 n_2 \{S_1^{(i)}, S_1^{(j)}\} \right) a_j^{(1)} + n_1 n_2 \{S_1^{(i)}, S_2^{(j)}\} a_j^{(2)} \right] = n_1 n_2 \alpha_i^{(1)}, \tag{14}$$

and

$$\sum_{j=1}^N \left[ \left( n_2^2 [S_2^{(i)}, S_2^{(j)}] + n_1 n_2 \{S_2^{(i)}, S_2^{(j)}\} \right) a_j^{(2)} + n_1 n_2 \{S_2^{(i)}, S_1^{(j)}\} a_j^{(1)} \right] = n_1 n_2 \alpha_i^{(2)}, \tag{15}$$

where

$$n_1 n_2 \alpha_i^{(\gamma)} = -\delta_{0i} A_0^{(\gamma)} - \delta_{1i} \frac{n_\gamma}{n} \sum_\gamma A_1^{(\gamma)} + A_i^{(\gamma)}. \tag{16}$$

The bracket matrix elements  $[S_\gamma^{(i)}, S_\gamma^{(j)}]$ , the brace matrix elements  $\{S_\gamma^{(i)}, S_\eta^{(j)}\}$  are defined explicitly elsewhere (see Eqs. (31) and (32) of Ref. [7]), and evaluated for a hard sphere elastic cross section. The integrals  $A_i^{(\gamma)}$ , defined by Eq. (38) of Ref. [7], are the Sonine moments of the reactive collision frequencies and evaluated for the line-of-centers reactive cross section. The concentration dependence in the middle term of Eq. (16) is particularly important. It is this term, arising from  $(dT/dt)^{(0)} \neq 0$  (see Eq. (12)), that gives rise to large effects when the two reactants are dissimilar, that is for unequal mass ratios or densities.

The density is defined in terms of  $f_\gamma^{(0)}$ , that is,

$$n_\gamma = \int f_\gamma^{(0)} d\mathbf{c}_\gamma, \tag{17}$$

so that  $\int f_\gamma^{(0)} \psi_\gamma d\mathbf{c}_\gamma = 0$  and hence  $a_0^{(0)} = 0$ . The temperature is defined by

$$\frac{3}{2} nkT = \int f_1^{(0)} \frac{1}{2} m_1 c_1^2 d\mathbf{c}_1 + \int f_2^{(0)} \frac{1}{2} m_2 c_2^2 d\mathbf{c}_2, \tag{18}$$

where  $n = n_1 + n_2$  and we have that

$$\int f_1^{(0)} m_1 c_1^2 \psi_1 d\mathbf{c}_1 + \int f_2^{(0)} m_2 c_2^2 \psi_2 d\mathbf{c}_2 = 0, \tag{19}$$

and hence

$$n_1 a_1^{(1)} + n_2 a_1^{(2)} = 0. \tag{20}$$

Consistent with this definition of the temperature is that the two equations in Eqs. (14) and (15) with  $i = 1$  are the negative of one another; their sum being equal to zero is a reflection of conservation of energy when both species are taken into account. Consequently, the set of equations that is solved, is the set with Eq. (20) replacing either of the two equations with  $i = 1$  in Eqs. (14) and (15).

The solution of Eqs. (14) and (15) together with Eq. (20) as discussed above yields the expansion coefficients and the fractional decrease in the equilibrium rate of reaction as given by

$$\eta = - \left[ \sum_{i=1}^N a_i^{(1)} A_i^{(1)} / A_0^{(1)} + \sum_{i=1}^N a_i^{(2)} A_i^{(2)} / A_0^{(2)} \right]. \quad (21)$$

For the hard sphere cross section models, since  $\eta$  is directly proportional to  $\sigma_R / \sigma_E$ , this ratio can be set equal to 1 and the  $\eta$  calculated is then multiplied by  $\sigma_R / \sigma_E$ . The calculation of the mean energy of each species yields the definition of species temperatures,  $T_\gamma$ , which is

$$T_\gamma = T [1 - a_1^{(\gamma)}], \quad (22)$$

where  $T$  is the temperature in the Maxwellians. Cukrowski et al. [15,16] refer to these species temperatures as the Shizgal–Karplus temperatures.

Cukrowski et al. [15] suggested that the nonequilibrium rate coefficient can be approximated with the use of the species temperatures as given by Eq. (22) with the  $a_1^{(\gamma)}$  determined to lowest order, that is, from the solution of Eqs. (14) and (15) with only one term. An estimate of the nonequilibrium rate coefficient is determined with Maxwellians characterized with the species temperatures, that is,

$$\hat{\eta} = \frac{k^{(0)} - k(T_1, T_2)}{k^{(0)}}. \quad (23)$$

Clearly, this result can only be useful if the two species are distinct and the species temperatures differ from the temperature  $T$ . It is anticipated that their procedure will be invalid when the two species are similar by virtue of their masses and number densities. Cukrowski *et al.* have employed this approach in several studies of nonequilibrium effects [45] and references therein. The relationship between  $\eta$  and  $\hat{\eta}$  can be understood by recognizing that the expansion of the local Maxwellians,  $F^{(0)}(T_\gamma)$ , at the species temperatures about the temperature  $T$  leads to an expansion in Sonine polynomials of the form

$$F^{(0)}(T_\gamma) = f^{(0)}(T) \left[ 1 + \sum_{i=1}^{\infty} \left( \frac{\Delta T_\gamma}{T} \right)^i S_\gamma^{(i)}(mc^2/kT) \right], \quad (24)$$

where  $\Delta T_\gamma = T - T_\gamma$ . Eq. (24) illustrates the use of the ratio  $F^{(0)}(T_\gamma) / f^{(0)}(T)$  as the generating function for the Sonine polynomials. This was used in a previous paper [7] to determine the brace bracket integrals. In this way, the approximation by Cukrowski et al. [15], consists of an expansion of the distribution function in Sonine polynomials with the expansion coefficients as powers of  $a_1^{(\gamma)}$ . It is correct only to lowest order when only one term is retained in the expansion. In this way, the use of the Shizgal–Karplus temperature as employed by Cukrowski et al. yields a nonequilibrium correction of the form

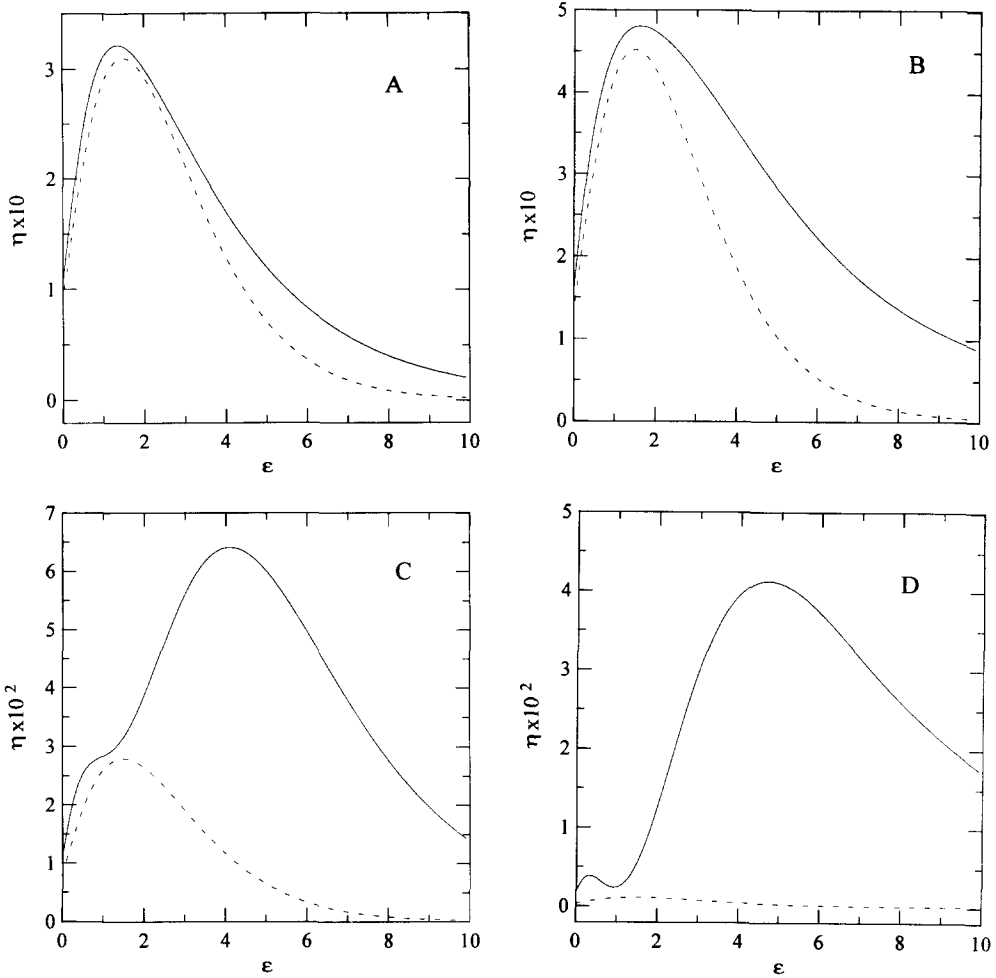


Fig. 1. Variation of  $\eta$  (—) and  $\hat{\eta}$  (---) versus  $\epsilon$  for  $A + C \rightarrow$  products. The mass ratio  $m_1/m_2$  and density ratio  $n_1/n_2$  are equal to (A) 2 and 8, (B) 10 and 1, (C) 2 and 1, (D) 10 and 1/8 respectively;  $\sigma_E = \sigma_{11} = \sigma_{12} = \sigma_{22}$  and  $\sigma_E/\sigma_R = 1$ .

$$\hat{\eta} = - \left[ \sum_{i=1}^N \left( \frac{\Delta T_1}{T} \right)^i A_i^{(1)}/A_0^{(1)} + \sum_{i=1}^N \left( \frac{\Delta T_2}{T} \right)^i A_i^{(2)}/A_0^{(2)} \right]. \quad (25)$$

It is expected that this approximation may be useful when the terms in  $a_1^{(\gamma)}$  dominate the solution in Eq. (21).

The variation of the correction  $\eta$  versus the system variables was reported at length in the previous paper [7]. Here we are interested in the comparison with  $\hat{\eta}$ , Eq. (25). Fig. 1 shows the variation of  $\eta$  (solid curve) obtained from Eq. (21) with retention of a sufficient number of terms to provide convergence to four significant figures, in comparison with the Cukrowski et al. [15] approximation, Eq. (25) (dashed curve). The

agreement between the converged solution,  $\eta$ , and the approximation, Eq. (25), varies considerably according to the ratios of the masses and densities of the reactants A and C. With Eq. (16) and the definition of  $A_i^{(\gamma)}$  defined by Eq. (38) of Ref. [7], it can be shown that  $\alpha_1^{(\gamma)}$  and  $a_1^{(\gamma)}$  are proportional to  $m_1 n_1 / m_2 n_2 - 1$ . The ratio  $m_1 n_1 / m_2 n_2$  is 16, 10, 2 and 5/4 in Figs. 1A to 1D, respectively. As the quantity  $m_1 n_1 / m_2 n_2 \rightarrow 1$  the agreement between  $\eta$  and  $\hat{\eta}$  becomes poorer. This is due to the fact that as  $m_1 n_1 / m_2 n_2 \rightarrow 1$ ,  $\alpha_1^{(\gamma)} \rightarrow 0$  resulting in  $\Delta T_\gamma \rightarrow 0$  and  $\hat{\eta} \rightarrow 0$ . This result holds for all orders of approximation. Consequently,  $\hat{\eta}$  is a reasonable approximation to  $\eta$  in Fig. 1A for which  $m_1 n_1 / m_2 n_2 = 16$ . The agreement worsens as  $m_1 n_1 / m_2 n_2$  tends to unity in Figs. 1B, 1C and 1D. For Fig. 1D where the temperature perturbation is extremely small, the  $a_1^{(\gamma)}$  contribution becomes insignificant,  $\Delta T_\gamma \approx 0$  and the approximation  $\hat{\eta}$  by Cukrowski et al. is not valid.

The dependence of  $\eta$  on the density is one of the important objectives of the present work, in particular with respect to the density of the products for the reactions considered in Sections 2.2 and 2.3. If only two terms in the expansion of the distribution functions are retained, approximate expressions can be obtained which show explicitly the concentration dependence. We consider equal mass ratios, set  $\sigma_E = \sigma_R$ , define  $\Delta = n_1 / n_2$  and eliminate common collision frequency factors on both sides of the equation. With only two terms retained in the expansions, we find that Eqs. (14) and (15) are approximated by the set of  $3 \times 3$  equations

$$\begin{pmatrix} -2(1 + \Delta) & \frac{1}{2} & -\frac{1}{2} \\ \frac{1}{2}(1 + \Delta) & -(2\Delta + \frac{31}{8}) & \frac{15}{8} \\ -\frac{1}{2}(1 + \Delta) & \frac{15}{8} & -(2/\Delta + \frac{31}{8}) \end{pmatrix} \begin{pmatrix} a_1^{(1)} \\ a_2^{(1)} \\ a_2^{(2)} \end{pmatrix} = \begin{pmatrix} \frac{1 - \Delta}{1 + \Delta} \hat{A}_1 / 2 \\ \hat{A}_2 / 4 \\ \hat{A}_2 / 4 \end{pmatrix}. \quad (26)$$

The solution of this set of equations is

$$\begin{aligned} a_1^{(1)} &= -\frac{1 - \Delta}{60(1 + \Delta)^2} [\hat{A}_2 + 31\hat{A}_1/2], \\ a_2^{(1)} &= -\frac{1}{60(1 + \Delta)^2} [(4 + 11\Delta)\hat{A}_2 + 2(1 - \Delta)\hat{A}_1], \\ a_1^{(2)} &= -\Delta a_1^{(1)}, \\ a_2^{(2)} &= -\frac{\Delta}{60(1 + \Delta)^2} [(11 + 4\Delta)\hat{A}_2 - 2(1 - \Delta)\hat{A}_1]. \end{aligned} \quad (27)$$

The fractional decrease in the rate of reaction 2 is then given by

$$\eta = \frac{1}{120(1 + \Delta)^2 \hat{A}_0} [(1 - \Delta)^2 (2\hat{A}_2 + 31\hat{A}_1/2) \hat{A}_1 + (2\Delta^2 + 11\Delta + 2) \hat{A}_2^2 / 2]. \quad (28)$$

For the line-of-centers reactive cross section, we have explicitly that

$$\hat{A}_0 = 2 \exp(-\epsilon),$$

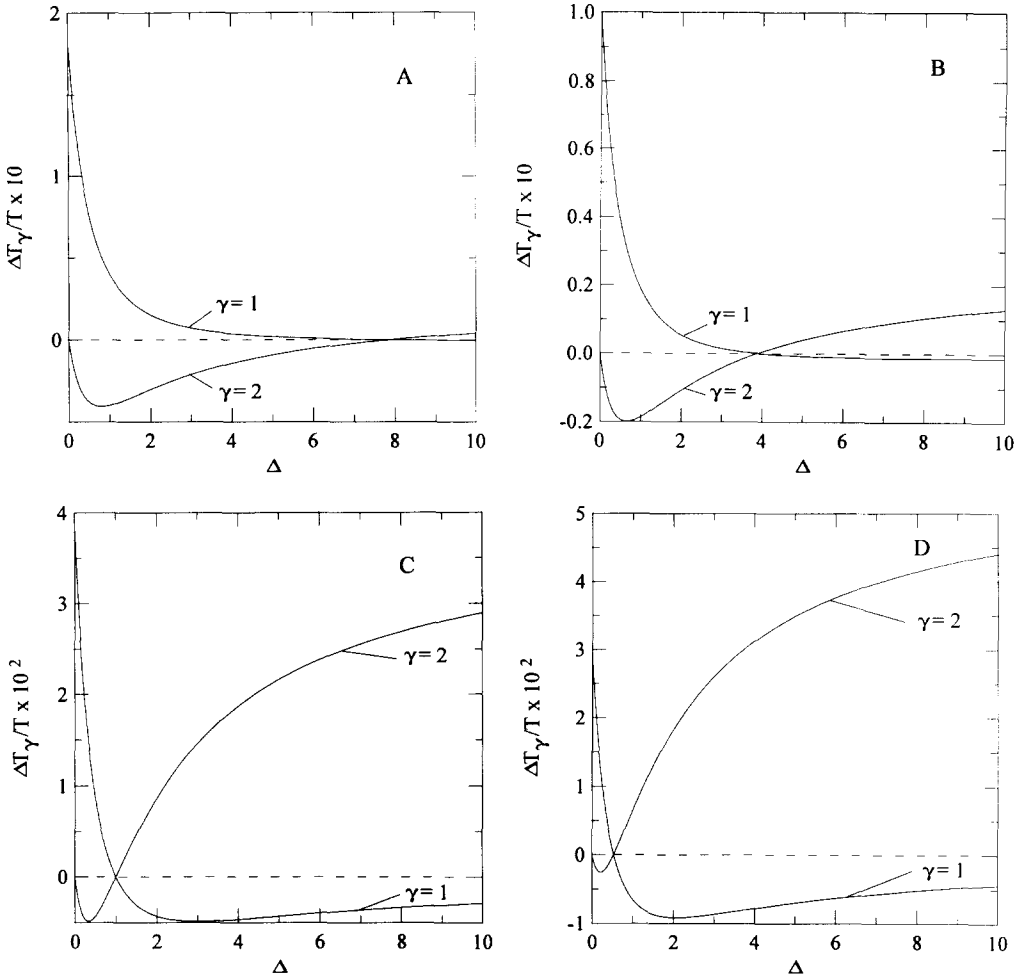


Fig. 2. Variation of  $\Delta T_\gamma/T$  versus density ratio  $\Delta = n_1/n_2$  for the system  $A + C \rightarrow$  products. The mass ratio  $m_1/m_2$  equals (A) 1/8, (B) 1/4, (C) 1 and (D) 2;  $\epsilon = 4$  and  $\sigma_E/\sigma_R = 1$ .  $\Delta T_\gamma = 0$  at  $m_1 n_1/m_2 n_2 = 1$ .

$$\begin{aligned} \hat{A}_1 &= -2(\epsilon + 1/2) \exp(-\epsilon), \\ \hat{A}_2 &= (\epsilon^2 - \epsilon - 1/4) \exp(-\epsilon), \end{aligned} \tag{29}$$

where  $\epsilon = E^*/kT$ . The two term result given by Eq. (28) is a very good approximation to the converged result.

Figs. 2 and 3 show the variation of  $a_1^{(\gamma)} = \Delta T_\gamma/T$  versus density and mass ratios, respectively. The energy conservation relation  $a_1^{(1)} = -\Delta a_1^{(2)}$  imposes the constraint that temperature perturbations  $\Delta T_\gamma$  for A and C must be opposite in sign. This property is common to all curves in Figs. 2 and 3. All the curves also show that there is no temperature perturbation,  $\Delta T_\gamma = 0$ , when  $(m_1/m_2)\Delta = 1$ , as discussed in connection with the results in Fig. 1. Fig. 2 shows that as  $\Delta \rightarrow 0$ , the temperature of the major species,  $T_2 \rightarrow T$ . However, the distribution of the minor species is strongly perturbed

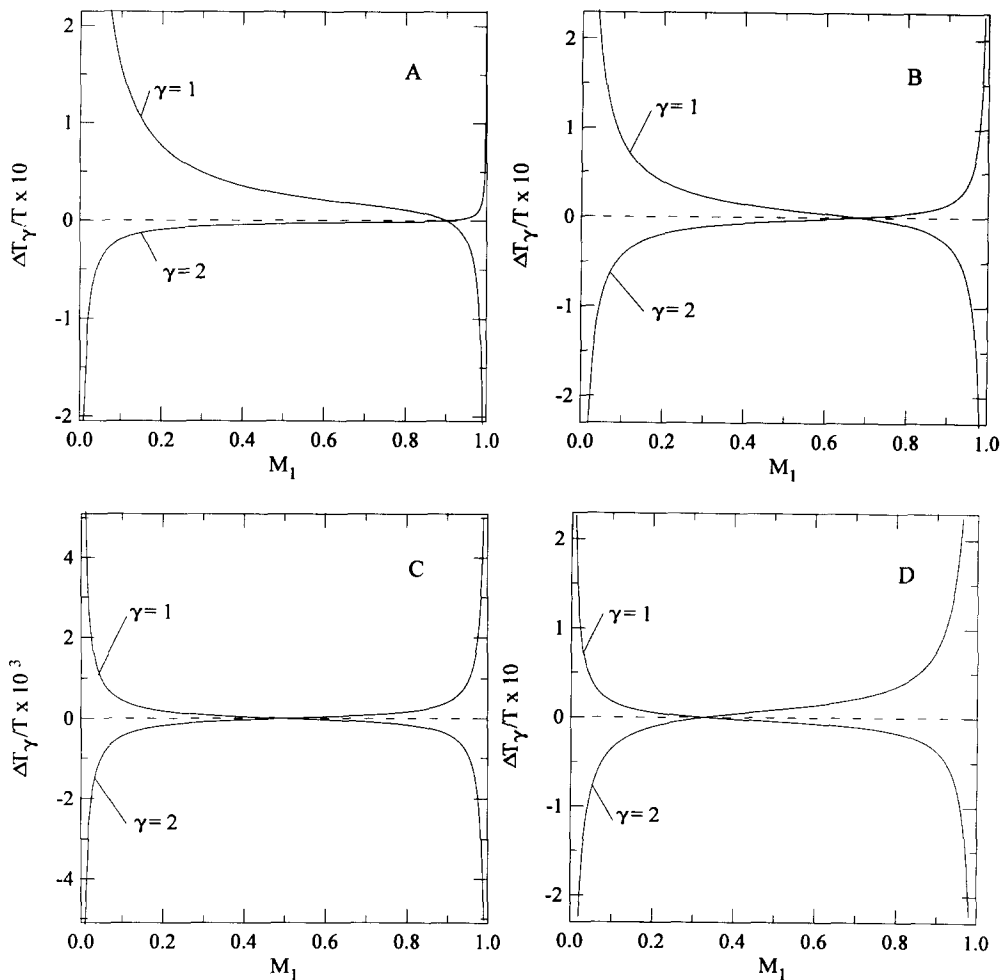


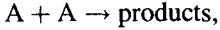
Fig. 3. Variation of  $\Delta T_\gamma/T$  versus  $M_1$ , mass fraction of A, for the system  $A + C \rightarrow$  products. The density ratio  $n_1/n_2$  equals (A)  $1/8$ , (B)  $1/2$ , (C)  $1$  and (D)  $2$ ;  $\epsilon = 4$  and  $\sigma_E/\sigma_R = 1$ .

and  $\Delta T_1$  is large. The point  $\Delta = 1$  in Fig. 2C ( $m_1 = m_2$ ) corresponds to the system  $A + A \rightarrow$  products. In this case, the species A and C become indistinguishable and are characterized by a single temperature,  $T_1 = T_2 = T$ .

The variation of temperature perturbation  $\Delta T_\gamma/T$  versus mass fraction of A,  $M_1 = m_1/(m_1 + m_2)$ , is shown in Fig. 3. A striking feature of Fig. 3 is that for a reaction involving reactants with dissimilar masses (i.e.  $M_1 \rightarrow 0$  or  $M_1 \rightarrow 1$ ) there are large temperature perturbations. As the density ratio  $\Delta$  increases in Figs. 3A–D, the mass fraction for which  $\Delta T_\gamma = 0$  shifts towards  $M_1 = 0$  in accordance with the dependence  $m_1\Delta/m_2 = 1$ . Fig. 3A has the smallest  $\Delta$  and as a consequence,  $\Delta T_\gamma = 0$  at  $M_1 = 8/9$ . With increasing  $\Delta$ , the mass fractions for which  $\Delta T_\gamma = 0$  are  $2/3$ ,  $1/2$  and  $1/3$  for Figs. 3B–D, respectively. Figs. 3B ( $n_1/n_2 = 1/2$ ) and 3D ( $n_1/n_2 = 2$ ) show the symmetry resulting from the interchange of species A and C. Fig. 3C corresponds to

the system  $A + A \rightarrow$  products for which  $n_1 = n_2$ , and  $\Delta T_\gamma = 0$  at  $m_1 = m_2$ .

In a subsequent paper, Cukrowski et al. [16] discussed further the role of the species temperatures in the determination of  $\eta$ . They concluded that the results of previous workers [2,3,6] for the one-component reactive system



is in error owing to the neglect of the effect given by Eq. (22). However, as we have shown, this temperature effect disappears when the reactants are identical and plays no role in the nonequilibrium effects. We show in the appendix that the system studied by Cukrowski et al. differs from the one-component system above. Their work corresponds to this reaction occurring in a large excess of a second (nonreactive) component (with the mass of A) that acts as an infinite heat bath so that the temperature of the system does not change. This was considered at length by Shizgal and Karplus [8]. For  $A + A \rightarrow$  products for which  $n_1 = n_2$ , the two term solution for  $\eta$  becomes

$$\lim_{A \rightarrow 1} \eta = \frac{\hat{A}_2^2}{32A_0}. \tag{30}$$

This is twice the result obtained from Eq. (28) because in this limit the two-component system has twice the number of elastic collisions as the one-component system [7]. Moreover since  $a_1^{(1)} = a_1^{(2)} = 0$  and  $\Delta T = 0$ , there is no perturbation of the temperature due to the reaction and no effect on the reaction rate.

### 2.2. The reaction $A + A \rightarrow B + B$

In this section, we are interested in the nonequilibrium effects in a model reactive system introduced by Cukrowski et al. [15,16]. The species A and B can be taken to be different internal states of some species and the reaction can be considered as an inelastic collision involving no mass transfer. Nonequilibrium effects for such processes have been considered previously [41,42]. The main objective here is to determine the influence of the products on the nonequilibrium effects in comparison with the results of Section 2.1. We also address the methodology of Cukrowski et al. and their conclusions. The effect of products has been previously discussed by Pyun and Ross [5] and by Fitzpatrick and Desloge [14].

For this reaction, the Boltzmann equations are similar to those in Section 2.1, except that the reactive term for the products is a gain term evaluated with the reactive cross section for the forward reaction. The coupled Boltzmann equations for this system are

$$\begin{aligned} \frac{\partial f_1}{\partial t} = & \int \int [f'_1 f' - f_1 f] \sigma_{11} g d\Omega d\mathbf{c} + \int \int [f'_1 f'_2 - f_1 f_2] \sigma_{12} g d\Omega d\mathbf{c}_2 \\ & - \int \int f_1 f \sigma^* g d\Omega d\mathbf{c}, \end{aligned} \tag{31}$$

$$\frac{\partial f_2}{\partial t} = \int \int [f'_2 f' - f_2 f] \sigma_{22} g d\Omega d\mathbf{c} + \int \int [f'_1 f'_2 - f_1 f_2] \sigma_{12} g d\Omega d\mathbf{c}_1$$

$$+ \int \int f'_1 f'_1 \sigma^* g d\Omega d\mathbf{c}'_1. \quad (32)$$

In Eq. (32), the reactive collision integral represents the production of product B species and the integration is over the velocity space of one of the two reactant A species. The primes on the distribution function refer to the A species that enter into a collision. All primed quantities in both Eq. (31) and (32) correspond to gain terms while all unprimed ones correspond to loss terms. The primes on the last term of the right-hand side of Eq. (32) are consistent with this convention. An important aspect of this model is that with the complete neglect of the reverse reaction, microscopic reversibility [37] for the reactive collisions cannot be employed. This reactive collision production rate is determined analogous to the calculations by Whipple [38], Riley and Matzen [39] and Shizgal and Lindenfeld [40].

The CE method of solution parallels the discussion in Section 2.1. The only modification is the nature of the reactive collision term for the product B in Eq. (32), which differs from the loss term of the reactant A in Eq. (31). We apply the CE method as in Section 2.1, and require the lowest order reactive collision frequencies evaluated with the Maxwellians and given by

$$f_2^{(0)} R_2'^{(0)} d\mathbf{c}_2 = \int \int f_1^{(0)'} f^{(0)'} \sigma^* g' d\Omega d\mathbf{c}'_1 d\mathbf{c}', \quad (33)$$

where the prime is used to distinguish this product collision frequency with the loss terms in Eq. (13). The reactive collision probability is determined by changing the integration to one over the velocity of one of the product B species. With energy conservation, we have that

$$f_2^{(0)} R_2'^{(0)} d\mathbf{c}_2 = e^{-\epsilon} \left( \frac{n_1}{n_2} \right)^2 \int \int f_2^{(0)} f^{(0)} \sigma^* g' d\Omega d\mathbf{g}' d\mathbf{G}, \quad (34)$$

where  $\mathbf{G}$  is the centre of mass velocity and is conserved in a reactive collision. This integral can be converted to an integration over the relative velocity of the products with energy conservation in differential form ( $g'dg' = gdg$ ) and with the reduced masses of the reactants and products equal, we get that

$$f_2^{(0)} R_2'^{(0)} d\mathbf{c}_2 = e^{-\epsilon} \left( \frac{n_1}{n_2} \right)^2 f_2^{(0)} \int f^{(0)} \sigma_{total}^* \frac{g'^2}{g} dg d\mathbf{G}. \quad (35)$$

We now specialize this to the line-of-centers cross section so that

$$f_2^{(0)} R_2'^{(0)} d\mathbf{c}_2 = \pi d_R^2 e^{-\epsilon} \left( \frac{n_1}{n_2} \right)^2 f_2^{(0)} \int f^{(0)} g dg d\mathbf{G}, \quad (36)$$

and

$$f_2^{(0)} R_2'^{(0)} = \pi d_R^2 e^{-\epsilon} \left( \frac{n_1}{n_2} \right)^2 f_2^{(0)} \int f^{(0)} g d\mathbf{c}, \quad (37)$$

where the integral is the hard sphere collision frequency [24] for unit total cross section. It is this form of the reactive production collision term (for the line-of-centers reactive

cross section) that determines the form of the CE equation for this model reaction. The work by Cukrowski et al. [15,16] considered this reactive collision frequency for product B equal to the loss term for reactant A.

We apply the CE method of solution based on the assumption Eq. (7). The time variation of the densities is determined from the Boltzmann equations, and given by

$$\left(\frac{dn_1}{dt}\right)^{(0)} = -\left(\frac{dn_2}{dt}\right)^{(0)} = -\int\int\int f_1^{(0)} f_2^{(0)} \sigma^* g d\Omega d\mathbf{c}_1 d\mathbf{c}_2. \quad (38)$$

For this reaction, there is no energy conservation in reactive collisions and the time rate of change of the temperature is non-zero and evaluated to lowest order with the use of the explicit form of the reactive collision frequency in Eq. (37). By evaluating the rate of change of the energy of each species from the Boltzmann equations and adding the results, we get that

$$\left(\frac{dT}{dt}\right)^{(0)} = \frac{2T}{3n} [A_1 - A_1(0)e^{-\epsilon}], \quad (39)$$

where the species designation on the  $A_i$  integrals is dropped since the masses are the same for both reactant and product. The quantities denoted by  $A_i(0)$  refer to the  $A_i$  integrals for zero threshold energy and arise from moments of the reactive collision frequency for species B, Eq. (37), that is,

$$\begin{aligned} A_i^{(2)} &= \int f_2^{(0)} R_2'^{(0)} S_2^{(i)} d\mathbf{c}_2 \\ &= e^{-\epsilon} A_i(0). \end{aligned} \quad (40)$$

Cukrowski et al. [15] assumed that translational energy is conserved in reactive collisions; the energy lost by the reactant is gained by the product and that  $dT/dt = 0$ . Their result is in contradiction to Eq. (39).

With the substitution of Eq. (6) into the Boltzmann equations, Eqs. (31) and (32) and use of Eqs. (7), (38) and (39), we find the CE equations for the perturbations  $\psi_\gamma$  are given by

$$\begin{aligned} &\int\int f_1^{(0)} f_2^{(0)} [\psi_1' + \psi_1' - \psi_1 - \psi] \sigma_{11} g d\Omega d\mathbf{c} \\ &+ \int\int f_1^{(0)} f_2^{(0)} [\psi_1' - \psi_1] \sigma_{12} g d\Omega d\mathbf{c}_2 + \int\int f_1^{(0)} f_2^{(0)} [\psi_2' - \psi_2] \sigma_{12} g d\Omega d\mathbf{c}_2 \\ &= f_1^{(0)} G_1(c_1), \end{aligned} \quad (41)$$

$$\begin{aligned} &\int\int f_2^{(0)} f_2^{(0)} [\psi_2' + \psi_2' - \psi_2 - \psi] \sigma_{22} g d\Omega d\mathbf{c} \\ &+ \int\int f_1^{(0)} f_2^{(0)} [\psi_2' - \psi_2] \sigma_{12} g d\Omega d\mathbf{c}_1 + \int\int f_1^{(0)} f_2^{(0)} [\psi_1' - \psi_1] \sigma_{12} g d\Omega d\mathbf{c}_1 \\ &= f_2^{(0)} G_2(c_2), \end{aligned} \quad (42)$$

where the inhomogeneous terms are defined by

$$G_1(c_1) = \left[ -\frac{1}{n_1} \left( \frac{dn_1}{dt} \right)^{(0)} - \frac{1}{T} \left( \frac{3}{2} - x_1^2 \right) \left( \frac{dT}{dt} \right)^{(0)} + R_1^{(0)}(c_1) \right], \quad (43)$$

$$G_2(c_2) = \left[ -\frac{1}{n_2} \left( \frac{dn_2}{dt} \right)^{(0)} - \frac{1}{T} \left( \frac{3}{2} - x_2^2 \right) \left( \frac{dT}{dt} \right)^{(0)} - R_2^{(0)}(c_2) \right]. \quad (44)$$

The CE equations, Eqs. (41) and (42) are analogous to Eqs. (10) and (11) in Section 2. The only distinction is the form of the reactive collision frequencies and the inhomogeneous terms Eqs. (43) and (44) in comparison with Eq. (12). The perturbations of the distribution function are expanded in Sonine polynomials  $S_\gamma^{(i)}(x_\gamma^2)$  as in Section 2.1 and result in the set of algebraic equations similar to Eqs. (14) and (15) given by

$$\sum_{j=1}^N \left[ \left( n_1^2 [S_1^{(i)}, S_1^{(j)}] + n_1 n_2 \{S_1^{(i)}, S_1^{(j)}\} \right) a_j^{(1)} + n_1 n_2 \{S_1^{(i)}, S_2^{(j)}\} a_j^{(2)} \right] = n_1^2 \beta_i^{(1)}, \quad (45)$$

and

$$\sum_{j=1}^N \left[ \left( n_2^2 [S_2^{(i)}, S_2^{(j)}] + n_1 n_2 \{S_2^{(i)}, S_2^{(j)}\} \right) a_j^{(2)} + n_1 n_2 \{S_2^{(i)}, S_1^{(j)}\} a_j^{(1)} \right] = -n_1^2 \beta_i^{(2)}, \quad (46)$$

where

$$n_1^2 \beta_i^{(1)} = -\delta_{0i} A_0 - \delta_{1i} \frac{n_1}{n} [A_1 - A_1(0) e^{-\epsilon}] + A_i, \quad (47)$$

and

$$n_1^2 \beta_i^{(2)} = -\delta_{0i} A_0 + \delta_{1i} \frac{n_2}{n} [A_1 - A_1(0) e^{-\epsilon}] + A_i(0) e^{-\epsilon}. \quad (48)$$

The fractional decrease in the forward reaction rate only involves the distribution function of species A and is given by

$$\eta = -2 \sum_{i=1}^{\infty} a_i^{(1)} A_i / A_0. \quad (49)$$

As was done in Section 2.1, it is useful to consider the approximate result with only two terms in the expansion of the distribution functions in Sonine polynomials. We set  $\sigma_E = \sigma_R$ , define  $\delta = n_2/n_1$ , and eliminate common collision frequency factors from both sides of Eqs. (45) and (46). The result is the set of  $3 \times 3$  equations

$$\begin{pmatrix} -2(1+\delta) & \frac{1}{2}\delta & -\frac{1}{2}\delta \\ \frac{1}{2}(1+\delta) & -(2+\frac{31}{8}\delta) & \frac{15}{8}\delta \\ -\frac{1}{2}(1+\delta) & \frac{15}{8}\delta & -(2\delta^2 + \frac{31}{8}\delta) \end{pmatrix} \begin{pmatrix} a_1^{(1)} \\ a_2^{(1)} \\ a_2^{(2)} \end{pmatrix}$$

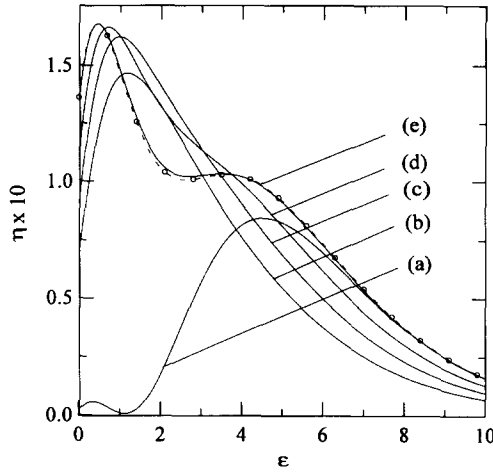


Fig. 4. Variation of  $\eta$  versus  $\epsilon$  for  $A + A \rightarrow B + B$  compared with  $A + A \rightarrow$  products.  $A + A \rightarrow$  products is shown by curve (a). For  $A + A \rightarrow B + B$ , the density ratio  $n_2/n_1$  equals (b) 1.0, (c) 0.5, (d) 0.1 and (e) 0.01;  $\sigma_E/\sigma_R = 1$ . The value of  $\eta$  for  $A + A \rightarrow B + B$  in the limit  $\delta \rightarrow 0$  is shown by  $--\circ--$ .

$$= \begin{pmatrix} \frac{1}{2(1+\delta)} [\hat{A}_1(0)e^{-\epsilon} + \delta\hat{A}_1] \\ \hat{A}_2/4 \\ -\hat{A}_2(0)e^{-\epsilon}/4 \end{pmatrix}. \tag{50}$$

The solution of this set of equations is

$$\begin{aligned} a_1^{(1)} &= -\frac{1}{60(\delta+1)^2} \left[ \frac{31}{2}(\hat{A}_1(0)e^{-\epsilon} + \delta\hat{A}_1) + (\hat{A}_2\delta + \hat{A}_2(0)e^{-\epsilon}) \right], \\ a_2^{(1)} &= -\frac{2}{60(\delta+1)^2} \left[ (\hat{A}_1(0)e^{-\epsilon} + \delta\hat{A}_1) - (2\delta + 15/4)\hat{A}_2 + \frac{7}{4}\hat{A}_2(0)e^{-\epsilon} \right], \\ a_1^{(2)} &= -a_1^{(1)}/\delta, \\ a_2^{(2)} &= -\frac{2}{60(\delta+1)^2\delta} \left[ (\hat{A}_1(0)e^{-\epsilon} + \delta\hat{A}_1) + (2 + \frac{15}{4}\delta)\hat{A}_2(0)e^{-\epsilon} - \frac{7}{4}\delta\hat{A}_2 \right]. \end{aligned} \tag{51}$$

With Eq. (51), we obtain an expression for  $\eta$  comparable to Eq. (28) which we do not report. It is important to note that the correction,  $\eta$  (Eq. (49)), depends only on the expansion coefficients,  $a_i^{(1)}$  of species A. The two term solution is accurate to within 5 percent of the converged values for the conditions discussed here. This two term analytic solution provides for a useful interpretation of the density dependence.

The variation of  $\eta$  versus  $\epsilon$  for several density ratios is shown in Fig. 4. The curve (a) of Fig. 4 shows the variation of  $\eta$  for the reaction  $A + A \rightarrow$  products. The curves (b)–(e) are for decreasing density ratio,  $\delta = n_2/n_1$ , of product to reactant. The  $\eta$  values calculated for  $A + A \rightarrow B + B$  are larger than those for  $A + A \rightarrow$  products, due to the contribution of the  $a_1^{(1)}$  terms, and the nonequilibrium effects generally increase with a decrease in  $\delta$ . Note that  $\eta$  attains a limiting value as  $\delta \rightarrow 0$  (dashed curve and

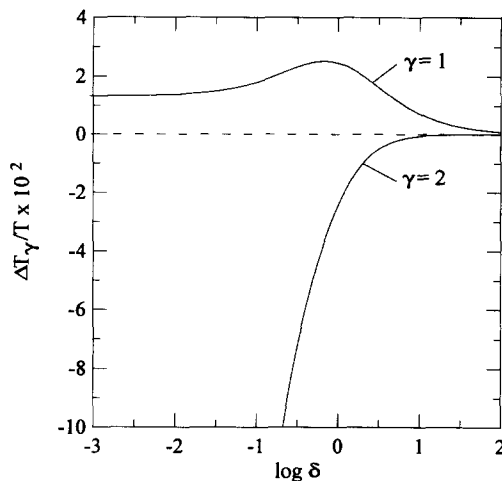


Fig. 5. Variation  $\Delta T_\gamma/T$  versus the log of density ratio  $\delta = n_2/n_1$  for  $A + A \rightarrow B + B$ ;  $\epsilon = 3$  and  $\sigma_E/\sigma_R = 1$ .

open circles). The peak near  $\epsilon = 1$  for the system  $A + A \rightarrow B + B$  is caused by the relatively large temperature difference,  $\Delta T_1 = a_1^{(1)}$ , between the two components A and B. This temperature difference does not occur for the system  $A + A \rightarrow$  products and results in small values of  $\eta$  for  $\epsilon \lesssim 2$ . There is good agreement in the values of  $\eta$  for the systems  $A + A \rightarrow$  products and  $A + A \rightarrow B + B$  as  $\delta \rightarrow 0$  and  $\epsilon$  becomes large.

Fig. 5 shows the variation of  $\Delta T_\gamma/T$  versus the log  $\delta$  for the reaction  $A + A \rightarrow B + B$  with  $\epsilon = 3$ . We are primarily interested in the behaviour in the limit of vanishing reactant or product. In the limit of vanishing reactant,  $n_1 \rightarrow 0$ ,  $\delta \rightarrow \infty$ , the product is in large excess and acts as a heat bath at temperature  $T$ , so that  $\Delta T_2 \rightarrow 0$  as  $1/\delta^2$  as shown in Fig. 5. The distribution function of the reactant is not a Maxwellian and  $\Delta T_1 \rightarrow 0$  as  $1/\delta$ . This limit corresponds to the isothermal reactive systems of Ref. [7]. In the limit of vanishing product,  $n_2 \rightarrow 0$ ,  $\delta \rightarrow 0$  and the perturbation of the distribution function of the product is large; the expansion coefficients  $a_i^{(2)}$  vary as  $1/\delta$  (see Eq. (51)). Similarly,  $\Delta T_2 \rightarrow \infty$  as  $1/\delta$  so that  $\Delta T_2/T$  shown in Fig. 5 is large and negative. By contrast, as  $\delta \rightarrow 0$ ,  $\Delta T_1/T$  remains finite. Since the correction  $\eta$  shown in Fig. 4 depends only on  $a_i^{(1)}$ , it remains finite. A comparison of these results with the results for the reaction  $A + A \rightarrow$  products is presented in Section 2.4.

### 2.3. The reaction $A + A \rightleftharpoons B + B$

In this section we consider the reaction of Section 2.2 but allow for the reverse reaction. This changes the nature of the Boltzmann equations since microscopic reversibility is valid and forward and reverse reactive collision terms are related. The formalism for the kinetic analysis for this system was treated in detail in an earlier paper [7]. Microscopic reversibility relates the cross sections for the forward and reverse reactive cross sections [37] as given by

$$\mu_f^2 \sigma_f^* g_f^2 = \mu_r^2 \sigma_r^* g_r^2, \quad (52)$$

where  $\mu$  is the reduced mass of the pair entering a reactive collision, and the subscripts  $f$  and  $r$  refer to the forward and reverse reactions, respectively. For the line-of-centers reactive collision cross section model for both forward and reverse reactions, this implies that  $d_f^2 \mu_f = d_r^2 \mu_r$ . Since for the present model the reduced mass of the reactants and products are equal, the corresponding reactive hard sphere diameters have to be equal,  $d_f = d_r$ . If the forward and reverse threshold energies are unequal, the “heat of reaction”,  $\Delta E = E_f^* - E_r^*$  has an important effect on the extent of the nonequilibrium.

The coupled Boltzmann equations for this system are of the form

$$\begin{aligned} \frac{\partial f_1}{\partial t} = & \int \int [f'_1 f' - f_1 f] \sigma_{11} g d\Omega dc + \int \int [f'_1 f'_2 - f_1 f_2] \sigma_{12} g d\Omega dc_2 \\ & - \int \int [f'_2 f' - f_1 f] \sigma_f^* g_f d\Omega dc, \end{aligned} \quad (53)$$

$$\begin{aligned} \frac{\partial f_2}{\partial t} = & \int \int [f'_2 f' - f_2 f] \sigma_{22} g d\Omega dc + \int \int [f'_1 f'_2 - f_1 f_2] \sigma_{12} g d\Omega dc_1 \\ & - \int \int [f'_1 f' - f_2 f] \sigma_r^* g_r d\Omega dc. \end{aligned} \quad (54)$$

The gain and loss terms in the reactive collision integral terms have been combined by using microscopic reversibility, Eq. (52). The equality of the reduced masses has been used. The reactive collision terms have the same formal appearance as the unlike elastic collision terms. It is important to mention that the integration over  $c$  in the reactive collision term is over the velocity of species A in Eq. (53) and over the velocity of species B in Eq. (54).

The application of the CE method of solution of the Boltzmann equations follows the discussion in Sections 2.1 and 2.2, and the earlier paper [7]. The important differences are that

$$\left( \frac{dn_1}{dt} \right)^{(0)} = - \left( \frac{dn_2}{dt} \right)^{(0)} = [k_r^{(0)} n_2^2 - k_f^{(0)} n_1^2] \quad (55)$$

and

$$\left( \frac{dT}{dt} \right)^{(0)} = - \frac{2\Delta E}{3kn} [k_r^{(0)} n_2^2 - k_f^{(0)} n_1^2] \quad (56)$$

are the equilibrium estimates of the density and temperature time derivatives employed in Eq. (7). The resulting CE equations are similar in form to Eqs. (10) and (11), with the inhomogeneous terms  $F_\gamma^{(0)}$  replaced with  $H_\gamma^{(0)}$  defined by

$$f_\gamma^{(0)} H_\gamma^{(0)} = \frac{f_\gamma^{(0)}}{n_\gamma} \left[ \tilde{A}_0^{(0)} + \frac{2\Delta E}{3nKT} \tilde{A}_0^{(\gamma)} - R_\gamma^{(0)} \right], \quad (57)$$

where the reactive collision frequencies include both forward and reverse rates, given by

$$f_1^{(0)} R_1^{(0)} = \int \int \left[ f_2^{(0)'} f^{(0)'} - f_1^{(0)} f^{(0)} \right] \sigma_f^* g_f d\Omega dc \quad (58)$$

and

$$f_2^{(0)} R_2^{(0)} = \int \int \left[ f_1^{(0)'} f^{(0)'} - f_2^{(0)} f^{(0)} \right] \sigma_r^* g_r d\Omega dc. \quad (59)$$

The  $\tilde{A}_i^{(\gamma)}$  are the moments of these reactive collision frequencies with Sonine polynomials. These can be related to the  $A_i^{(\gamma)}$  quantities for the forward reaction of Section 2.1. We have that

$$n_1^2 \tilde{A}_i^{(1)} = \left[ 1 - \left( \frac{n_2}{n_1} \right)^2 \exp(\Delta E/kT) \right] A_i^{(1)}(\epsilon_f) \quad (60)$$

and

$$n_2^2 \tilde{A}_i^{(2)} = \left[ 1 - \left( \frac{n_1}{n_2} \right)^2 \exp(-\Delta E/kT) \right] A_i^{(2)}(\epsilon_r), \quad (61)$$

where  $\epsilon_f = E_f^*/kT$  and  $\epsilon_r = E_r^*/kT$ ,  $E_f^*$  and  $E_r^*$  are the forward and reverse activation energies respectively. The CE equations for this model system are very similar to those in Sections 2.1 and 2.2 and given by

$$\sum_{j=1}^N \left[ \left( n_1^2 \left[ S_1^{(i)}, S_1^{(j)} \right] + n_1 n_2 \left\{ S_1^{(i)}, S_1^{(j)} \right\} \right) a_j^{(1)} + n_1 n_2 \left\{ S_1^{(i)}, S_2^{(j)} \right\} a_j^{(2)} \right] = n_1^2 \tilde{\alpha}_i^{(1)}, \quad (62)$$

and

$$\sum_{j=1}^N \left[ \left( n_2^2 \left[ S_2^{(i)}, S_2^{(j)} \right] + n_1 n_2 \left\{ S_2^{(i)}, S_2^{(j)} \right\} \right) a_j^{(2)} + n_1 n_2 \left\{ S_2^{(i)}, S_1^{(j)} \right\} a_j^{(1)} \right] = n_2^2 \tilde{\alpha}_i^{(2)}, \quad (63)$$

where

$$n_1^2 \tilde{\alpha}_i^{(1)} = -\delta_{0i} n_1^2 \tilde{A}_0^{(1)} + \delta_{1i} \frac{n_1}{n} \frac{\Delta E}{2kT} n_1^2 \tilde{A}_0^{(1)} + n_1^2 \tilde{A}_i^{(1)} \quad (64)$$

and

$$n_2^2 \tilde{\alpha}_i^{(2)} = -\delta_{0i} n_2^2 \tilde{A}_0^{(2)} - \delta_{1i} \frac{n_2}{n} \frac{\Delta E}{2kT} n_2^2 \tilde{A}_0^{(2)} + n_2^2 \tilde{A}_i^{(2)}. \quad (65)$$

The  $\tilde{A}_i^{(\gamma)}$  integrals which involve both forward and reverse reactions can be written in terms of the  $A_i^{(\gamma)}$  integrals for either the forward or reverse reaction as a consequence of microscopic reversibility.

The approximate solution with only two terms in the expansions leads to the  $3 \times 3$  equation of the form

$$\begin{pmatrix} -2(1+\delta) & \frac{1}{2}\delta & -\frac{1}{2}\delta \\ \frac{1}{2}(1+\delta) & -(2+\frac{31}{8}\delta) & \frac{15}{8}\delta \\ -\frac{1}{2}(1+\delta) & \frac{15}{8}\delta & -(2\delta^2+\frac{31}{8}\delta) \end{pmatrix} \begin{pmatrix} a_1^{(1)} \\ a_2^{(1)} \\ a_2^{(2)} \end{pmatrix} = \begin{pmatrix} \tilde{A}_1^{(1)} + \frac{1}{1+\delta} \frac{\Delta E}{2kT} \tilde{A}_0^{(1)} \\ \tilde{A}_2^{(1)} \\ \delta^2 \tilde{A}_2^{(2)} \end{pmatrix}. \tag{66}$$

The system is solved to give

$$\begin{aligned} a_1^{(1)} &= -\frac{1}{60(\delta+1)^2} \left\{ 31 \left[ \tilde{A}_1^{(1)}(1+\delta) + \tilde{A}_0^{(1)} \left( \frac{\Delta E}{2kT} \right) \right] + 4(\tilde{A}_2^{(1)} - \tilde{A}_2^{(2)}\delta)\delta \right\}, \\ a_2^{(1)} &= -\frac{2}{60(\delta+1)^2} \left\{ 2 \left[ \tilde{A}_1^{(1)}(1+\delta) + \tilde{A}_0^{(1)} \left( \frac{\Delta E}{2kT} \right) \right] \right. \\ &\quad \left. - \tilde{A}_2^{(1)}(8\delta+15) - 7\tilde{A}_2^{(2)}\delta^2 \right\}, \\ a_1^{(2)} &= -a_1^{(1)}/\delta, \\ a_2^{(2)} &= -\frac{2}{60(\delta+1)^2\delta} \left\{ 2 \left[ \tilde{A}_1^{(1)}(1+\delta) + \tilde{A}_0^{(1)} \left( \frac{\Delta E}{2kT} \right) \right] \right. \\ &\quad \left. - \tilde{A}_2^{(2)}(8\delta+15)\delta^2 - 7\delta\tilde{A}_2^{(1)} \right\}. \end{aligned} \tag{67}$$

Using the solutions Eq. (67), two term approximations of  $\eta_f$  and  $\eta_r$  (the fractional decrease for forward and reverse reactions, respectively) can be obtained with Eqs. (66) and (67). The converged corrections to the reactive rate coefficient are given by

$$\eta_f = -\sum_{i=1}^N a_i^{(1)} A_i^{(1)} / A_0^{(1)}, \tag{68}$$

and

$$\eta_r = -\sum_{i=1}^N a_i^{(2)} A_i^{(2)} / A_0^{(2)}. \tag{69}$$

The two term solutions give very good approximations to the converged values of  $\eta$ .

This reversible reactive system differs from the systems studied in Sections 2.1 and 2.2 in that the reaction can attain chemical equilibrium whenever the forward and reverse rates are equal, that is when  $k_f^{(0)}n_1^2 = k_r^{(0)}n_2^2$  and the equilibrium density ratio is given by  $\delta^2 = \exp(-\Delta E/kT)$ . At chemical equilibrium the distribution functions are Maxwellian and  $\eta_f = \eta_r = 0$  [4,7]. For other density ratios,  $\eta_f$  and  $\eta_r$  are finite and can be either positive or negative, the sign depending on the factors  $(1 - \delta^2 \exp(\Delta E/kT))$  and

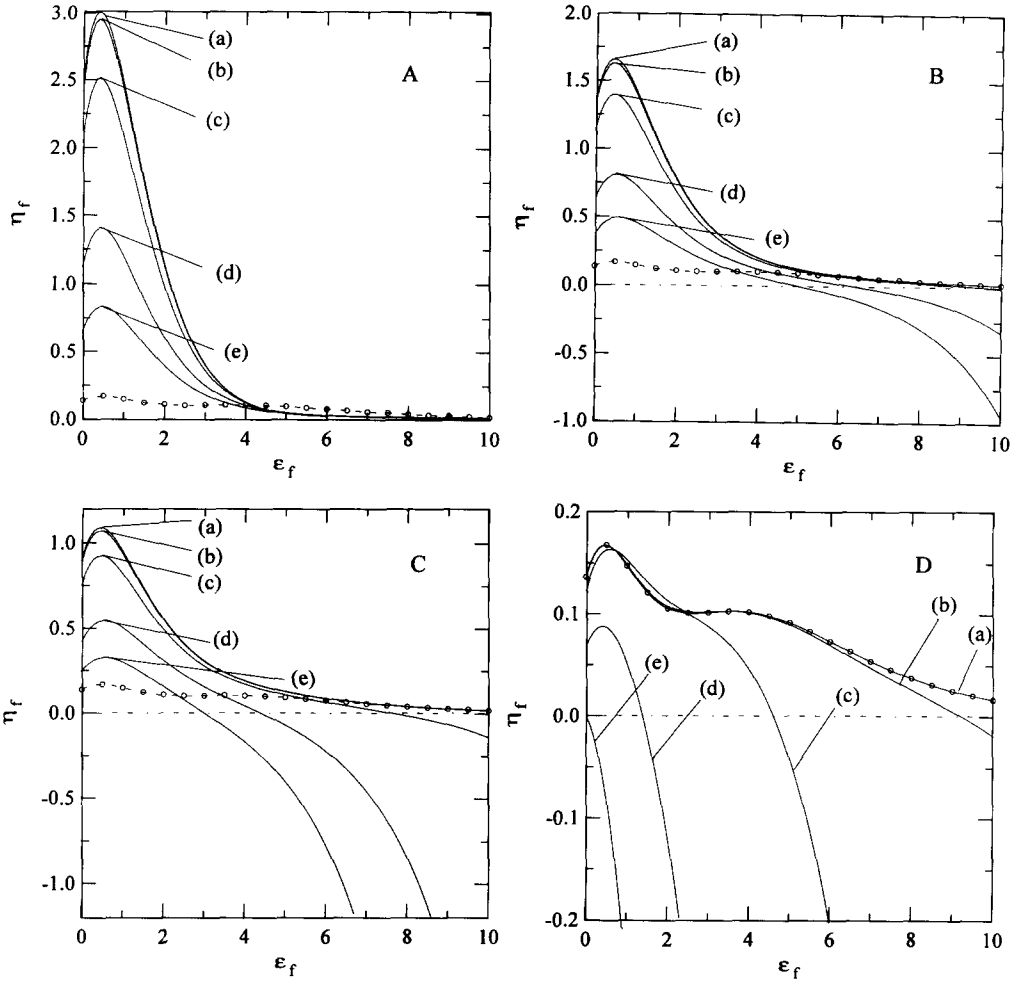


Fig. 6. Variation of  $\eta_f$  for  $A + A \rightleftharpoons B + B$  versus  $\epsilon_f$ . The reverse activation energy,  $\epsilon_r$ , equals (A) 10, (B) 5, (C) 3 and (D) 0;  $\sigma_E/\sigma_R = 1$ . The density ratio  $n_2/n_1$  equals (a) 0, (b) 0.01, (c) 0.1, (d) 0.5 and (e) 1. The variation of  $\eta$  for the system  $A + A \rightarrow B + B$  in the limit  $\delta \rightarrow 0$  is shown by  $--\circ--$ .

$(1 - 1/\delta^2 \exp(-\Delta E/kT))$  in Eqs. (60) and (61). These features are demonstrated in Fig. 6 where the variation of  $\eta_f$  versus  $\epsilon_f$  is shown for several values of  $\epsilon_r$  (Figs. 6A–D) and various density ratios (curves (a)–(e)). The correction  $\eta_f$  equals zero for values of  $\epsilon_f$  where chemical equilibrium exists, that is,  $\delta^2 = \exp(-\Delta E/kT)$ . For  $\delta = 1$ , curve (e),  $\eta_f = 0$  for  $\epsilon_f = \epsilon_r$  as seen in Fig. 6. For  $\epsilon_f > \epsilon_r$ ,  $\eta_f < 0$  and for  $\epsilon_f < \epsilon_r$ ,  $\eta_f > 0$  as discussed above. For the other density ratios, curves (a)–(d),  $\eta_f > 0$  for values of  $\delta^2 > \exp(-\Delta E/kT)$ . The maxima in  $\eta_f$  in Fig. 6 near  $\epsilon_f = 1$  are due to temperature effects resulting from the separation of the temperatures of the two species. The dashed curves and open circles correspond to the limit of vanishing product,  $n_2 \rightarrow 0$ . This limiting behaviour is discussed in Section 2.4 in comparison with the results in Sections 2.1 and 2.2.

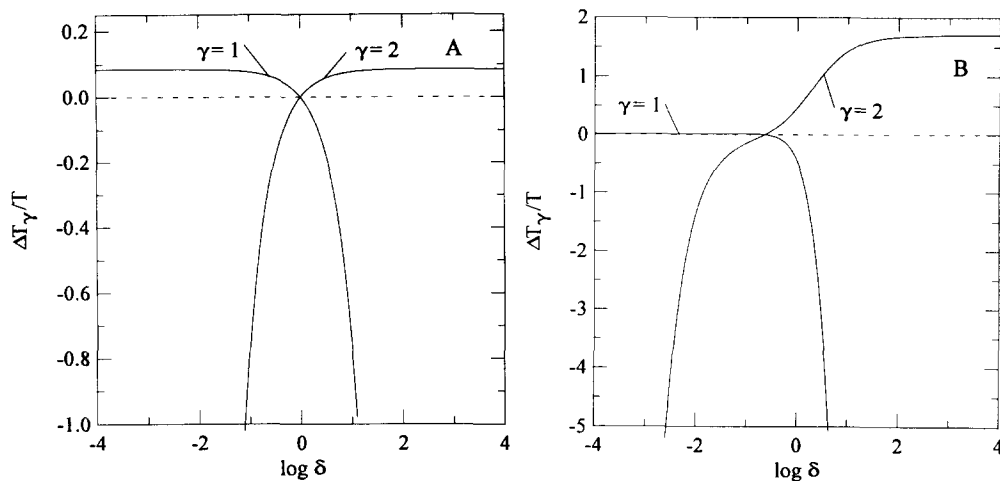


Fig. 7. Variation of  $\Delta T_\gamma/T$  versus the log of density ratio  $\delta = n_2/n_1$  for  $A + A \rightleftharpoons B + B$ . Forward and reverse activation energies are (A)  $\epsilon_f = 3$  and  $\epsilon_r = 3$  and (B)  $\epsilon_f = 3$  and  $\epsilon_r = 0$ ;  $\sigma_E/\sigma_R = 1$ .

The variation in the temperature perturbation  $\Delta T_\gamma/T$  versus the density ratio  $\delta = n_2/n_1$  is shown in Fig. 7 for two pairs of values of  $\epsilon_f$  and  $\epsilon_r$ . Fig. 7 shows that as one species disappears ( $\log \delta \rightarrow \infty$  or  $\log \delta \rightarrow -\infty$ ), the temperature perturbation for that species becomes extremely large, while the temperature perturbation of the more abundant species approaches a finite limiting value. This behaviour is due to  $a_i^{(\gamma)}$  and  $\Delta T_1$  varying as  $\delta$  and  $\Delta T_2$  varying as  $1/\delta$  as given by Eqs. (67). The coefficients  $a_i^{(\gamma)}$  and  $\Delta T_\gamma$  vanish at chemical equilibrium, that is for  $\delta^2 = \exp(-\Delta E/kT)$ . The sign of  $\Delta T_\gamma$  follows the sign of  $\eta$  as discussed above. Fig. 7A, for which  $\epsilon_f = \epsilon_r$ , shows a symmetry for  $\Delta T_\gamma$  versus  $\log \delta$  whereas Fig. 7B, for which  $\epsilon_f \neq \epsilon_r$ , is asymmetric. Note that A and B are interchangeable by interchanging the labels 1 and 2 and  $\epsilon_f$  with  $\epsilon_r$ .

The dependence of the perturbation to the reaction rate,  $\eta_f$ , on the system parameters is more complicated than for the two irreversible systems. The parameters that drive the equilibrium towards A or B are now not merely the forward activation energy but also the reverse activation energy as well as the ratio of densities of the components A and B. The irreversible system  $A + A \rightarrow B + B$  in the limit of vanishing products,  $\delta \rightarrow 0$ , is shown as a dashed curve and open circles in Figs. 6A–D. The reversible and irreversible systems do not coincide in the limit of vanishing product, with the notable exception of the case of vanishing product in Fig. 6D. One obtains identical  $\eta$  and  $\Delta T_\gamma$  values for  $A + A \rightleftharpoons B + B$  and its irreversible equivalent in the limit of  $\delta \rightarrow 0$  and  $\Delta E = \epsilon_f$  (i.e.  $\epsilon_r = 0$ ). These conditions represent a reversible process with no reverse activation threshold for a vanishing back reaction  $B + B \rightarrow A + A$ . This yields a special set of circumstances where  $\epsilon_r = 0$ ,  $\epsilon_f = \Delta E$  and  $\alpha_i^{(2)} = 0$  in Eq. (66), giving rise to identical forms for the matrix equations (50) and (66). This yields identical results for  $a_i^{(1)}$  to all orders of approximation. A detailed discussion of the effect of products is presented in the next section.

#### 2.4. The limit of vanishing product

It is important to note that each of the three systems described here involve specific assumptions in the formalisms that lead to the form of the Boltzmann equations and the application of the CE method. The different solutions derived in Sections 2.1–2.3 are dictated by the explicit expressions for  $(dT/dt)^{(0)}$  in the implementation of the CE method. The elastic collision operators for the three systems are formally similar. The time rate of change of the temperature is given by Eqs. (9), (39) and (56) for the reactions  $A + A \rightarrow$  products,  $A + A \rightarrow B + B$  and  $A + A \rightleftharpoons B + B$ , respectively. In the limit of vanishing product, Eq. (56) does not coincide with Eq. (39), and similarly Eq. (39) does not coincide with Eq. (9) (for  $m_1 = m_2$ ). The different results for  $(dT/dt)^{(0)}$  lead to the different inhomogeneous terms in the CE equations, Eqs. (16), (47) and (48), and (64) and (65) for the three different reactions. These are similar except for the terms in  $\delta_{li}$  that arise from  $(dT/dt)^{(0)}$ . These factors do not coincide in the limit of vanishing products. Hence, the results for the corrections,  $\eta$ , do not correspond in the limit of vanishing products.

The dependence of  $\eta$  versus  $\epsilon$  for increasingly small density of product for  $A + A \rightarrow B + B$  was shown in Fig. 4. The limit of vanishing product shown by the open circles and dashed curve does not coincide with the curve (a) for  $A + A \rightarrow$  products. An approximation to the dashed curve is obtained with the two-term results, Eqs. (51), and for  $\delta \rightarrow 0$  we get

$$\lim_{\delta \rightarrow 0} \eta = -\frac{1}{60A_0} [(31\hat{A}_1(0)e^{-\epsilon} + 2\hat{A}_2(0)e^{-\epsilon})\hat{A}_1/2 + 2(\hat{A}_1(0)e^{-\epsilon} - 15/4\hat{A}_2 + 7/4\hat{A}_2(0)e^{-\epsilon})\hat{A}_2/4], \quad (70)$$

which differs from the result, Eq. (30), for the system  $A + A \rightarrow$  products. The terms in  $\hat{A}_i(0)$  in Eq. (70) are the terms relating to the production of product B. This is a manifestation of the nonvanishing effect of vanishing products discussed by Fitzpatrick and Desloge [14]. The nonvanishing temperature effect of vanishing product B for  $A + A \rightarrow B + B$  is caused by the fact that  $a_1^{(1)}$  (Eq. (51)) is not zero for  $n_2 \rightarrow 0$ .

For  $A + A \rightarrow B + B$ , in the limits  $\delta \rightarrow 0$  and  $\epsilon$  large,

$$\lim_{\delta \rightarrow 0, \epsilon \rightarrow \infty} a_2^{(1)} \approx \hat{A}_2/8$$

and

$$\lim_{\delta \rightarrow 0, \epsilon \rightarrow \infty} \eta \approx \frac{\hat{A}_2^2}{32A_0}.$$

In the large  $\epsilon$  limit, the terms in  $\hat{A}_i(0)$  are neglected relative to the terms in  $\hat{A}_i$  which vary as  $\epsilon^i \exp(-\epsilon)$ . In Fig. 8, the ratio of the corrections for these two reactions versus  $\epsilon$  in the  $\delta \rightarrow 0$  limit is shown. Although there is no agreement for small  $\epsilon$ , the ratio is very close to unity for  $\epsilon \gtrsim 8$ , consistent with the analysis leading to Eq. (70). The dashed curve is the two term result. The results for these two cases discussed above are

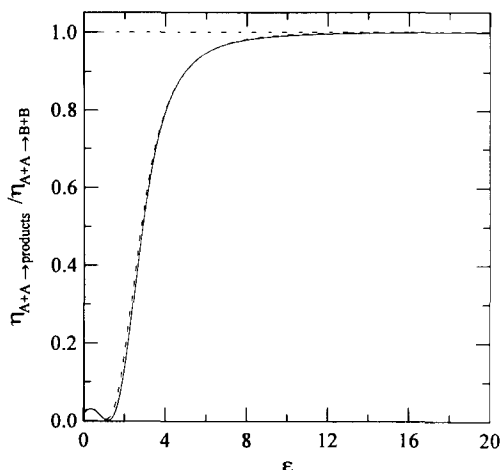


Fig. 8. Variation versus  $\epsilon$  of the ratio of  $\eta$  for  $A + A \rightarrow \text{products}$  to  $\eta$  for  $A + A \rightarrow B + B$ , in the limit  $\delta \rightarrow 0$ ,  $\sigma_E/\sigma_R = 1$ ; (—) is the ratio of converged values of  $\eta$ ; (---) is the ratio of two-term solutions.

identical in the limit of large  $\epsilon$ . This result holds to all orders of approximation. Hence, we observe a region for which the system  $A + A \rightarrow B + B$  corresponds to the system  $A + A \rightarrow \text{products}$ .

Similarly, the limit of vanishingly small reverse reaction for the system  $A + A \rightleftharpoons B + B$  does not coincide with the irreversible reaction  $A + A \rightarrow B + B$ . The irreversible case  $\sigma_r \rightarrow 0$  violates the principle of microscopic reversibility (Eq. (52)) and cannot be applied in this case. As with  $A + A \rightarrow B + B$ , the limit of  $\delta \rightarrow 0$  results in the coefficients  $a_i^{(2)}$  becoming infinite. The matrix equations Eqs. (50) and (66) corresponding to the two term solutions of the reversible and irreversible systems differ only in the inhomogeneous component arising from the form of  $(dT/dt)^{(0)}$ , Eq. (56). There appears to be no limiting procedure whereby the results for the system  $A + A \rightleftharpoons B + B$  go over to  $A + A \rightarrow B + B$ . Fig. 6 shows that the perturbations become significantly large if  $\delta$  departs far enough from the equilibrium value. We have demonstrated that the choice for  $(dT/dt)^{(0)}$  in the CE method of solution of the Boltzmann equation for the reactive system leads to somewhat different results. The CE method in each case is carried out consistent with the basic assumptions of the method [3–8,24]. It provides the asymptotic solutions of the Boltzmann equations on the reactive time scale. The transient time variation on an elastic time scale is assumed to be extremely short so as not to affect the long time dependence. A verification of the CE results requires an explicit time-dependent solution of the Boltzmann equation for different values of the reactive to elastic relaxation time scales. When the time scales are well separated we expect the time-dependent calculation will give results in agreement with the CE results.

### 3. Time-dependent solutions of the Boltzmann equation

The reaction  $A + A \rightarrow B + B$

The CE method provides a very special solution of the Boltzmann equation which gives the long time behaviour on the reactive time scale. The time dependence is implicit through the variation of the density and the temperature. In this section, we are concerned with the explicit time-dependent solution of the Boltzmann equation and the comparison of the time-dependent solutions with the CE results for different values of  $\epsilon$  and  $\sigma_R/\sigma_E$ . We are interested in a comparison of the results for the reaction  $A + A \rightarrow$  products and  $A + A \rightarrow B + B$ , especially in the limit of vanishing B. Similar studies for model reactive systems with neglect of the products have been reported previously [9,10].

The distribution functions are expanded about local Maxwellians,  $F_\gamma^{(0)}$ , characterized by time-dependent number densities,  $n_\gamma(t)$ , and temperatures,  $T_\gamma(t)$ . We have that

$$F_\gamma = F_\gamma^{(0)} [1 + \psi_\gamma(x, t)], \quad (71)$$

where  $\psi_\gamma(x, t)$  is the time-dependent perturbation from Maxwellian. The present approach parallels a study of temperature relaxation in binary gases [36] and the application to hot atom reactions [44].

With Eq. (71) in Eqs. (31) and (32), we have that

$$\begin{aligned} \frac{dF_\gamma^{(0)} [1 + \psi_\gamma]}{dt} &= \int \int [F_\gamma^{(0)'} F_\eta^{(0)'} - F_\gamma^{(0)} F_\eta^{(0)}] g \sigma_{\gamma\eta} d\Omega d\mathbf{c}_\eta \\ &+ \int \int F_\gamma^{(0)} F_{\gamma'}^{(0)} [\psi_\gamma' + \psi_{\gamma'}' - \psi_\gamma - \psi_{\gamma'}] g \sigma_{\gamma\gamma'} d\Omega d\mathbf{c}_{\gamma'} \\ &+ \int \int [F_\gamma^{(0)'} F_\eta^{(0)'} [\psi_\gamma' + \psi_\eta'] - F_\gamma^{(0)} F_\eta^{(0)} [\psi_\gamma - \psi_{\eta'}]] g \sigma_{\gamma\eta} d\Omega d\mathbf{c}_{\eta'} \\ &+ R_\gamma(c_\gamma), \quad (\gamma, \eta) = 1, 2, \end{aligned} \quad (72)$$

where

$$R_1(c_1) = -R_1^{(0)}(c_1) - 2 \int \int F_1^{(0)'} F^{(0)} \psi_1 g \sigma^* d\Omega d\mathbf{c} \quad (73)$$

and

$$R_2(c_2) = R_2^{(0)'}(c_2) + 2 \int \int F_1^{(0)'} F^{(0)'} \psi_1' g \sigma^* d\Omega d\mathbf{c}. \quad (74)$$

The reactive collision frequency  $R_2(c_2)$  for the product is a function of  $c_2$  and its evaluation requires the transformation to product velocities as discussed in Section 2.2 and elsewhere [4,38].

With the expansion in Sonine polynomials, we have that

$$\psi_\gamma(x_\gamma, t) = \sum_{i=2}^N b_i^{(\gamma)}(t) S^{(i)}(x_\gamma^2), \quad (75)$$

where the expansion coefficients are time dependent. It is important to note that  $b_1^{(\gamma)} = 0$  owing to the definition of the species temperature,  $T_\gamma$ . The coupled set of Boltzmann equations is reduced to the set of equations of the form

$$\frac{1}{N_i} \frac{db_i^{(\gamma)}}{dt} = \lambda_i^{(\gamma)} + \sum_{j=2}^N \left[ B_{ij}^{(\gamma)} b_j^{(\gamma)} + C_{ij}^{(\eta)} b_j^{(\eta)} \right], \quad i = 2, 3, \dots, N, \quad (76)$$

where

$$\begin{aligned} \lambda_i^{(1)} &= n_1 \langle S_1^{(i)}, S_1^{(0)} \rangle - A_i^{(1)} / n_1, \\ \lambda_i^{(2)} &= n_2 \langle S_2^{(i)}, S_2^{(0)} \rangle + D_i^{(2)} / n_2, \\ B_{ij}^{(\gamma)} &= n_\gamma [ S_\gamma^{(i)}, S_\gamma^{(j)} ] + n_\eta \langle S_\gamma^{(i)}, S_\gamma^{(j)} \rangle - \frac{2}{n_\gamma} R_{ij}^{(\gamma)} \delta_{\gamma 1} \\ &\quad - (H_{ij1} + \frac{3}{2} \delta_{ij}) \frac{1}{T_\gamma} \frac{dT_\gamma}{dt} - \frac{1}{n_\gamma} \frac{dn_\gamma}{dt} \delta_{ij}, \\ C_{ij}^{(\eta)} &= n_\eta \langle S_\gamma^{(i)}, S_\eta^{(j)} \rangle + \frac{2}{n_\gamma} R_{ij}^{(\eta)} \delta_{\eta 1}. \end{aligned} \quad (77)$$

The angle integrals,  $\langle S_\gamma^{(i)}, S_\eta^{(j)} \rangle$  in Eq. (77) are the two-temperature matrix elements of the collision operators as defined in Ref. [43], and evaluated for the hard sphere cross section. The integrals  $A_i^{(1)}$  are the moments of the equilibrium reactive collision frequencies,  $R_1^{(0)}$ , evaluated as in Ref. [7]. The corresponding integrals for product species B are given by

$$D_i^{(2)} = \int \int \int F_1^{(0)'}(T_1) F^{(0)'}(T_1) S_2^{(i)}(T_2) \sigma^* g d\Omega d\mathbf{c} d\mathbf{c}_2,$$

and can be evaluated as in [7] for the special case  $m_1 = m_2$  and we have that

$$D_i^{(2)} = 4n_1^2 Q_{11} \left( \frac{T_2}{T_1} \right)^{3/2} \sum_{k=0}^i \left( 1 - \frac{1}{2} \frac{T_1}{T_2} \right)^{i-k} \left( \frac{1}{2} \right)^k S_{ik} K_k(0) e^{-\epsilon}.$$

Note that  $K_k(0)$  represents the zero threshold energy integral,  $K_k$  in Eq. (41) in Ref. [7], and  $\epsilon$  is  $\exp(-E^*/kT_1)$ . The two-temperature  $D_i^{(2)}$  reduces to  $A_i(0)e^{-\epsilon}$  for  $T_1 = T_2$ . The quantities  $R_{ij}^{(\gamma)}$  are the matrix elements of the reactive collision operator in Eq. (73), (74). These have been found to be of second order and can be neglected. The quantities  $H_{ijk}$  are the integrals of products of Sonine polynomials that arise from  $dF_\gamma^{(0)}/dt$ , and  $dS_\gamma^{(i)}/dt$ . These details of the calculation have been discussed in a previous paper [43]. All the coefficients in Eq. (76) are time dependent since the temperatures characterizing these matrix elements as well as the densities are time dependent. Hence Eq. (76) is coupled to the equations for the densities

$$dn_1/dt = -dn_2/dt = -n_1^2 \left[ A_0^{(1)} + 2 \sum_{j=2}^N b_j(t) A_j^{(1)} \right], \quad (78)$$

and the temperatures

$$\frac{dT_1}{dt} = -\frac{2n_2T_1}{3} \left[ \langle S_1^{(1)}, S_2^{(0)} \rangle - \frac{A_1^{(1)}}{n_1n_2} + \sum_{j=2}^N \left( \left[ \langle S_1^{(1)}, S_1^{(j)} \rangle - 2\frac{R_{1j}^{(1)}}{n_1n_2} \right] b_j^{(1)} + \langle S_1^{(1)}, S_2^{(j)} \rangle b_j^{(2)} \right) \right], \quad (79)$$

$$\frac{dT_2}{dt} = -\frac{2n_1T_2}{3} \left[ \langle S_2^{(1)}, S_1^{(0)} \rangle + \frac{D_1^{(2)}}{n_1n_2} + \left( \left( \frac{T_2}{T_1} \right)^{3/2} - 1 \right) \frac{T_2}{n_2} \left( \frac{dn_2}{dt} \right)^{(0)} + \sum_{j=2}^N \left( \left[ \langle S_2^{(1)}, S_2^{(j)} \rangle + 2\frac{R_{1j}^{(2)}}{n_1n_2} + 2\frac{A_i^{(1)}}{n_1n_2} \right] b_j^{(1)} + \left[ \langle S_2^{(1)}, S_1^{(j)} \rangle - 2\frac{D_i^{(2)}}{n_1n_2} \right] b_j^{(2)} \right) \right]. \quad (80)$$

The perturbation of the distribution function and the fractional change in the rate of reaction,  $\eta(t)$ , are determined from the numerical time integration of Eq. (76), and the equations for the densities and temperatures, Eqs. (78)–(80). The calculations by Cukrowski et al. [16] did not include the departure from the local Maxwellians, that is, the perturbation of the distribution functions was assumed to be zero. Hence their analysis is based solely on the hydrodynamic equations, Eqs. (78)–(80) with  $b_i^{(\gamma)}(t) = 0$ , and in a sense cannot be considered as a solution to the Boltzmann equation. These authors use the time dependent species temperatures (referred to as the Shizgal–Karplus temperatures) to determine a time-dependent correction to the rate of reaction as given by Eq. (23).

For the numerical integration of Eqs. (79)–(80), a dimensionless time variable,  $t_E$ , is defined given by  $td_2^2n_1^{(0)}(0)/[2\pi kT_1(0)/m]^{1/2}$ . The initial conditions assume Maxwellian distribution of reactants and products and therefore all coefficients  $b_i^{(\gamma)} = 0$  at  $t = 0$ . The set of Eqs. (76)–(80) are integrated with a fourth-order Runge–Kutta integration procedure. Fig. 9 shows the time variation of  $\eta(t)/\eta_{CE}$  versus the dimensionless elastic collision time. The value of  $\eta_{CE}$  varies with time implicitly through  $n(t)$  and  $T(t)$ , Eqs. (78)–(80). The different curves are for different choices of the activation energy and the ratio of elastic and reactive collision hard sphere diameters, that is, for different values of the elastic and reactive time scales. When these time scales are well separated, we expect that the long time or asymptotic value of the time-dependent result, that is  $\lim_{t \rightarrow \infty} \eta(t) \rightarrow \eta_{asy}$ , coincides with the CE result. For the topmost curve (a) in Fig. 9, with  $\epsilon = 13$  and  $\sigma_E/\sigma_R = 200$ , this separation of relaxation times is satisfied and the time-dependent result coincides with the CE result. The subsequent curves, from top to bottom, are for decreasing reduced activation energy. In each case, except for the bottom curve, a steady value of  $\eta$  is obtained but does not coincide with  $\eta_{CE}$ , even for arbitrarily large ratios for  $\sigma_E/\sigma_R$ . In Table 1, we have listed the values of  $\sigma_E/\sigma_R$ ,  $\epsilon$ , the ratio of relaxation times and the ratio  $\eta(t)/\eta_{CE}$ . For example,

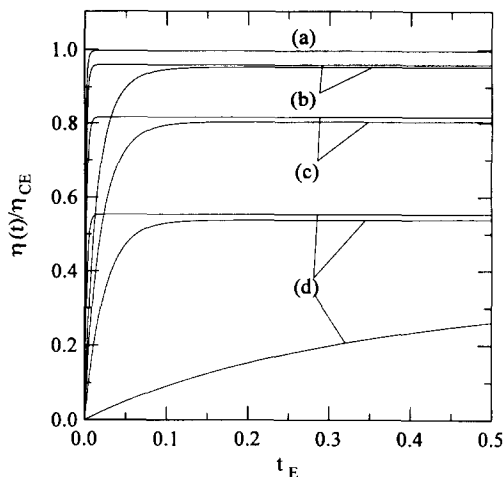


Fig. 9. Ratio of the time-dependent  $\eta(t)$  and corresponding CE  $\eta_{CE}$  for the system  $A + A \rightarrow B + B$ . The reduced activation energy  $\epsilon$  equals (a) 13, (b) 9, (c) 6 and (d) 4. The elastic collision cross sections for each curve are listed on Table 1.

Table 1

Comparison of  $\eta$  values calculated from CE,  $\eta_{CE}$ , and asymptotic values from the time-dependent two-temperature approach  $\eta_{asy}$  for the system  $A + A \rightarrow B + B$ . The ratio of initial product to reactant density  $n_1(0)/n_2(0)$  is 1. See Fig. 9

Curve	$\epsilon$	$\sigma_E/\sigma_R$	$\tau_R/\tau_E$	$\eta_{asy}$	$\eta_{CE}$	$\eta_{asy}/\eta_{CE}$
	2	1	7.3(0)	8.15(-4)	2.18(-2)	0.049
(d)	4	1	5.5(1)	1.53(-2)	2.24(-2)	0.514
(d)	4	20	1.1(3)	1.20(-3)	2.19(-3)	0.546
(d)	4	200	1.1(4)	1.78(-4)	3.20(-4)	0.554
(c)	6	20	8.1(3)	1.50(-3)	1.86(-3)	0.803
(c)	6	200	8.1(4)	1.52(-4)	1.86(-4)	0.817
(b)	9	20	1.6(5)	4.96(-4)	5.21(-4)	0.953
(b)	9	200	1.6(6)	5.00(-5)	5.21(-5)	0.960
(a)	13	200	8.8(7)	8.27(-6)	8.29(-6)	0.997

for the curve (d) in Fig. 9,  $\epsilon = 4$  and the ratio  $\eta(t)/\eta_{CE} \approx 0.55$  even for arbitrarily large  $\sigma_E/\sigma_R$ . This result is unexpected and was not observed in the previous study for a one-component system [9,10]. The phenomenon arises from the separation in temperatures,  $\Delta T_\gamma(t)$ , which is shown in Fig. 10 for different values of  $\epsilon$  and  $\sigma_E/\sigma_R$ . These attain steady values which agree remarkably well with the corresponding CE values when the required separation of relaxation times is obtained. The ratio  $\tau_E/\tau_R$  decreases in Figs. 10A–D. As a consequence of this steady temperature separation, the quantity  $\langle S_\gamma^{(i)}, S_\gamma^{(0)} \rangle \alpha \Delta T_\gamma$  (see [43]) differs from zero. This two-temperature matrix

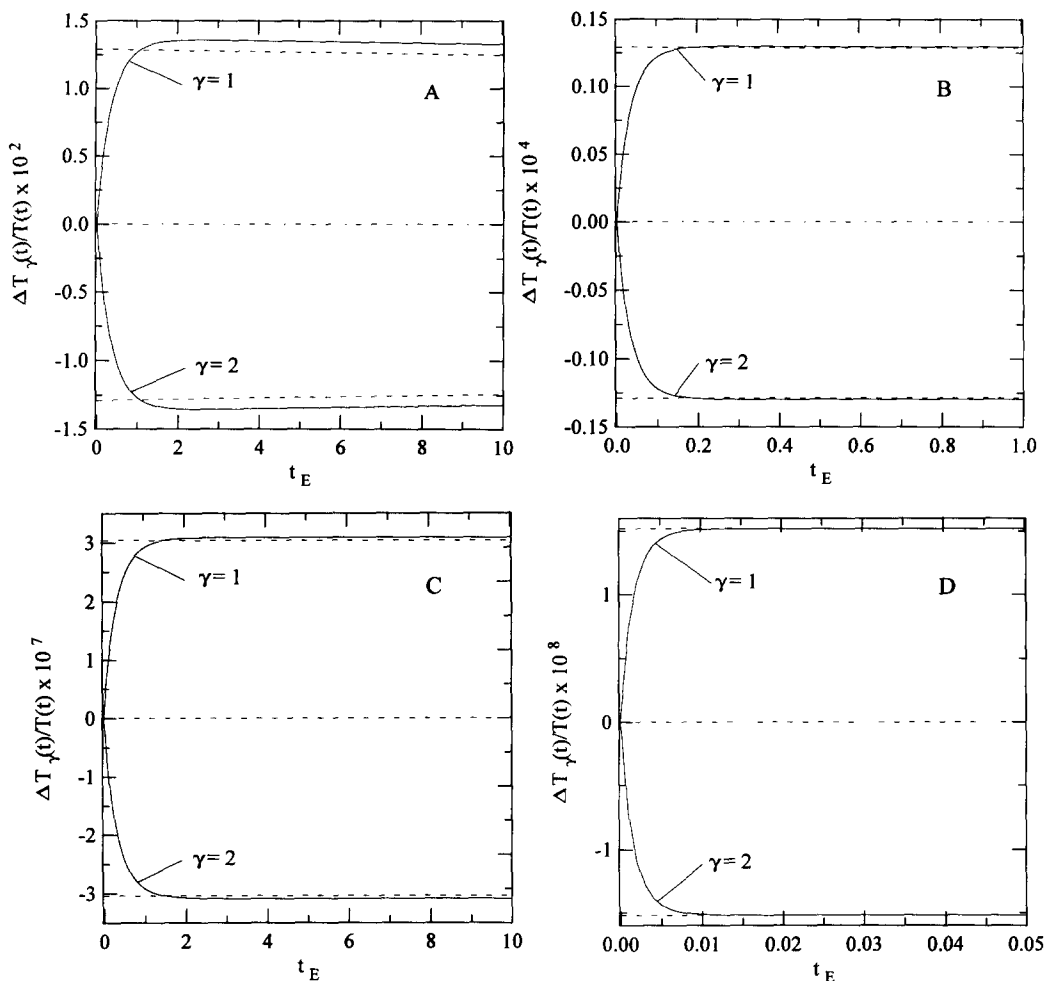


Fig. 10. Time-dependent  $\Delta T_\gamma/T$  (—), and corresponding CE values  $a_1^{(\gamma)}$  (---) for  $A + A \rightarrow B + B$ . The ratio of elastic to reactive hard sphere collision cross sections,  $\sigma_E/\sigma_R$ , and reduced activation energy,  $\epsilon$ , are equal to (A) 1, 9; (B) 10, 9; (C) 1, 13 and (D) 200, 13.

element occurs in  $\lambda_i^{(\gamma)} = n_\gamma \langle S_\gamma^{(i)}, S_\gamma^{(0)} \rangle - A_i^{(\gamma)}/n_\gamma$  in Eq. (76), which becomes independent of  $\sigma_E/\sigma_R$  for large  $\sigma_E/\sigma_R$ . It is the finite values of  $\langle S_\gamma^{(i)}, S_\gamma^{(0)} \rangle$  which leads to the  $\eta(t)/\eta_{CE}$  values in Fig. 9 and Table 1 which are less than unity. For larger values of  $\epsilon$ ,  $\langle S_\gamma^{(i)}, S_\gamma^{(0)} \rangle$  vanishes more rapidly than  $A_i^{(\gamma)}$ , and has a reduced effect so that for  $\epsilon \gtrsim 13$  shown in Fig. 9 and Table 1,  $\eta(t)/\eta_{CE} \approx 1$ . The physical explanation for this result is that  $\eta_{asy}$  includes the effect of the reaction and temperature relaxation [35,36]. There is a perturbation of the distribution function that arises from both processes. The CE result,  $\eta_{CE}$ , does not include this two-temperature effect.

The use of local Maxwellians characterized by the species temperature,  $T_\gamma$ , in the present time-dependent calculations can also be employed in a CE-type solution of the Boltzmann equation. A similar procedure was used by Pascal and Brun [46] for the

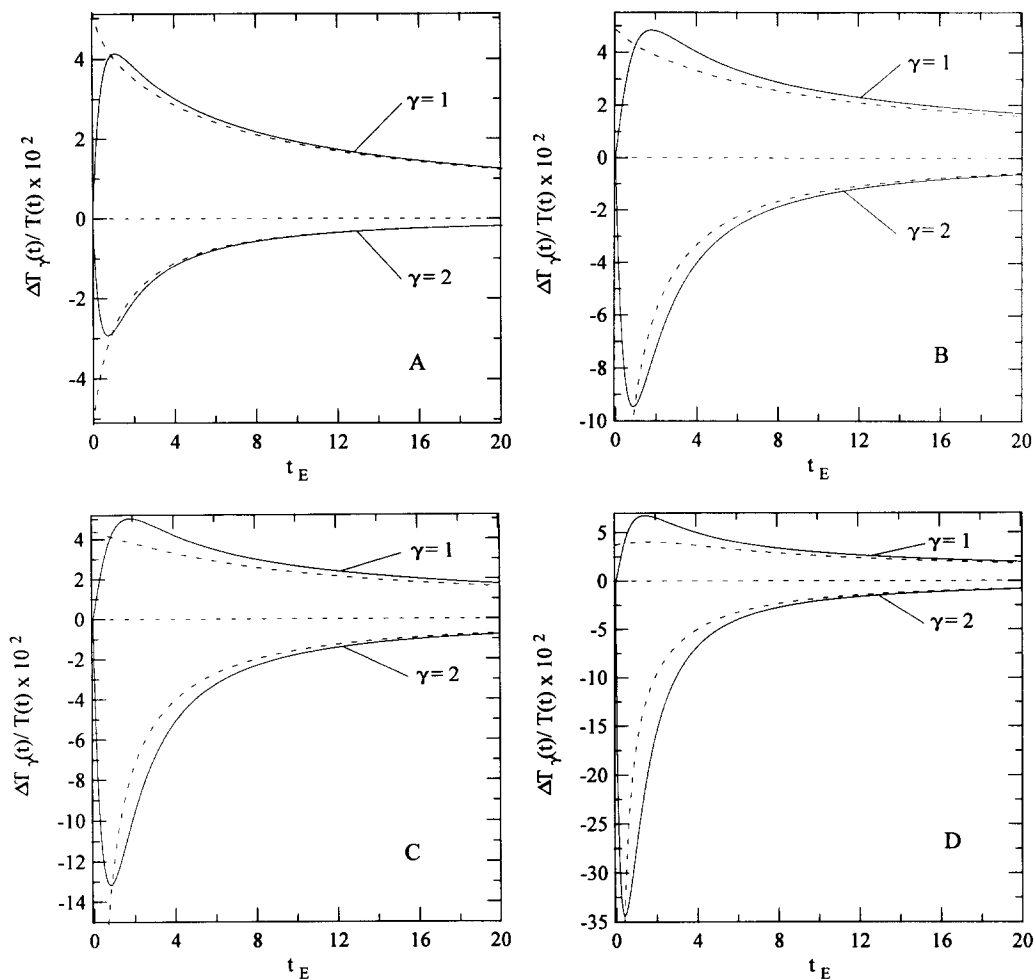


Fig. 11. Time dependence of  $\Delta T_\gamma/T$  (—), and the corresponding CE values  $a_1^{(\gamma)}$  (---), for  $A + A \rightarrow B + B$ . The density ratios  $n_2/n_1$  equal (A) 1, (B) 0.5, (C) 0.1 and (D) 0.01;  $\epsilon = 2$  and  $\sigma_E/\sigma_R = 1$ .

calculation of transport coefficients in molecular systems. The different temperatures for translational and vibrational degrees of freedom in their paper correspond to the different species temperatures in this paper. They referred to their approach as strong nonequilibrium (SNE). The CE procedure in Sections 2.1–2.3 that involves an expansion about Maxwellians at the common system temperature is called weak nonequilibrium (WNE) [46]. A detailed analysis of these different methods of solution of the Boltzmann equations for reactive systems will be presented elsewhere [47].

In Fig. 11, we show the time variation of  $\Delta T_\gamma$  with decreasing product density. The dashed curves are the corresponding CE results with the time variation implicit through  $n_\gamma(t)$  and  $T(t)$ . The reduced activation energy  $\epsilon$  is equal to 2 and  $\sigma_E/\sigma_R$  is unity so that the elastic and reactive time scales are similar. The agreement between the CE results for all but the shortest times in Fig. 11 is somewhat unexpected since  $\tau_E/\tau_R \approx 1$ , unlike

Table 2

Comparison of asymptotic values,  $[\Delta T_1(t)]_{asy}$ , calculated from integration of the Boltzmann equation and corresponding CE values  $[\Delta T_1(t)]_{CE}$ , for the reaction  $A + A \rightarrow B + B$

$\epsilon$	$\sigma_E/\sigma_R$	$n_2(0)/n_1(0)$	$[\Delta T_1]_{asy}/[\Delta T_1]_{CE}^a$	$[\Delta T_1]_{asy}/[\Delta T_1]_{CE}^b$
2	1	0.5	1.000	0.992
2	1	0.1	1.000	1.000
2	1	0.01	1.000	1.000
4	1	1.0	0.998	0.870
4	20	1.0	1.000	0.990
4	200	1.0	1.000	0.999

<sup>a</sup> First order approximation.

<sup>b</sup> Converged solution.

the conditions of Fig. 10. Although there is no steady state, the ratio  $[\Delta T_1]_{asy}/[\Delta T_1]_{CE}$  becomes time-independent on the  $t_E$  time scale. It is useful to notice the increasingly large perturbation of  $T_2$  as  $n_2 \rightarrow 0$ . This can be inferred from Eq. (80), where  $dT_2/dt$  varies as  $1/\delta$  and becomes infinite as  $\delta \rightarrow 0$  for nonzero values of  $n_1$ .

In Table 2, we show for several values of  $\epsilon$ ,  $\sigma_E/\sigma_R = 1$  and the initial density ratio,  $n_1(0)/n_2(0)$  the steady state  $[\Delta T_1]_{asy}/[\Delta T_1]_{CE}$  ratios which are very close to unity. It is clear that there is very good agreement irrespective of the value  $\tau_E/\tau_R$ , unlike the behaviour shown in Table 1. The explanation for this behaviour is that the equation for  $T_1$ , Eq. (79), to lowest order ( $b_j^{(1)} = 0$ ) evolves only on the reactive time scale. In Table 2, the first entry corresponds to the first order approximation to  $[\Delta T_1]_{asy}/[\Delta T_1]_{CE}$ , whereas the second entry corresponds to a higher order approximation with sufficient number of terms to give agreement to four decimal places. To first order, the time-dependent and CE results coincide. The departures from unity in the last column of Table 2 arise from the perturbations from the local Maxwellians.

We conclude this discussion and show in Fig. 12 the time variation of the ratios for  $\eta(t)$  for  $A + A \rightarrow B + B$  (in the limit of vanishing products) in comparison with  $\eta_{CE}$  for  $A + A \rightarrow$  products (with complete neglect of products). The time-dependent results in Fig. 12 are for  $\delta = n_1/n_2 = 10^{-5}$  for various  $\epsilon$  and  $\sigma_E/\sigma_R$  values. The time-dependent equations cannot be integrated for the initial condition with no product since the temperature  $T_2$  is undefined. This is in sharp contrast to the previous works by Cukrowski et al. [15,16] which show that  $T_2(0) = T(7/6 + \epsilon/3)$  for  $n_2 \rightarrow 0$ , obtained with the assumption  $(dT/dt)^{(0)} = 0$ . Since this isothermal constraint does not apply,  $T_2(0)$  is indeterminate for  $n_2 \rightarrow 0$ . The ratio of the CE results for these reactions is shown in Fig. 8. The lack of agreement at small  $\epsilon$  is the nonvanishing effect of vanishing products. The time-dependent results in Fig. 12 are completely consistent with the CE result. There is agreement for  $\eta$  for the two reactive models in the limit of vanishing product for large  $\epsilon$ . For small  $\epsilon$ , the time-dependent results demonstrate, as does the CE approach, the nonvanishing effect of vanishing product. This effect is not a consequence

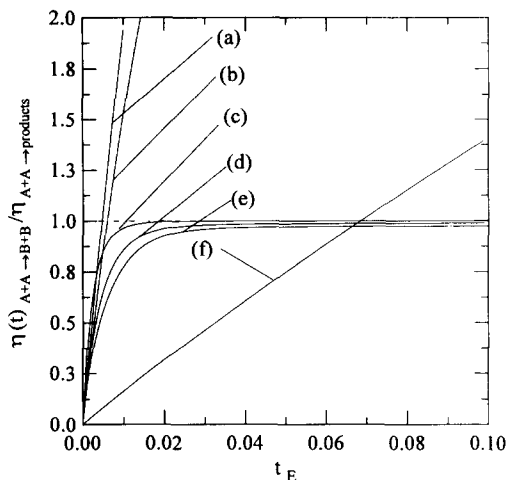


Fig. 12. Time dependence of the ratio  $\eta(t)$  ( $A + A \rightarrow B + B$ ) to the CE value of  $\eta$  ( $A + A \rightarrow \text{products}$ ). The reduced activation energy,  $\epsilon$ , and the ratio of elastic to reactive hard sphere collision cross section,  $\sigma_E/\sigma_R$ , are equal to (a) 6, 20p; (b) 4, 20; (c) 13, 200; (d) 6, 200; (e) 4, 200 and (f) 2, 1;  $n_2(0)/n_1(0) = 10^{-5}$ .

of the assumptions of the CE method, but arises from the different nature of the two reactive systems.

#### 4. Summary of results

In the present paper, we have considered the calculation of the perturbation of the distribution function from the Maxwellian from the Boltzmann equation using a CE method of solution. The model reactive systems  $A + A \rightarrow \text{product}$ ,  $A + A \rightarrow B + B$  and  $A + A \rightleftharpoons B + B$  were studied. A hard sphere elastic cross section was chosen for all elastic collisions and a line-of-centers reactive section with a reduced activation energy  $\epsilon = E^*/kT$  was used. The corrections to the rate coefficients from the equilibrium values were calculated and the role of the departure of the species temperatures from the system temperature was studied in detail. We showed that for small  $\epsilon$  the results for the reaction  $A + A \rightarrow B + B$  do not coincide with  $A + A \rightarrow \text{product}$  which has been termed the nonvanishing effect of vanishing products [5,14]. For large values of  $\epsilon$ , the results for these two reactions do agree. We also showed that the results for the reversible reaction  $A + A \rightleftharpoons B + B$  do not coincide with those for  $A + A \rightarrow B + B$  when the reverse reaction is made negligible. The reason for this is that microscopic reverseability holds for the reversible reaction and not for the irreversible reaction.

A two-temperature time-dependent solution of the Boltzmann equation for the reactions  $A + A \rightarrow B + B$  was carried out to study the validity of the CE method. We have shown that when the ratio of the elastic to reactive time scales is sufficiently small, the time-dependent calculations show a steady state. The steady state coincides with the CE result for sufficiently large  $\epsilon$  and  $\sigma_E/\sigma_R$ . However, for moderate values of  $\epsilon$ , the steady state value does not agree with the CE result owing to the departure of the

species temperature,  $T_\gamma$ , from the system temperature,  $T$ . A similar study was carried out for the limit of vanishing B and the results compared with that for  $A + A \rightarrow$  product. We found agreement at large  $\epsilon$  but not at small  $\epsilon$ , consistent with our findings in the comparison of the CE results for the two systems.

The formalism of the present paper can be applied to reactive systems with realistic elastic and reactive cross sections. The collision matrix elements that are required in the solution of the Boltzmann equation can be evaluated for arbitrary collision cross section sets. This was done previously by Shizgal and Karplus [6] for the microscopic reactions  $H_2(v_1) + H_2(v_2)$ , where  $v_1$  and  $v_2$  are the vibrational states. The nonequilibrium kinetics of translational hot  $O(^3P)$  formed from photodissociation of  $O_2$  and  $O_3$  in the Earth's atmosphere was carried out several years ago by Lindenfeld and Shizgal [48] with a realistic cross section set. The quantitative results for some particular reactive system will differ from the results for the model systems presented here but one should find a very similar dependence on the system variables. The behavior of model systems permits a better understanding of the results for physically interesting systems with a fixed set of parameters. In particular, the results obtained in this paper in terms of the effects of the products on the nonequilibrium corrections, the role of the species temperatures and the usefulness of the CE approach will be qualitatively similar in other systems. The magnitudes of the corrections will be different but the trends discussed here will be similar. For realistic systems where the nonequilibrium effects might be large, the time-dependent approach would be preferred over the CE method which is restricted to very small departures from equilibrium. There are important applications to disequilibrium of the vibrational states for molecular systems for which the formalism of this paper will have practical applications [46].

These nonequilibrium effects have had a very long history beginning with the classic papers by Kramers [1] and Prigogine [2], and only recently have there been experimental developments that may permit the direct verification of these effects in realistic systems. The direct measurements of velocity distribution functions in reacting systems have been reported recently by several groups [49]. These generally involve the determination of the details of the velocity distribution function of a product of a reaction (often hydrogen) from the Doppler profile of an emission line. Similar methods have been used to characterize the distribution of atomic hydrogen about the Earth at altitudes above 500 km [50]. The methods discussed in this paper have been used by Lindenfeld and Shizgal [51] to study the escape of atomic hydrogen from Earth; a process with an activation energy analogous to the model reactive systems of this paper. In particular, the cooling of the escaping hydrogen over the background major species which is atomic oxygen has been estimated and measured from the Doppler profiles of Lyman- $\beta$  emission [52]. There is an excellent example of the departure of the temperatures of different species from the system temperature; see Eq. (21). We cautiously speculate that it may be possible to experimentally observe similar effects in reactive systems modeled in this paper.

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## Appendix A

Cukrowski et al. [16] suggested in a recent paper that the neglect of the different species temperatures in the treatment of the one-component reactive system



is in error. Cukrowski et al. [16] argued that even for this one-component system, there must be a contribution from the  $a_1$  expansion coefficient owing to a difference in the temperature of species A and the temperature in the Maxwellian (Eq. (22)). In order to introduce this effect they replaced reaction (A.1) with the reaction



For this system, they set  $dT/dt = 0$  so that this term is no longer included in the inhomogeneous function (compare with Eqs. (12) and (13) in the CE equation). This assumption is not correct as discussed in Section 2.2.

The elastic A–A collision operator that was used in their work is given by Eq. (20) of the earlier paper [15], and to first order is of the form

$$I_{el}^{(1)}[f^{(1)}] = \iint [f^{(1)'} f_1^{(0)'} - f^{(1)} f_1^{(0)}] \sigma_{11} g d\Omega d\mathbf{c}_1. \quad (\text{A.3})$$

This is not the same linearized operator used in the other works [2,5,6] (see also Eqs. (10), (11), (41) and (42)) since one of the distribution functions of the *same* species has been set equal to the Maxwellian. With the substitution,  $f^{(1)} = f^{(0)}\phi$ , the elastic A–A collision operator is

$$I_{el}^{(1)}[\phi] = \iint f^{(0)} f_1^{(0)} [\phi' - \phi] \sigma_{11} g d\Omega d\mathbf{c}_1 \quad (\text{A.4})$$

and is not the correct linearized one-component collision operator. The correct operator is the one given by the first term on the left-hand side of Eq. (10). The operator in Eq. (10) conserves both the number density and the energy whereas the operator given by Eq. (A.4) conserves only the number density. With the neglect of  $dT/dt$  and the way in which the operator was linearized, the system studied by Cukrowski et al. [15] corresponds to the reaction Eq. (A.1) occurring in a large excess of a second species (with the same mass as A) that acts as a heat bath. This is the isothermal system studied in the paper by Shizgal and Karplus [8]. The CE equation considered by Cukrowski et al. [15] is of the form

$$\begin{aligned} & \int \int f^{(0)} f_1^{(0)} [\phi' - \phi] \sigma_{11} g d\Omega d\mathbf{c}_1 \\ &= f_1^{(0)} \left[ -\frac{1}{n_1} \left( \frac{dn_1}{dt} \right)^{(0)} + \int \int f^{(0)} \sigma^* g d\Omega d\mathbf{c} \right]. \end{aligned} \quad (\text{A.5})$$

The Boltzmann equation for the product is not included so that there is no density dependence considered.

It is important to notice that in this equation the cross section that appears in the collision operator on the LHS is for A–A elastic collisions, and not A–B collisions if B were in large excess and acted as a constant temperature heat bath. For the system studied by Cukrowski et al. [15] (and in [7]), the temperature of the one-component reactive species is *different* from the bath temperature as given by Eq. (22). The leading term in the expansion is indeed  $a_1$  and a first approximation to the correction to the equilibrium rate of reaction is given by

$$\eta = A_1^2 / 4A_0, \quad (\text{A.6})$$

which, with Eq. (29), is given explicitly by

$$\eta = \frac{1}{2} \left[ \epsilon + \frac{1}{2} \right]^2 \exp(-\epsilon), \quad (\text{A.7})$$

which is given by Eq. (3.2) of Cukrowski et al. [16].

The CE equation for the one-component system, Eq. (A.1), is given by

$$\begin{aligned} & \int \int f_1^{(0)} f^{(0)} [\psi'_1 + \psi' - \psi_1 - \psi] \sigma_{11} g d\Omega d\mathbf{c} \\ &= f_1^{(0)} \left[ -\frac{1}{n_\gamma} \left( \frac{dn_\gamma}{dt} \right)^{(0)} - \frac{1}{T} \left( \frac{3}{2} - x_\gamma^2 \right) \left( \frac{dT}{dt} \right)^{(0)} \right. \\ & \quad \left. + \int \int f_\eta^{(0)} \sigma^* g d\Omega d\mathbf{c}_\eta \right]. \end{aligned} \quad (\text{A.8})$$

The important distinction between this equation and Eq. (A.5) is that the energy is not a summational invariant of the first equation whereas it is for the second equation. The coefficient  $a_1$  is nonzero for the solution of Eq. (A.5) but it is zero for Eq. (A.8). The lowest order estimate of the fractional decrease of the rate coefficient from the equilibrium value is obtained with  $a_2$  and is given by

$$\eta = \frac{1}{32} \left( \epsilon^4 - 2\epsilon^3 + \epsilon^2/2 + \epsilon/2 + \frac{1}{16} \right) \exp(-\epsilon), \quad (\text{A.9})$$

which appears as Eq. (3.3) in Cukrowski et al. [16]. This result is twice the result given by Eq. (30) as explained in Section 2.1. The results Eqs. (A.7) and (A.9) are for different systems and cannot be compared directly.

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