

44X-3780-31

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Nonequilibrium Contribution to the Rate of Reaction

III. Isothermal Multicomponent Systems<sup>†</sup>

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## ABSTRACT

The nonequilibrium contribution to the reaction rate of an isothermal multicomponent system is obtained by solution of the appropriate Chapman-Enskog equation; the system is composed of reactive species in contact with a heat bath of inert atoms M. It is found that the perturbation of the velocity distribution functions is determined by the extent of the departure of the reactive collision frequency  $R^{(o)}(c_\gamma)$  for each reactive component  $\gamma$  from  $\bar{R}^{(o)}(c_\gamma)$ , the collision frequency that leaves the distribution function unaltered by reaction; the function  $\bar{R}^{(o)}(c_\gamma)$  obtained for an isothermal systems is different from that introduced previously for an isolated system. An illustrative application is made to a model system corresponding to the  $H_2 + Cl \rightleftharpoons HCl + H$  reaction without internal degrees of freedom; the deviation of the rate coefficient ration  $(k_f/k_r)$  from the equilibrium value  $(k_f^{(o)}/k_r^{(o)})$  is a few percent.

## I. INTRODUCTION

The perturbation of the velocity distribution function by reaction for the reactive system



was studied in two previous papers.<sup>1,2</sup> It was pointed out that a treatment of the nonequilibrium behavior of reactive systems with the nonlinear Boltzmann equation implies that the system is isolated. In this paper, we construct an isothermal constraint on a corresponding reactive system by dispersing the reactants and products in a heat bath of inert atoms M in such large excess that the heat bath remains unperturbed by the reaction. The system consisting of reactive species plus heat bath is held at a constant temperature, so that the reaction can be considered to take place under isothermal conditions; that is, the overall temperature of the reactive system remains essentially constant, although variation of the "temperatures" of the individual reactants and products does take place during the course of the reaction. This model corresponds more closely to the usual experimental situation than the one described in I and II.

The model reactive systems considered by Pyun and Ross<sup>3</sup> did not include an explicit mechanism for maintaining a constant temperature; instead, they made the assumption that the components in the isolated reactive system all have the translational temperature of the gas mixture. In the work by Pyun,<sup>4</sup> the reactive system was placed in contact with a heat bath, and the perturbation of the heat bath was included together with the assumption that the translational temperatures of the reactive components and the heat bath are all equal. This assumption clearly differs from the isothermal and constraint used in the present work; moreover,

it is not evident how such an equal temperature constraints is to be introduced into a real system of the type considered by Pyun.

The Chapman-Enskog method of solution of the Boltzmann equation for the model isothermal system is described in Sec. II. The effect on the form of the Chapman-Enskog equation of the isothermal character of the system is discussed. Comparison is made with the methods adopted by the earlier workers. In Sec. III the Sonine polynomial method of solution is outlined. Illustrative applications are made to reactions with and without activation energy and to the two model systems corresponding to the  $H_2+Cl=HCl+H$  and  $H_2+I_2=2HI$  reactions introduced in II. A discussion of the results is given in Sec. IV. In the appendix, the effect of including the perturbation of the heat bath particles is studied and comparison is made with the results obtained by Pyun.<sup>4</sup>

## II. THEORY

With the assumption that the heat bath particles M are distributed according to a Maxwell-Boltzmann velocity distribution function  $f_M^{(0)}$ , the velocity distribution functions for the reactive components  $f_Y$  obey the set of Boltzmann-like transport equations of the form (see II)<sup>5</sup>

$$\frac{\partial f_Y}{\partial t} = \iint (f_Y' f_M^{(0)'} - f_Y f_M^{(0)}) \sigma_{YM} g d\Omega dc - R_Y f_Y \quad (1)$$

Since the heat bath particles are assumed to be in large excess, elastic collisions between reactive species are neglected in comparison to the more frequent elastic collisions between the reactive components and the heat bath particles. In terms of the distribution functions, the number densities  $n_Y$  and the temperature T of the system are given by

$$n_Y = \int f_Y dc_Y \quad (2)$$

$$T = \frac{2}{3nk} \int f_M^{(o)} \frac{1}{2} m_M c_M^2 dc_M + \frac{2}{3nk} \sum_Y \int f_Y \frac{1}{2} m_Y c_Y^2 dc_Y \quad (3)$$

where  $n = n_M + \sum_Y n_Y$  and the sum over  $Y$  is over the reactive components. Since  $n_M \gg n_Y$ , Eq. (3) reduces to

$$T = \frac{2}{3n_M k} \int f_M^{(o)} \frac{1}{2} m_M c_M^2 dc_M \quad (4)$$

Solutions to Eq. (1) are obtained following the Chapman-Enskog method, which assumes that the only time dependence of  $f_Y$  is implicit through  $n_Y(t)$  and  $T(t)$ . Since the presence of a large excess of nonreacting species ensures that the gas mixture is at a constant temperature  $T$ , we can write

$$\frac{\partial f_Y}{\partial t} = \frac{\partial f_Y}{\partial n_Y} \frac{dn_Y}{dt} \quad (5)$$

where  $(dn_Y/dt)$  is obtained by integrating Eq. (1) over  $c_Y$ ; that is,

$$\frac{dn_Y}{dt} = -\int f_Y R_Y dc_Y \quad (6)$$

Equation (6) is the hydrodynamic equation of transport theory for the present problem. Expanding  $f_Y$  about the Maxwellian distribution function  $f_Y^{(o)}$

$$f_Y = f_Y^{(o)} (1 + \psi_Y) \quad (7)$$

substituting Eq. (7) into Eq. (1), and making use of Eqs. (5) and (6), we obtain the equation for  $f_Y^{(o)}$  (zero order in  $\psi_Y$ ),

$$\iint (f_Y^{(o)'} f_M^{(o)'} - f_Y^{(o)} f_M^{(o)}) \sigma_{YM} g d\Omega d\tilde{c}_M = 0 \quad (8)$$

The solution of Eq. (8) with the standard condition

$$n_Y = \int f_Y^{(o)} d\tilde{c}_Y \quad (9)$$

is the Maxwell-Boltzmann distribution function

$$f_Y^{(o)} = n_Y(t) \left| \frac{m_Y}{2\pi kT} \right|^{3/2} \exp(-m_Y c_Y^2 / 2kT) \quad (10)$$

where T is the heat bath temperature.

The equation linear in  $\psi_Y$  is

$$n_Y n_M K_{YM}(\psi_Y) = f_Y^{(o)} F_Y^{(o)} \quad (11)$$

with the definition

$$n_Y n_M K_{YM}(\psi_Y) = \iint f_Y^{(o)} f_M^{(o)} (\psi_Y' - \psi_Y) \sigma_{YM} g d\Omega d\tilde{c}_M \quad (12)$$

$$F_Y^{(o)} = -\frac{1}{n_Y} \int f_Y^{(o)} R_Y^{(o)} d\tilde{c}_Y + R_Y^{(o)} \quad (13)$$

It is important to notice that the equations for  $\psi_Y$  [Eq. (11)] are not coupled; this uncoupled set of equations contrasts with the coupled set obtained for a multicomponent system in the absence of a heat bath (see II). As a consequence of the definition of  $n_Y$  [Eq. (2)] and of Eq. (9),  $\psi_Y$  must satisfy the single auxiliary condition

$$\int f_Y^{(o)} \psi_Y d\tilde{c}_Y = 0 \quad (14)$$



Equation (14) selects a unique solution to Eq. (11) by requiring that the solutions to the homogeneous equation  $K_{YM}(\chi_Y) = 0$  do not contribute to  $\psi_Y$ . There is only one such condition in the present case since there is only one solution to the homogeneous equation; i.e.,  $\chi_Y = \text{constant}$ . In I, the energy is also a solution to the homogeneous equation of that problem and there are two auxiliary conditions.

Through terms listed in the functions  $\psi_Y$ , the forward and reverse rates of reaction are

$$J_f = J_f^{(o)} + \iiint f_1^{(o)} f_2^{(o)} (\psi_1 + \psi_2) \sigma_{12}^* g d\Omega dc_1 dc_2 \quad (15)$$

$$J_r = J_r^{(o)} + \iiint f_3^{(o)} f_4^{(o)} (\psi_3 + \psi_4) \sigma_{34}^* g d\Omega dc_3 dc_4 \quad (16)$$

where  $J_f^{(o)}$  and  $J_r^{(o)}$  are the equilibrium rates.

### III. CALCULATIONS

When  $\psi_Y$  is expanded in Sonine polynomials (i.e.,  $\psi_Y = \sum_{i=0}^N a_i^{(Y)} S_Y^{(i)}$ ), the expansion coefficients obtained by substituting into Eq. (11) are (see II)

$$n_Y n_M \sum_i a_i^{(Y)} \{S_Y^{(j)}, S_Y^{(i)}\} = n_Y n_j \alpha_j^{(Y)} \quad (17)$$

where

$$n_Y n_j \alpha_j^{(Y)} = \int f_Y^{(o)} F_Y^{(o)} S_Y^{(j)} dc_Y = [A_j^{(Y)} - A_o^{(Y)} \delta_{oj}] G_Y \quad (18a)$$

and

$$n_Y n_M \{S_Y^{(j)}, S_Y^{(i)}\} = \iiint f_Y^{(o)} f_M^{(o)} S_Y^{(j)} [S_Y^{(i)'} - S_Y^{(i)}] \sigma_{YM} g d\Omega dc_M dc_Y \quad (18b)$$

In terms of the  $a_i^{(\gamma)}$ , the fractional decrease in the forward and reverse rates of reaction  $\eta_f = (J_f^{(0)} - J_f) / J_f^{(0)}$  and  $\eta_r = (J_r^{(0)} - J_r) / J_r^{(0)}$ , respectively, are

$$\eta_f = - \sum_{\gamma=1}^2 \sum_{i=1}^N a_i^{(\gamma)} A_i^{(\gamma)} / A_o^{(\gamma)} \quad (19)$$

$$\eta_r = - \sum_{\gamma=3}^4 \sum_{i=1}^N a_i^{(\gamma)} A_i^{(\gamma)} / A_o^{(\gamma)} \quad (20)$$

where  $a_o^{(\gamma)} = 0$  by Eq. (14).

The cross sections used in I and II [Eqs. (II44), (II45), and I51)] are employed in the present paper. From the form of Eqs. (17), (18), and (II38), one observes that the dependence of the expansion coefficients  $a_i^{(\gamma)}$  on  $\eta_\gamma$ ,  $d_{\gamma\eta}$  and the steric factors  $q_f$  and  $q_r$  for the forward and reverse rates of reaction has a simple form. This dependence can be factored out by defining a new set of expansion coefficients  $a_i'^{(\gamma)}$

$$a_i'^{(1)} = \frac{1}{q_f} [(n_M d_{1M}^2) / (n_2 d_{12}^2)] a_i^{(1)}, \quad a_i'^{(2)} = \frac{1}{q_f} [(n_M d_{2M}^2) / (n_1 d_{12}^2)] a_i^{(2)}$$

$$a_i'^{(3)} = \frac{1}{q_r} [(n_M d_{3M}^2) / (n_4 d_{34}^2)] a_i^{(3)}, \quad a_i'^{(4)} = \frac{1}{q_r} [(n_M d_{4M}^2) / (n_4 d_{34}^2)] a_i^{(4)}$$

where from Eq. (17) the  $a_i'^{(\gamma)}$  coefficients depend on the component masses, the cross section parameters in  $p(2)$  and the number of terms retained in the expansion of  $\psi_\gamma$ . We can now write the fractional decrease in the reaction rate in the form

$$\eta_f = q_f \{ [(n_2 d_{12}^2) / (n_M d_{1M}^2)] \eta^{(1)} + [(n_1 d_{12}^2) / (n_M d_{2M}^2)] \eta^{(2)} \} G_f \quad (21)$$

$$\eta_r = q_r \left[ \left\{ (n_4 d_{34}^2) / (n_M d_{3M}^2) \right\} \eta^{(3)} + \left\{ (n_4 d_{34}^2) / (n_M d_{4M}^2) \right\} \eta^{(4)} \right] G_r \quad (22)$$

where

$$\eta^{(\gamma)} = - \sum_{i=1}^N a_i^{(\gamma)} A_i^{(\gamma)} / A_o^{(\gamma)}$$

The assumption that the distribution function of the heat bath particles is Maxwellian could be relaxed and the perturbation of the heat bath calculated with the formalism of II (see Appendix). However, the concentration and elastic cross section dependence is then more complicated and cannot be written down as given by Eqs. (21) and (22).

#### a. Applications and Results

Since the dependence of  $\eta_f$  and  $\eta_r$  on the concentration and on the hard-sphere diameters is known, and since the convergence of the expansion of  $\psi_\gamma$  has been demonstrated in I and II, we need only study the dependence of the quantities  $\eta^{(\gamma)}$  on the masses and on the cross section parameters  $\epsilon^*/kT$  and  $\beta$ . The nature of the solutions of Eq. (11) for a particular component  $\gamma$  is sufficient for an understanding of the possible effects in the multi-component systems since the equations for  $\psi_\gamma$  are not coupled.

In Fig. 1, the effect of changes in the ratio of the heat bath particle mass relative to the reactant mass  $M/m$  for  $A=B$  on  $\eta^{(\gamma)}$  is studied. The dependence of  $\eta^{(1)}$  versus  $\epsilon^*/kT$  shown in Fig. 1a can be compared with the dependence of  $\eta_f$  shown in Fig. IIIa for the isolated system reaction  $A+A \rightarrow \text{products}$ . The maximum in  $\eta^{(1)}$  in Fig. 1a is seen to occur for smaller  $\epsilon^*/kT$  and there is no oscillatory behavior in the region  $0 \leq \epsilon^*/kT < 2$ . The effect of the reactant mass ratio is shown for reactions with activation energy in Fig. 2 and for reactions without activation energy in Fig. 3.

It is important to compare the dependence of  $\eta^{(\gamma)}$  versus  $\beta$  in Fig. 3 with the dependence of  $\eta_f$  shown in Fig. II5; the difference in the results obtained for  $0 \leq \beta < 2$  are of primary interest.

For the  $H_2 + Cl = HCl + H$  reaction<sup>6</sup> and the hypothetical bimolecular reaction  $H_2 + I_2 = 2HI$  (which is now known to actually involve I atoms rather than  $I_2$  in the forward reaction<sup>7</sup>), the coefficients  $\eta_f$  and  $\eta_r$  given by Eqs. (21) and (22) are listed in Table 1. The calculations were carried out with the parameters used in II and the heat bath properties chosen to correspond to helium or argon as in the experimental investigation of the  $H_2 + Cl \rightleftharpoons HCl + H$  reaction by Westenberg and de Haas.<sup>6</sup>

In I, preliminary estimates of the forward rate of the ionic recombination reaction  $H^+ + H^- \rightarrow H_2$  indicated that the nonequilibrium correction can be large and the Chapman-Enskog expansion of the distribution function may converge very slowly or not at all. Since the earlier treatment could not account for the concentration dependence of  $\eta_f$ , the nonequilibrium effects have been reinvestigated. With the cross section parameters of I,  $\eta_f$  was calculated and the results are shown in Table 1.

#### IV. DISCUSSION

As in our previous papers, we begin by investigating systems for which nonequilibrium effects do not occur. The reaction collision frequencies  $R_Y^{(0)} = G_Y \int f_Y^{(0)} g \sigma_t^* dc_Y$  for which  $\eta^{(\gamma)} = 0$  are obtained for cross section  $\sigma_t^*$  that yield zero for  $F_Y^{(0)}$  in Eq. (11). Thus, from Eq. (13), and Sec. V of II, we have

$$\bar{R}_Y^{(0)} = A_o^{(\gamma)} / n_Y \quad (23)$$

Perturbations of the distribution functions are determined by the departure of  $R_Y^{(o)}$  from  $\bar{R}_Y^{(o)}$ , where

$$R_Y^{(o)} - \bar{R}_Y^{(o)} = -(\xi_Y^2 - 3/2) \frac{1}{T} \left( \frac{dT_Y}{dt} \right)_R^{(o)} + \frac{\sqrt{\pi}}{2n_Y} \sum_{k=2}^{\infty} \frac{\gamma! A_k^{(\gamma)} S_Y^{(k)} (\xi_Y^2)}{\Gamma(k + 3/2)} \quad (24)$$

with  $(dT_Y/dt)_R^{(o)} = (2T/3n_Y) A_1^{(\gamma)}$ . Equations (23) and (24) show that only when  $R_Y^{(o)}$  is independent of  $\xi$ , which corresponds to uniform removal of particles by reaction, is there no perturbation of the distribution functions. This is the case for systems without activation energy and  $\beta = -1$  as shown in Fig. 3 [ $\eta^{(\gamma)} (\beta = -1) = 0$ ], since  $A_j^{(\gamma)} = 0$ ,  $j \geq 1$  and  $R_Y^{(o)} = \bar{R}_Y^{(o)}$ , independent of the other system variables (see II).

The dependence of  $R_Y^{(o)} - \bar{R}_Y^{(o)}$  and  $\eta^{(\gamma)}$  on the cross section parameters is through the  $A_j^{(\gamma)}$  integrals. Since  $A_j^{(\gamma)}$  is proportional to  $(1 - m_Y/m_o)^j$ , there is a dependence on the reactant mass ratio in the form of a power series in  $m_Y/m_o$ . There is an additional mass dependence of  $\eta^{(\gamma)}$  that arises from the dependence of  $\{S_Y^{(i)}, S_Y^{(j)}\}$  on the ratio of the reactant and heat bath particles mass ratio  $m_Y/M$ . In Figs. 2 and 3, the decrease in  $\eta^{(1)}$  with increasing  $m_1$  ( $m_2=1$ ) is due primarily to the decrease in the difference  $R_1^{(o)} - \bar{R}_1^{(o)}$  arising from the decreasing reactant mass ratio ( $m_2/m_o$ ) in the  $A_j^{(1)}$  integrals. Similarly, the increase in  $\eta^{(2)}$  is due to the increase in  $R_2^{(o)} - \bar{R}_2^{(o)}$  arising from the increase in the  $A_j^{(2)}$  integrals; in the limit  $m_1/m_2 \rightarrow \infty$   $\eta^{(1)} \rightarrow 0$  and  $\eta^{(2)}$  approaches a finite non-zero value. The increase in  $\eta^{(1)} = \eta^{(2)}$  with an increase in  $M/m$  shown in Fig. 1 [or decrease in  $M/m$  since  $\eta^{(\gamma)} (m_1=m_2=1)$  is invariant under the transformation  $M/m \rightarrow m/M$ ] is due to the decrease in the matrix elements  $\{S_Y^{(i)}, S_Y^{(j)}\}$ ; i.e.,

the momentum relaxation times are longer and there is a decreased coupling between the reactant and the heat bath.

Inspection of the results for the  $H_2+Cl=HCl+H$  and the  $H_2+I_2=2HI$  reactions listed in Table 1 indicates that they are in qualitative agreement with the above observations. The corrections  $\eta^{(\gamma)}$  are largest for the lighter reactive component and the dependence on the heat bath variables is as given by Eqs. (21) and (22) and as shown in Fig. 1. From the list of rate coefficients, it is clear that even for the extreme case  $n_Y/n_M = 0.1^9$  and for systems not too far removed from chemical equilibrium ( $G_f = .1$ ),  $\eta_f$  and  $\eta_r$  are still small and represent less than a 1% decrease in the equilibrium rates. The deviation of  $(k_f/k_r)$  from  $(k_f^{(o)}/k_r^{(o)})$  is also very small. In particular, if we compare  $k_f$  calculated for a large excess of  $H_2$  (i.e.,  $G_f = 1, G_r = 0$ ) with  $k_r$  calculated for a large excess of  $HCl$  (i.e.,  $G_r = 1, G_f = 0$ ) corresponding to the conditions under which these rates were separately measured,<sup>6</sup> we find that

$$k_f/k_r = k_f^{(o)}/k_r^{(o)} \left\{ (1 - 10^{-5} n_{H_2}/n_{He}) / (1 - .19 \times 10^{-2} n_{HCl}/n_{He}) \right\}$$

$$k_f/k_r = k_f^{(o)}/k_r^{(o)} \left\{ (1 - .57 \times 10^{-5} n_{H_2}/n_{Ar}) / (1 - .95 \times 10^{-2} n_{HCl}/n_{Ar}) \right\}$$

in He and Ar, respectively. Even for an extreme choice of the concentrations, the deviation of  $k_f/k_r$  from  $k_f^{(o)}/k_r^{(o)}$  is very small. However, it must be emphasized that only the translational degrees of freedom have been taken into account. Since there is some theoretical evidence that vibrational energy may be very important in  $H_2+Cl \rightarrow HCl+H$  and related reactions,<sup>10</sup> a non-equilibrium calculation including vibrational effects is required for further analysis of this case.

For the  $H^+ + H^- \rightarrow$  products reaction, the effects are small for very dilute systems. However, for higher ionic concentrations, the non-equilibrium rates effects become large. This suggests, as already suggested in I, that the Burnett term in the expansion of the distribution function can be significant.

Comparison of Isothermal and Isolated Reactive Systems. The difference in the results obtained in this paper and those found in II for the isolated reactive system are dominated by the effect on  $\bar{R}_Y^{(o)}$  of the fact that  $(dT/dt)$  equals zero in the former and not in the latter. To illustrate this point, we consider the one-component reactive system  $A+A \rightarrow$  products and employing the relaxation time approximation,<sup>11</sup> which assumes that one can write

$$\psi = \tau F^{(o)} \quad (25)$$

With Eqs. (11) and (25) we find that

$$\eta_{\text{isothermal}} = 2\tau_{\text{isothermal}} \{ \langle R^{(o)2} \rangle - \langle R^{(o)} \rangle^2 \} / \langle R^{(o)} \rangle \quad (26)$$

where  $n\langle \rangle = \int f^{(o)}(\underline{c}) d\underline{c}$  and  $\tau_{\text{isothermal}} = \{ R_A^{(o)}, R_A^{(o)} \} / \langle (F^{(o)})^2 \rangle$ . Equation (26) is identical in form to an expression derived by Widom<sup>12</sup> for the correction to the forward rate of reaction due to the perturbation of the vibrational distribution function of a system of diatomics dilutely dispersed in a heat bath of atoms; though the interpretation of the relaxation times is different. From Eq. (26),  $\eta_{\text{isothermal}} = 0$  for  $R^{(o)} = \text{constant}$  which is in agreement with the results discussed earlier in this section. The corresponding result for the isolated system with Eqs. (II3) and II5) is

$$\eta_{\text{isolated}} = 2\tau_{\text{isolated}} \{ \langle R^{(o)2} \rangle - \langle R^{(o)} \rangle^2 - \frac{2}{3} \langle S^{(1)} R^{(o)} \rangle^2 \} \quad (27)$$

where  $\tau_{\text{isolated}} = [R_A^{(0)}, R_A^{(0)}] / \langle (F^{(0)})^2 \rangle$ .  $\eta_{\text{isolated}}$  is zero not only if  $R^{(0)}$  is a constant but also if  $R^{(0)}$  is of the form  $R^{(0)} = a + \frac{2}{3} b S^{(1)}$ ; (see Eq. (158)). Therefore  $\eta_{\text{isolated}} = 0$  for  $\beta = \pm 1$  whereas  $\eta_{\text{isothermal}} = 0$  only for  $\beta = -1$ .

The above analysis could be extended to multicomponent systems though it becomes more complicated. For the two component system  $A+B \rightarrow$  products, the fundamental difference between the isolated and isothermal systems is that in the isolated system the two nonequilibrium "systems" A and B are coupled, in some instances, predominantly through exchange of translational energy and the nonequilibrium effects are sensitive to this coupling as expressed by the values of the  $a_1^{(\gamma)}$  coefficients in the Sonine expansions; when  $A \rightarrow B$ ,  $a_1^{(\gamma)} \rightarrow 0$ . In the isothermal system, the nonequilibrium systems A and B are coupled to an equilibrium heat bath and the nonequilibrium effects in this case are due predominantly to energy exchange between the reactants and the heat bath. The  $a_1^{(\gamma)}$  coefficients express this important interaction but in this case for  $A \rightarrow B$ ,  $a_1^{(\gamma)} \neq 0$ .

The different results of  $\beta=1$  is now clear since for this case  $\eta_f = a_1^{(1)} A_1^{(1)} / A_0^{(1)} + a_1^{(2)} A_1^{(2)} / A_0^{(2)}$  in both systems and vanishes for  $A=B$  in the isolated case since  $a_1^{(\gamma)} = 0$  and is non-zero in the isothermal case since  $a_1^{(\gamma)} \neq 0$ .

Since all of the above features arise from the use of the Chapman-Enskog method of solution of the transport equations, it is of considerable interest to investigate these effects by an alternate approach as a test of the Chapman-Enskog assumptions. In a subsequent paper,<sup>13</sup> the explicit time-dependent solutions of the linearized transport equations are obtained and compared with these results.



ACKNOWLEDGMENTS

One of us (B.S.) is grateful to the National Research Council of Canada for the award of an Overseas Postdoctoral Fellowship (1968-70). The facilities of the Centraal Rekeninstituut at the Rijksuniversiteit at Leiden are appreciated. Thanks are also due to Professor P. Mazur for helpful discussions.

## APPENDIX

In this appendix we discuss the calculation of the correction to the equilibrium rate of reaction of the reactive system  $A+A \rightarrow \text{products}$ , where A is dispersed in a gas of inert atoms M not necessarily in large excess. The M-type particles are not assumed to be distributed according to a Maxwell-Boltzmann distribution function. The main purpose of the calculation is to obtain an estimate of how small  $n_A/n_M$  must be so that the heat bath is essentially unperturbed by the reaction. The Boltzmann equations for the two components are

$$\frac{\partial f_1}{\partial t} = \iint (f_1' f_1' - f_1 f) \sigma_{11} g d\Omega d\tilde{c} + \iint (f_1' f_2' - f_1 f_2) \sigma_{12} g d\Omega d\tilde{c}_2 \quad (\text{A1})$$

$$\frac{\partial f_2}{\partial t} = \iint (f_2' f_2' - f_2 f) \sigma_{22} g d\Omega d\tilde{c} + \iint (f_1' f_2' - f_1 f_2) \sigma_{12} g d\Omega d\tilde{c}_1 \quad (\text{A2})$$

where 1 and 2 denote A and M, respectively. With the formalism of II, the Chapman-Enskog equations for the perturbations  $\psi_1$  and  $\psi_2$  are

$$n_1^2 I(\psi_1) + n_1 n_2 K_{12}(\psi_1 + \psi_2) = -\frac{A_0}{n_1} f_1^{(0)} - \frac{2A_1}{3n} S_1^{(1)} f_1^{(0)} + R_1^{(0)} f_1^{(0)} \quad (\text{A3})$$

$$n_2^2 I(\psi_2) + n_1 n_2 K_{12}(\psi_1 + \psi_2) = -\frac{2A_1}{3n} S_2^{(1)} f_2^{(0)} \quad (\text{A4})$$

It is sufficient here to retain terms up to  $S_Y^{(2)}$  in the expansions of  $\psi_Y$ . Since we are primarily interested in the concentration dependence, the masses and hard-sphere diameters of the reactant and heat bath atoms are chosen equal. Taking moments of Eqs. (A3) and (A4), we obtain four equations, two of which are the same, for the four expansion coefficients. With the additional equation  $n_1 a_1^{(1)} + n_2 a_1^{(2)} = 0$  and with the homogeneous equation resulting from taking the moment of Eq. (A4) with  $S_2^{(2)}$ , we obtain

$$a_1^{(2)} = -\delta a_1^{(1)} \quad (A5)$$

$$a_2^{(2)} = \delta \left\{ \frac{15}{8} a_2^{(1)} - \frac{1}{2} a_1^{(1)} (1+\delta) \right\} / \left( \frac{31}{8} \delta + 2 \right) \quad (A6)$$

where  $\delta = n_1/n_2$ . With Eqs. (A5) and (A6) and the remaining two moment equations, one finds that

$$a_1^{(1)} = -\delta \{ 31A_1 + 4A_2 \} / 60(1+\delta)^2 \quad (A7)$$

$$a_2^{(1)} = -\delta \{ (30\delta + 16)A_2 + 4A_1 \} / 60(1+\delta)^2 \quad (A8)$$

The correction to the rate of reaction is then given by

$$\begin{aligned} \eta_f &= -(2a_1^{(1)}A_1 + 2a_2^{(1)}A_2) / A_0 \\ &= \frac{\delta}{30(1+\delta)^2 A_0} \{ 31A_1^2 + 12A_1A_2 + 16A_2^2 \} + \frac{\delta^2 A_2^2}{(1+\delta)^2 A_0} \end{aligned} \quad (A9)$$

In the limit  $\delta \rightarrow 0$ , the reactant is dilutely dispersed in a heat bath and  $\eta_f \xrightarrow{\delta \rightarrow 0} \delta(31A_1^2 + 12A_1A_2 + 16A_2^2) / 30A_0$  which is the result for the isothermal system. The other limit  $\delta \rightarrow \infty$  corresponds to the isolated system and we find that  $\eta_f \xrightarrow{\delta \rightarrow \infty} A_2^2 / A_0$ . Since the expansions converge rapidly, these results are qualitatively in agreement with those in Figs. 1a and IIIa corresponding to the  $\delta \rightarrow 0$  and the  $\delta \rightarrow \infty$  limits, respectively. The result Eq. (A9) can be used to obtain an estimate of the error introduced by assuming that the heat bath is unperturbed by reaction; i.e.,  $\eta_f$  varies linearly with  $\delta$ . From the expansion of  $\eta_f$  in  $\delta$ , the ratio of the coefficient of  $\delta^2$  to the coefficient of  $\delta$  is found to be

$$8\{4+3(\frac{A_2}{A_1})+4(\frac{A_2}{A_1})^2\}/\{31+12(\frac{A_2}{A_1})+16(\frac{A_2}{A_1})^2\}$$

For reactions with activation energy, we find that  $\delta$  must be less than  $10^{-2}$  in order that an error of only 1-2% is introduced by neglecting the perturbation of the heat bath.

The calculations by Pyun<sup>4</sup> set the  $a_1^{(1)}$  expansion coefficients equal to zero and his result is (in our notation)  $\eta_f = \delta\{(16+31\delta)/(31(1+\delta)^2)\}A_2^2/A_0$ , which has the limits  $\eta_f \xrightarrow{\delta \rightarrow 0} \delta(16/31)A_2^2/A_0$  and  $\eta_f \xrightarrow{\delta \rightarrow \infty} A_2^2/A_0$ . The agreement between the two methods for the limit  $\delta \rightarrow \infty$  is due to the fact that the  $a_1^{(1)}$  coefficients vanish in this limit (pure A). However, if the two methods were separately applied to the system  $A+B \rightarrow$  products (in a heat bath M) there would not be agreement since the  $a_1^{(\gamma)}$  ( $\gamma=A,B$ ) coefficients are non-zero even in the limit  $\delta \rightarrow \infty$ . This fact has been discussed in II where it was shown that the  $a_1^{(\gamma)}$  ( $\gamma=A,B$ ) terms (for the isolated system  $\delta \rightarrow \infty$ ) depend on the mass density difference  $\rho_A - \rho_B$ , so that significant differences can result between the present model ( $a_1^{(\gamma)} \neq 0$ ) and calculations with  $a_1^{(\gamma)} = 0$ .

REFERENCES

- † Supported in part by a contract with the U. S. Atomic Energy Commission.
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1. B. Shizgal and M. Karplus, J. Chem. Phys. 52, 4262 (1970); henceforth referred to as I; equations quoted from this paper are preceded by I.
  2. B. Shizgal and M. Karplus, J. Chem. Phys. (in press; preceding paper; henceforth referred to as II; equations quoted from this paper are preceded by II).
  3. C. W. Pyun and J. Ross, J. Chem. Phys. 40, 2572 (1964).
  4. C. W. Pyun, J. Chem. Phys. 48, 1306 (1968); ibid, 50, 2782 (1969).
  5. Quantities defined in I and II have the same definition in this paper.
  6. A. A. Westenbergh and N. deHaas, J. Chem. Phys. 48, 4405 (1968).
  7. J. H. Sullivan, J. Chem. Phys. 46, 73 (1967); 51, 2288 (1969).
  8. D. R. Bates and J. T. Lewis, Proc. Phys. Soc. (London) A68, 173 (1959).
  9. The calculations in the appendix indicate how large an excess of heat bath particles is required for the heat bath to remain unperturbed by reaction.
  10. R. N. Porter and L. M. Raff (private communication); K. Morokuma, G. W. Koepl and M. Karplus (unpublished calculation).
  11. F. Reif, Fundamentals of Statistical Mechanics and Thermal Physics (McGraw Hill, New York, 1965).
  12. B. Widom, J. Chem. Phys. 34, 2050 (1961).
  13. B. Shizgal (in preparation).

FIGURE CAPTIONS

Fig. 1: Variation of  $\eta^{(1)}$  versus  $\epsilon^*/kT$  as a function of the mass ratio of the heat bath particle and the reactant mass;  $M/m$  equal to (a) 1.0 (b) 2.0 (c) 4.0 and (d) 8.0;  $m=m_1=m_2$ ; all other unspecified quantities are equal to unity.

Fig. 2: Variation of  $\eta^{(\gamma)}$  versus  $\epsilon^*/kT$  as a function of the mass ratio of the reactants;  $m_2=1$  and  $m_1/m_2$  equal to (a) 1.25 (b) 2.0 and (c) 4.0; all the other system variables are equal to 1; —  $\eta^{(2)}$ , ----  $\eta^{(1)}$ , .....  $\eta^{(1)}=\eta^{(2)}$  for  $m_1=m_2$ .

Fig. 3: Variation of  $\eta^{(\gamma)}$  with  $\beta$  as a function of the mass ratio of the reactants;  $m_2=1$  and  $m_1/m_2$  equal to (a) 2.0 and (b) 4.0; all the other systems variables are equal to 1; —  $\eta^{(2)}$ , ----  $\eta^{(1)}$ , .....  $\eta^{(1)}=\eta^{(2)}$  for  $m_1=m_2$ .

Table 1. Nonequilibrium Effects in Some Gas Phase Reactions

Heat Bath	T(°K)	Reaction	Nonequilibrium Rate Coefficients
He	500	$H_2 + Cl = HCl + H^a$	$\eta_f = (.79 \times 10^{-3} n_{Cl} + 10^{-5} n_{H_2}) G_f / n_{He}$ $\eta_r = (.24 \times 10^{-5} n_H + .19 \times 10^{-2} n_{HCl}) G_r / n_{He}$
Ar			$\eta_f = (.35 \times 10^{-2} n_{Cl} + .57 \times 10^{-5} n_{H_2}) G_f / n_{Ar}$ $\eta_r = (.14 \times 10^{-5} n_H + .95 \times 10^{-2} n_{HCl}) G_r / n_{Ar}$
He	4000	$H_2 + I_2 = HI + HI^b$	$\eta_f = (.14 \times 10^{-1} n_{H_2} + .45 \times 10^{-5} n_{I_2}) G_f / n_{He}$ $\eta_r = .51 \times 10^{-2} n_{HI} G_r / n_{He}$
Ar			$\eta_f = (.58 \times 10^{-1} n_{H_2} + .14 \times 10^{-5} n_{I_2}) G_f / n_{Ar}$ $\eta_r = .20 \times 10^{-2} n_{HI} G_r / n_{Ar}$
H <sub>2</sub>	100	$H^+ + H^- \rightarrow H_2^c$	$\eta_f = 20.49 (n_{H^+} + n_{H^-}) / n_{H_2}$
Ar			$\eta_f = 251 (n_{H^+} + n_{H^-}) / n_{Ar}$

<sup>a,b</sup> See footnotes, Table II 4.

<sup>c</sup> The theoretical rate constants of ref. 8 were fitted to the model reactive cross section  $\sigma_t^*(g) = \pi d_R^2 \{1 + (2kT/\mu g^2)\alpha\}$  from 250°K-8000°K;  $d_R$  and  $\alpha(T)$  were found to be equal to  $23 \times 10^{-6}$  cm and  $73/T$ , respectively;  $d_E$  was assigned the value of  $4 \times 10^{-8}$  cm; see footnote d of Table XI in I.