

## Application of the generalized Chapman-Enskog method to the transport-coefficient calculation in a reacting gas mixture

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In this paper we investigate the calculation of the kinetic coefficients for a nonequilibrium mixture of chemically reacting gases. This study is based on the generalized Chapman-Enskog method (GCEM) proposed by Alexeev. An alternative method for the resolution of the basic linearized integral equations of the GCEM is developed in this paper. The algorithm of this method is adjusted to include triple inelastic collisions and the resolution method of the integral equation with non-self-adjoint operator was found to be the most effective for practical use. Some issues and examples of calculation are discussed.

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### I. INTRODUCTION

Transport processes in gas mixtures with chemical reactions is one of the most studied problems of the modern kinetic theory of gases. Chemically reacting-flow studies are necessary for a deep understanding of plasma chemistry, atmosphere physics, laser physics, chemical technology, and other fields. It should be noted that the problem of reacting-flow investigation is related inseparably to the problem of the transport coefficient calculations. In the past the processes in nonequilibrium gas mixtures were considered from two points of view. First, from a "chemical" point of view (since 1949, Prigogine *et al.* [1,2]) the aim of these investigations was to find the perturbation of the Maxwellian distribution function in nonequilibrium systems and therefore to construct "non-Arrhenius" chemical kinetics. Second, from a "physical" point of view (mainly the initiative papers of Wang-Chang, Uhlenbeck, and de Boer [3,4]) it was connected with calculations of the transport processes in polyatomic gases. Later it was understood [6] that these two directions of investigation had to be unified in the frame of a universal theory (see also [7]). The history of the different studies before 1982 is given in detail in Ref. [7]. As a rule all the investigations were based on different variants of the Chapman-Enskog method (CEM); in our opinion this method is more thoroughly developed than the others, e.g., the moment method.

The well-known idea of Enskog is that near the state of local thermodynamic equilibrium all the time derivatives in the linearized Boltzmann equation should be excluded using the hydrodynamic equations and therefore only an implicit dependence on time exists for the transport coefficients. The second proposition consists in the fact that the time derivatives  $\partial n_\alpha / \partial t$ ,  $\partial \mathbf{v}_0 / \partial t$ ,  $\partial T / \partial t$  [where  $n_\alpha, \mathbf{v}_0, T$  are concentration of species  $\alpha$  ( $\alpha=1, \dots, \mu$ ), mean hydrodynamic velocity, and temperature, respectively] as well as the distribution function  $f_\alpha$  can be performed as a power series of the Knudsen number. These two propositions must be considered in any modification or generalization of the Chapman-Enskog method.

When the energy threshold of various conversions (excitation, chemical reactions, ionization) in a moving gas is of the order of the thermal particle energy, then it is necessary to take into account the great number of inelastic processes. In early generalizations of the CEM for chemically reacting systems only two limit cases were considered [1–6]: the cases of "slow" and "fast" inelastic processes. But obviously even in the same chemical reacting flow the physical system may undergo several qualitatively physical states, so the transport coefficients should be calculated in the frame of a unified theory valid through all these states.

The derivation of the linearized Boltzmann equation valid over all the cases mentioned above was considered for the first time by Alexeev [8]. In Ref. [8] and the following papers [9–11], the basic linearized Boltzmann equation for reacting gases and the corresponding resolution method (titled by Alexeev as generalized CEM) were proposed. This integral equation can be considered as an "interpolating" equation for all the limit cases in kinetic theory. The basic equation of the generalized CEM (in the following  $A$  equation) has a complicated form because it contains a non-self-adjoint operator. Multiple methods of solution of the  $A$  equation were proposed; however, this equation remains the starting point of all variants of the generalized Chapman-Enskog method (GCEM) [12–22].

### II. THE $A$ EQUATION AND GENERALIZED CHAPMAN-ENSKOG METHOD

Let us consider the main ideas of the generalized Chapman-Enskog method for chemically reacting gas mixture with bimolecular reactions

$$A_\alpha + A_{\beta \rightleftharpoons \gamma} A_\gamma + A_\delta, \quad (1)$$

triple collisions will be considered later. The Boltzmann equation for such a system can be expressed as follows:

$$\frac{Df_\alpha}{Dt} = \sum_{i,j} I_{\alpha j}(f, f) + \frac{1}{2} \sum_r \sum_{\beta, \gamma, \delta} {}^r I_{\alpha \beta}^{\gamma \delta}(f, f), \quad (2)$$

where  $I_{\alpha j}$  and  $I_{\alpha\beta}^{\gamma\delta}(f, f)$  are the integral collision terms corresponding to elastic and inelastic processes respectively. For example [7],

$$I_{\alpha\beta}^{\gamma\delta}(f, f) = \int [\xi_{\alpha\beta}^{\gamma\delta} f_{\gamma}^{\prime} f_{\delta}^{\prime} - f_{\alpha} f_{\beta}] g_{\alpha\beta} d(\sigma_{\alpha\beta}^{\gamma\delta}) d\mathbf{v}_{\beta}, \quad (3)$$

$$\frac{D}{Dt} \equiv \frac{\partial}{\partial t} + \mathbf{v}_{\alpha} \cdot \frac{\partial}{\partial \mathbf{r}} + \mathbf{F}_{\alpha} \cdot \frac{\partial}{\partial \mathbf{v}_{\alpha}}.$$

In Eq. (3)

$$\xi_{\alpha\beta}^{\gamma\delta} = \frac{s_{\alpha} s_{\beta}}{s_{\gamma} s_{\delta}} \left[ \frac{m_{\alpha} m_{\beta}}{m_{\gamma} m_{\delta}} \right]^3 \quad (4)$$

and  $s_i$  is the statistical weight for energetic states of particles of the  $i$  species,  $g_{\alpha\beta}$  is the relative velocity of  $\alpha$  and  $\beta$  particles, and  $\sigma_{\alpha\beta}^{\gamma\delta}$  is the collision cross section for inelastic process (1). The elastic collision integral in Eq. (2) is a particular case of the relation (3); we should only write  $\gamma = \alpha, \beta = \delta = j$  and,  $d\sigma_{\alpha j}$  instead of  $d(\sigma_{\alpha\beta}^{\gamma\delta})$ .

We first built the basic equation of the generalized Chapman-Enskog method using the physical considerations given in the first paper of this branch in the transport theory [8]. Following this paper, we consider the Boltzmann equation in the dimensionless form

$$\frac{D\tilde{f}_{\alpha}^{\text{eff}}}{Dt} = \frac{1}{\text{Kn}_{\text{el}}} \tilde{I}_{\text{el}} + \frac{1}{\text{Kn}_r} \tilde{I}_r, \quad (5)$$

where  $\tilde{I}_{\text{el}}$  and  $\tilde{I}_r$  are the integral collision terms for elastic and inelastic collisions, respectively. For simplicity we consider the reacting system with only one characteristic

$$\begin{aligned} \frac{Df_{\alpha}^{(0)}}{Dt} - \frac{1}{2} \sum_r \sum_{\beta, \gamma, \delta} \int [\xi_{\alpha\beta}^{\gamma\delta} f_{\gamma}^{(0)'} f_{\delta}^{(0)'} - f_{\alpha}^{(0)} f_{\beta}^{(0)}] g_{\alpha\beta} d(\sigma_{\alpha\beta}^{\gamma\delta}) d\mathbf{v}_{\beta} \\ = \sum_j \int [h'_{\alpha} + h'_j - h_{\alpha} - h_j] f_{\alpha}^{(0)} f_{\beta}^{(0)} g_{\alpha j} d\sigma_{\alpha j}^{\alpha j} d\mathbf{v}_j \\ + \frac{1}{2} \sum_r \sum_{\beta, \gamma, \delta} \int [\xi_{\alpha\beta}^{\gamma\delta} f_{\gamma}^{(0)'} f_{\delta}^{(0)'} (h'_{\gamma} + h'_{\delta}) - f_{\alpha}^{(0)} f_{\beta}^{(0)} (h_{\alpha} + h_{\beta})] g_{\alpha\beta} d(\sigma_{\alpha\beta}^{\gamma\delta}) d\mathbf{v}_{\beta}, \end{aligned} \quad (8)$$

where for the first-order approximation

$$f_{\alpha} = f_{\alpha}^{(0)} (1 + h_{\alpha}).$$

In this form, the  $A$  equation was written by Alexeev [8]. It is the basis in all the applications and modifications of the theory devoted to the generalized Chapman-Enskog method in the scientific literature.

Let us consider now the well-known particular cases in the kinetic theory of reacting gases.

(i) In the case pointed out in [7] as the Prigogine one and corresponding to “slow” reactions the last term on the right-hand side of Eq. (8) is very small and therefore we have

“inelastic” Knudsen number  $\text{Kn}_r$ . We suppose that it is much greater than the “elastic” Knudsen number  $\text{Kn}_{\text{el}}$ ,  $\text{Kn}_r \gg \text{Kn}_{\text{el}}$ . Therefore the distribution function could be expanded in the series

$$f_{\alpha} = \sum_{k=0}^{\infty} \text{Kn}_{\text{el}}^k f_{\alpha}^{(k)}. \quad (6)$$

Substituting the expansion (6) into Eq. (5) we have as usual for the zeroth approximation

$$\tilde{I}_{\text{el}}^{(0)} = 0,$$

which leads to the Maxwellian function  $f_{\alpha}^{(0)}$  and in a common case for the first approximation

$$\frac{Df_{\alpha}^{(0)}}{D\tilde{t}} + \text{Kn}_{\text{el}} \frac{Df_{\alpha}^{(1)}}{D\tilde{t}} = \tilde{I}_{\text{el}}^{(1)} + \frac{1}{\text{Kn}_r} \tilde{I}_r^{(0)} + \frac{\text{Kn}_{\text{el}}}{\text{Kn}_r} \tilde{I}_r^{(1)}. \quad (7)$$

This equation has multiple interesting features. Formally the last terms in both the left- and right-hand sides of Eq. (7) should be neglected because  $\text{Kn}_{\text{el}}$  is a small parameter. In the left-hand side the term  $\text{Kn}_{\text{el}} (Df_{\alpha}^{(1)}/D\tilde{t})$  is proportional to  $\text{Kn}_{\text{el}}$  only, but the term  $(\text{Kn}_{\text{el}}/\text{Kn}_r) \tilde{I}_r^{(1)}$  is proportional to  $\text{Kn}_{\text{el}}/\text{Kn}_r$ . Therefore with increasing the inelastic collision process this term could be of the same order than  $\tilde{I}_{\text{el}}^{(1)}$ . On the other hand, this term leaves all considerations in the limit of the first approximation and in the case of small value  $\text{Kn}_{\text{el}}/\text{Kn}_r$  cannot spoil the first approximation as the out of order term.

Therefore we have in the dimensional form

$$\begin{aligned} \frac{Df_{\alpha}^{(0)}}{Dt} - \frac{1}{2} \sum_r \sum_{\beta, \gamma, \delta} \int [\xi_{\alpha\beta}^{\gamma\delta} f_{\gamma}^{(0)'} f_{\delta}^{(0)'} - f_{\alpha}^{(0)} f_{\beta}^{(0)}] \\ \times g_{\alpha\beta} d(\sigma_{\alpha\beta}^{\gamma\delta}) d\mathbf{v}_{\beta} \\ = \frac{1}{2} \sum_j \int [h'_{\alpha} + h'_j - h_{\alpha} - h_j] f_{\alpha}^{(0)} f_j^{(0)} g_{\alpha j} d\sigma_{\alpha j}^{\alpha j} d\mathbf{v}_j. \end{aligned}$$

We should remind the reader that in 1949 Prigogine had formulated the well-known problem of definition of the perturbation of the Maxwellian distribution function in the reaction  $A + A$ , giving the reaction products for a hypothetical case where all the formed molecules leave the physical system immediately. In the past this hypothetical reaction was considered in chemistry as an upper limit of possible perturbations, which could be realized in

any chemical reacting system. Incidentally this opinion was wrong; an exhaustive solution of Prigogine's problem is developed in [7].

(ii) In the case of "fast" reactions in the system near the chemical equilibrium [6] we have

$$\xi f_{\gamma}^{(0)'} f_{\delta}^{(0)'} = f_{\alpha}^{(0)} f_{\beta}^{(0)}$$

and therefore from Eq. (8)

$$\begin{aligned} \frac{Df_{\alpha}^{(0)}}{Dt} = & \sum_j \int [h'_{\alpha} + h'_j - h_{\alpha} - h_j] f_{\alpha}^{(0)} f_j^{(0)} g_{\alpha j} d\sigma_{\alpha j}^{\alpha j} d\mathbf{v}_j \\ & + \frac{1}{2} \sum_r \sum_{\beta, \gamma, \delta} \int [h'_{\gamma} + h'_{\delta} - h_{\alpha} - h_{\beta}] \\ & \times f_{\alpha}^{(0)} f_{\beta}^{(0)} g_{\alpha\beta} d(\sigma_{\alpha\beta}^{\gamma\delta}) d\mathbf{v}_{\beta}. \end{aligned}$$

(iii) In the case of "very fast" reactions in the mixture of reacting gases  $\text{Kn}_r \ll \text{Kn}_{el}$ ,

$$\begin{aligned} \frac{Df_{\alpha}^{(0)}}{Dt} = & \frac{1}{2} \sum_r \sum_{\beta, \gamma, \delta} \int [h'_{\gamma} + h'_{\delta} - h_{\alpha} - h_{\beta}] \\ & \times f_{\alpha}^{(0)} f_{\beta}^{(0)} g_{\alpha\beta}^d(\sigma_{\alpha\beta}^{\gamma\delta}) d\mathbf{v}_{\beta}. \end{aligned}$$

Therefore for different limit cases in kinetic theory of gases we obtain from  $A$  equation the exact integral equations. We can state now that the  $A$  equation should be considered as an interpolating equation in kinetic theory of gases. This equation should be applied for the calculation of transport processes in gases if it is possible to use the Maxwellian distribution as the main term in the expansion of the distribution functions in the mixture of reacting gases. Thus we do not have to consider any particular limit case in the kinetic theory of reacting gases and make any assumption for a procedure of interpolating the solutions of linearized equations corresponding to limit cases. It is of course an impossible task.

In the following, we built a strict formal theory of the GCEM and the method of resolution of the  $A$  equation for any order of approximation. The dimensionless form of the Boltzmann equation will be considered and the characteristic scales are  $\bar{n}_{\alpha}$  for the concentration of  $\alpha$  species and  $\bar{c}_{\alpha}$  for the mean velocity of  $\alpha$  molecules. The distribution function scale is  $\bar{n}_{\alpha}/\bar{c}_{\alpha}^3$ . Introducing the notations  $\bar{g}_{\alpha\beta}$  and  $d_{\alpha\beta}^2$  for the characteristic values of the relative velocity and the collision cross section, the microscopic reversibility principle

$$\xi \bar{g}_{\alpha\beta}^{\gamma\delta} g_{\alpha\beta} d(\sigma_{\alpha\beta}^{\gamma\delta}) d\mathbf{v}_{\alpha} d\mathbf{v}_{\beta} = g'_{\gamma\delta} d(\sigma_{\gamma\delta}^{\alpha\beta}) d\mathbf{v}'_{\gamma} d\mathbf{v}'_{\delta}. \quad (9)$$

We obtain the estimation

$$\xi \bar{g}_{\alpha\beta}^{\gamma\delta} \bar{g}_{\alpha\beta} (d_{\alpha\beta}^2) \bar{c}_{\alpha}^3 \bar{c}_{\beta}^3 \sim \bar{g}_{\gamma\delta} (d_{\gamma\delta}^2) \bar{c}_{\gamma}^3 \bar{c}_{\delta}^3 \quad (10)$$

and using this relation, the collisional integral can be written as follows:

$$I_{\alpha\beta}^{\gamma\delta}(f, f) = \frac{1}{\bar{c}_{\alpha}^3} [{}^r\bar{N}_{\gamma\delta} {}^r\bar{J}_{\gamma\delta}^{\alpha\beta} - {}^r\bar{N}_{\alpha\beta} {}^r\bar{J}_{\alpha\beta}^{\gamma\delta}], \quad (11)$$

where

$${}^r\bar{J}_{\alpha\beta}^{\gamma\delta} = \int \tilde{f}_{\alpha} \tilde{f}_{\beta} d(\sigma_{\alpha\beta}^{\gamma\delta}) d\mathbf{v}_{\beta} \quad (12)$$

and the tilde indicates the dimensionless value. In Eq. (11) the term

$${}^r\bar{N}_{\alpha\beta} = \bar{n}_{\alpha} \bar{n}_{\beta} g_{\alpha\beta} d_{\alpha\beta}^2 \quad (13)$$

is the characteristic number of collisions per unit volume and unit time. It is convenient to take  $L$  as the macroscopic length,  $\tau_L$  as the hydrodynamical time, and  $\bar{F}_{\alpha}$  as the characteristic external force. We also introduce the following notations:

$$C = \max_{\{\alpha\}} \bar{c}_{\alpha}, \quad \bar{N} = \sum_{\alpha} \bar{n}_{\alpha}. \quad (14)$$

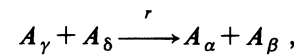
The left-hand side of the kinetic equation (2) can be written

$$\begin{aligned} \frac{D\tilde{f}_{\alpha}}{D\tilde{t}} = & \bar{n}_{\alpha} \frac{C}{L} \left[ \frac{L}{C\tau_L} \frac{\partial \tilde{f}_{\alpha}}{\partial \tilde{t}} + \frac{\bar{c}_{\alpha}}{C} \mathbf{v}_{\alpha} \cdot \frac{\partial \tilde{f}_{\alpha}}{\partial \tilde{\mathbf{r}}} \right. \\ & \left. + \frac{L\bar{F}_{\alpha}}{\bar{c}_{\alpha}^2} \frac{\bar{c}_{\alpha}}{C} \tilde{\mathbf{F}}_{\alpha} \cdot \frac{\partial \tilde{f}_{\alpha}}{\partial \mathbf{v}_{\alpha}} \right] \frac{1}{\bar{c}_{\alpha}^3} \quad (15) \end{aligned}$$

and thus the dimensionless form of the kinetic equation (2) is expressed as follows:

$$\begin{aligned} \frac{\bar{n}_{\alpha}}{\bar{N}} \left[ \frac{L}{C\tau_L} \frac{\partial \tilde{f}_{\alpha}}{\partial \tilde{t}} + \frac{c_{\alpha}}{C} \mathbf{v}_{\alpha} \cdot \frac{\partial \tilde{f}_{\alpha}}{\partial \tilde{\mathbf{r}}} + \frac{L\bar{F}_{\alpha}}{\bar{c}_{\alpha}^2} \frac{c_{\alpha}}{C} \tilde{\mathbf{F}}_{\alpha} \cdot \frac{\partial \tilde{f}_{\alpha}}{\partial \mathbf{v}_{\alpha}} \right] \\ = \frac{L}{C\bar{N}} \sum_{j=1}^{\mu} \bar{N}_{\alpha j} \tilde{I}_{\alpha j} \\ + \frac{1}{2} \sum_r \sum_{\beta, \gamma, \delta} \left[ \frac{L}{C\bar{N}} {}^r\bar{N}_{\gamma\delta} {}^r\bar{J}_{\gamma\delta}^{\alpha\beta} - \frac{L}{C\bar{N}} {}^r\bar{N}_{\alpha\beta} {}^r\bar{J}_{\alpha\beta}^{\gamma\delta} \right], \quad (16) \end{aligned}$$

where  ${}^r\bar{N}_{\gamma\delta}/\bar{N}$  is the characteristic number of collisions in the reaction



calculated on one particle of the mixture and the inverse value has the order of the free mean time between collisions and  $C\bar{N}/{}^r\bar{N}_{\gamma\delta}$  is the mean free path. As a result we obtain

$${}^r\bar{N}_{\gamma\delta} \frac{L}{C\bar{N}} = \frac{1}{\text{Kn}_{\gamma\delta}}, \quad (17)$$

where  $\text{Kn}_{\gamma\delta}$  is the Knudsen number for the above reactive collision type. We notice that

$$\frac{\bar{c}_{\alpha}}{C} \leq 1, \quad \frac{\bar{n}_{\alpha}}{\bar{N}} \leq 1. \quad (18)$$

The external force  $\mathbf{F}_{\alpha}$  should not be too strong

$$\frac{L\bar{F}_{\alpha}}{\bar{c}_{\alpha}^2} \leq 1. \quad (19)$$

Taking into account that  $L \sim C\tau_L$  we find that the left-hand side of Eq. (16) is of the first order. The hydrodynamic description is possible if for each  $\alpha$  species we can find as a minimum one type of the collision for which

$\text{Kn}_{\alpha\beta} \ll 1$ . Equation (16) can be written in the form

$$\frac{D\tilde{f}_\alpha}{D\tilde{t}} = \frac{1}{2} \sum_r \sum_{\beta, \gamma, \delta} \left\{ \frac{1}{\text{Kn}_{\gamma\delta}^{\alpha\beta}} r \tilde{f}_{\gamma\delta}^{\alpha\beta} - \frac{1}{\text{Kn}_{\alpha\beta}^{\gamma\delta}} r \tilde{f}_{\alpha\beta}^{\gamma\delta} \right\}. \quad (20)$$

In Eq. (20) the elastic collision integral is considered as a particular case of the inelastic one. As usual the factor  $\frac{1}{2}$  is introduced to eliminate the necessary terms in the sum by formal mutual interchanging of two indices  $\gamma$  and  $\delta$ .

Let us consider the following:

$$\text{Kn}_\alpha = \min_{\{r, \beta, \gamma, \delta\}} \text{Kn}_{\alpha\beta}^{\gamma\delta}, \quad (21)$$

$$\text{Kn} = \max_{\{\alpha\}} \text{Kn}_\alpha, \quad (22)$$

and rewrite Eq. (20):

$$\frac{\text{Kn}_\alpha}{\text{Kn}} \frac{D\tilde{f}_\alpha}{D\tilde{t}} = \frac{1}{\text{Kn}} \frac{1}{2} \sum_r \sum_{\beta, \gamma, \delta} \frac{\text{Kn}_\alpha}{\text{Kn}_{\alpha\beta}^{\gamma\delta}} \left[ \frac{\text{Kn}_{\alpha\beta}^{\gamma\delta}}{\text{Kn}_{\alpha\beta}^{\gamma\delta}} r \tilde{f}_{\gamma\delta}^{\alpha\beta} - r \tilde{f}_{\alpha\beta}^{\gamma\delta} \right]. \quad (23)$$

The relations (21) and (22) lead to the affirmations that

$$\frac{\text{Kn}_k}{\text{Kn}} \leq 1, \quad \frac{\text{Kn}_\alpha}{\text{Kn}} \sim O(1), \quad (24)$$

$$\frac{\text{Kn}_\alpha}{\text{Kn}_{\alpha\beta}^{\gamma\delta}} \leq 1. \quad (25)$$

Therefore we can estimate the value

$$\frac{\text{Kn}_{\alpha\beta}^{\gamma\delta}}{\text{Kn}_{\gamma\delta}^{\alpha\beta}} r \tilde{f}_{\gamma\delta}^{\alpha\beta} - r \tilde{f}_{\alpha\beta}^{\gamma\delta} = O(\text{Kn}). \quad (26)$$

Let us assume now that for each  $\alpha$  species, there exists  $\text{Kn}_\alpha \ll 1$ ; in this case of course  $\text{Kn} \ll 1$ . We can separate all collisional processes in two kinds: “fast” processes (for which  $\text{Kn}_{\alpha\beta}^{\gamma\delta} < \text{Kn}$ ) and “slow” processes.

Now we can introduce the usual preposition of the Chapman-Enskog method connected with performance of the distribution function  $f_\alpha$  as power series in  $\text{Kn}$ :

$$f_\alpha = \sum_{k=0}^{\infty} \text{Kn}^k \tilde{f}_\alpha^{(k)}. \quad (27)$$

Expanding the collisional integral  $I_{\alpha\beta}^{\gamma\delta}$ , we find

$$I_{\alpha\beta}^{\gamma\delta}(\tilde{f}, \tilde{f}) = \sum_{k=0}^{\infty} \text{Kn}^k \sum_{m=0}^k I_{\alpha\beta}^{\gamma\delta}(\tilde{f}^{(m)}, \tilde{f}^{(k-m)}), \quad (28)$$

where

$$\begin{aligned} I_{\alpha\beta}^{\gamma\delta}(\tilde{f}, \tilde{g}) = & \frac{1}{2} \int \left[ \frac{1}{\text{Kn}_{\alpha\beta}^{\gamma\delta}} \xi_{\alpha\beta}^{\gamma\delta} (\tilde{f}'_\gamma \tilde{g}'_\delta + \tilde{f}'_\delta \tilde{g}'_\gamma) \right. \\ & \left. - (\tilde{f}_\alpha \tilde{g}_\beta + \tilde{f}_\beta \tilde{g}_\alpha) \frac{1}{\text{Kn}_{\alpha\beta}^{\gamma\delta}} \right] \\ & \times \tilde{g}_{\alpha\beta} d(\tilde{\sigma}_{\alpha\beta}^{\gamma\delta}) d\tilde{\mathbf{v}}_\beta. \end{aligned} \quad (29)$$

Substituting the relation (28) into (23), we obtain

$$\begin{aligned} \frac{\text{Kn}_\alpha}{\text{Kn}} \frac{D\tilde{f}_\alpha}{Dt} - \frac{1}{\text{Kn}} \frac{1}{2} \sum_r \sum_{\beta, \gamma, \delta} \frac{\text{Kn}_\alpha}{\text{Kn}_{\alpha\beta}^{\gamma\delta}} \int & \left[ \frac{\text{Kn}_{\alpha\beta}^{\gamma\delta}}{\text{Kn}_{\alpha\beta}^{\gamma\delta}} \xi_{\alpha\beta}^{\gamma\delta} \tilde{f}_\gamma^{(0)} \tilde{f}_\delta^{(0)} - \tilde{f}_\alpha^{(0)} \tilde{f}_\beta^{(0)} \right] \tilde{g}_{\alpha\beta} d(\tilde{\sigma}_{\alpha\beta}^{\gamma\delta}) d\tilde{\mathbf{v}}_\beta \\ = & \frac{1}{2} \sum_{k=1}^{\infty} \text{Kn}^{k-1} \sum_{m=0}^k \sum_r \sum_{\beta, \gamma, \delta} \frac{\text{Kn}_\alpha}{\text{Kn}_{\alpha\beta}^{\gamma\delta}} \int \left[ \frac{\text{Kn}_{\alpha\beta}^{\gamma\delta}}{\text{Kn}_{\alpha\beta}^{\gamma\delta}} \xi_{\alpha\beta}^{\gamma\delta} (\tilde{f}_\gamma^{(m)} \tilde{f}_\delta^{(k-m)} + \tilde{f}_\gamma^{(k-m)} \tilde{f}_\delta^{(m)}) \right. \\ & \left. - (\tilde{f}_\alpha^{(m)} \tilde{f}_\beta^{(k-m)} - \tilde{f}_\alpha^{(k-m)} \tilde{f}_\beta^{(m)}) \right] \tilde{g}_{\alpha\beta} d(\tilde{\sigma}_{\alpha\beta}^{\gamma\delta}) d\tilde{\mathbf{v}}_\beta. \end{aligned} \quad (30)$$

Now we transform the left-hand side of Eq. (30). The distribution function can be written as an explicit function of the velocity and a hydrodynamic parameter  $\tilde{\Gamma}$ :

$$\tilde{f}_\alpha(\tilde{\mathbf{r}}, \tilde{\mathbf{v}}, \tilde{t}) = \tilde{f}_\alpha(\tilde{\mathbf{v}}_\alpha | \tilde{\Gamma}, \tilde{\nabla} \tilde{\Gamma}, \dots, \tilde{\nabla}^{(s)} \tilde{\Gamma}, \dots), \quad (31)$$

where  $\tilde{\nabla}^{(s)}$  denotes the dimensionless space gradient of  $s$  order. As usual in the CEM on the hydrodynamic stage of evolution we assume that

$$\frac{\partial}{\partial \tilde{t}} \tilde{\Gamma}(\tilde{\mathbf{r}}, \tilde{t}) = \tilde{\Phi}(\tilde{\Gamma}, \tilde{\nabla} \tilde{\Gamma}, \dots, \tilde{\nabla}^{(s)} \tilde{\Gamma}, \dots) \quad (32)$$

and

$$\Phi = \sum_{k=0}^{\infty} \text{Kn}^k \tilde{\Phi}^{(k)}. \quad (33)$$

The expression  $D\tilde{f}_\alpha/D\tilde{t}$  on the left-hand of Eq. (30) can be expanded in a power series of  $\text{Kn}$  and initially the time derivative  $\partial \tilde{f}_\alpha / \partial \tilde{t}$  is transformed as follows:

$$\begin{aligned}
\frac{\partial \tilde{f}_\alpha}{\partial \tilde{t}} &= \sum_{s=0}^{\infty} \frac{\partial \tilde{f}_\alpha}{\partial (\tilde{\nabla}^{(s)} \tilde{\Gamma})} : \frac{\partial}{\partial \tilde{t}} \tilde{\nabla}^{(s)} \tilde{\Gamma} = \sum_{s=0}^{\infty} \frac{\partial \tilde{f}_\alpha}{\partial (\tilde{\nabla}^{(s)} \tilde{\Gamma})} : \tilde{\nabla}^{(s)} \frac{\partial \tilde{\Gamma}}{\partial \tilde{t}} = \sum_{s=0}^{\infty} \frac{\partial \tilde{f}_\alpha}{\partial (\tilde{\nabla}^{(s)} \tilde{\Gamma})} : \tilde{\nabla}^{(s)} \tilde{\Phi} \\
&= \sum_{s=0}^{\infty} \left[ \sum_{l=0}^{\infty} \text{Kn}^l \frac{\partial \tilde{f}_\alpha^{(l)}}{\partial (\tilde{\nabla}^{(s)} \tilde{\Gamma})} \right] : \sum_{m=0}^{\infty} \text{Kn}^m \tilde{\nabla}^{(s)} \tilde{\Phi}^{(m)} = \sum_{s=0}^{\infty} \sum_{l,m=0}^{\infty} \text{Kn}^{l+m} \frac{\partial \tilde{f}_\alpha^{(l)}}{\partial (\tilde{\nabla}^{(s)} \tilde{\Gamma})} : \tilde{\nabla}^{(s)} \tilde{\Phi}^{(m)} \\
&= \sum_{s=0}^{\infty} \sum_{k=0}^{\infty} \sum_{l=0}^k \text{Kn}^k \frac{\partial \tilde{f}_\alpha^{(l)}}{\partial (\tilde{\nabla}^{(s)} \tilde{\Gamma})} : \tilde{\nabla}^{(s)} \tilde{\Phi}^{(k-l)} = \sum_{k=0}^{\infty} \text{Kn}^k \sum_{l=0}^k \left\{ \sum_{s=0}^{\infty} \tilde{\nabla}^{(s)} \tilde{\Phi}^{(k-l)} : \frac{\partial \tilde{f}_\alpha^{(l)}}{\partial (\tilde{\nabla}^{(s)} \tilde{\Gamma})} \right\}. \quad (34)
\end{aligned}$$

The colon denotes the scalar product of the corresponding vectors or tensors. Introducing the operator

$$\frac{\partial_i}{\partial \tilde{t}} = \sum_{s=0}^{\infty} \tilde{\nabla}^{(s)} \tilde{\Phi}^{(i)} : \frac{\partial}{\partial (\tilde{\nabla}^{(s)} \tilde{\Gamma})}, \quad (35)$$

the time derivative of the distribution function expresses as

$$\frac{\partial \tilde{f}_\alpha}{\partial \tilde{t}} = \sum_{k=0}^{\infty} \text{Kn}^k \sum_{l=0}^k \frac{\partial_{k-l} \tilde{f}_\alpha^{(l)}}{\partial \tilde{t}}, \quad (36)$$

where

$$\frac{\partial_{k-l} \tilde{f}_\alpha^{(l)}}{\partial \tilde{t}} = \sum_{s=0}^{\infty} \tilde{\nabla}^{(s)} \tilde{\Phi}^{(k-l)} : \frac{\partial \tilde{f}_\alpha^{(l)}}{\partial (\tilde{\nabla}^{(s)} \tilde{\Gamma})}, \quad (37)$$

and using Eqs. (27) and (37) we obtain

$$\frac{D \tilde{f}_\alpha}{D \tilde{t}} = \sum_{k=0}^{\infty} \text{Kn}^k \frac{D_k \tilde{f}_\alpha}{D \tilde{t}} \quad (38)$$

and the dimensional form of the derivative  $D_k \tilde{f}_\alpha / D \tilde{t}$  can be written as

$$f_\alpha^{(0)} \mathcal{L}_\alpha[h] = \frac{1}{2} \sum_{\beta, \gamma, \delta} \int [\xi_{\alpha\beta}^{\gamma\delta} f_\gamma^{(0)'} f_\delta^{(0)'} (h'_\gamma + h'_\delta) - f_\alpha^{(0)} f_\beta^{(0)} (h_\alpha + h_\beta)] g_{\alpha\beta} d(r\sigma_{\alpha\beta}^{\gamma\delta}) d\mathbf{v}_\beta,$$

$$f_\alpha^{(0)} \mathcal{P}_\alpha^{(k-1)} = \frac{1}{2} \sum_{\beta, \gamma, \delta} \left\{ (1 - \delta_{k1}) \sum_{m=1}^{k-1} \int [\xi_{\alpha\beta}^{\gamma\delta} f_\gamma^{(0)'} f_\delta^{(0)'} (h_\gamma^{(m)'} h_\delta^{(k-m)'} + h_\delta^{(m)'} h_\gamma^{(k-m)'}) - f_\alpha^{(0)} f_\beta^{(0)} (h_\alpha^{(m)} h_\beta^{(k-m)} + h_\beta^{(m)} h_\alpha^{(k-m)})] g_{\alpha\beta} d(r\sigma_{\alpha\beta}^{\gamma\delta}) d\mathbf{v}_\beta \right.$$

$$\left. + \delta_{k1} \int (\xi_{\alpha\beta}^{\gamma\delta} f_\gamma^{(0)'} f_\delta^{(0)'} - f_\alpha^{(0)} f_\beta^{(0)}) g_{\alpha\beta} d(r\sigma_{\alpha\beta}^{\gamma\delta}) d\mathbf{v}_\beta \right\}, \quad (42)$$

$$h_\alpha^{(k)} = f_\alpha^{(k)} / f_\alpha^{(0)}, \quad h = \{h\}^\mu \quad \alpha=1; k=1, \dots \quad (43)$$

$$\mathcal{L}_\alpha = \frac{1}{2} \sum_r \mathcal{L}_\alpha \quad (44)$$

$$\mathcal{P}_\alpha^{(k-1)} = \frac{1}{2} \sum_r \mathcal{P}_\alpha^{(k-1)}. \quad (45)$$

The zeroth-order approximation of the distribution function  $f_\alpha^{(0)}$  can be found from Eq. (30) as a result of identifying the coefficients according to  $\text{Kn}^{-1}$  for the fast processes. All the terms in the sum over  $r$  on the left-hand side of Eq. (30) for which  $\text{Kn}_\alpha \ll \text{Kn}_{\alpha\beta}^{\gamma\delta}$  (slow process) must be connected with the next order of approximation.

$$\frac{D_k f_\alpha}{Dt} = \sum_{l=0}^k \frac{\partial_{k-l} f_\alpha^{(l)}}{\partial t} + \mathbf{v}_\alpha \cdot \frac{\partial f_\alpha^{(k)}}{\partial \mathbf{r}} + \mathbf{F}_\alpha \cdot \frac{\partial f_\alpha^{(k)}}{\partial \mathbf{v}_\alpha}, \quad (39)$$

$$\frac{\partial_{k-l} f_\alpha^{(l)}}{\partial t} = \sum_{s=0}^{\infty} \nabla^{(s)} \Phi^{(k-l)} : \frac{\partial f_\alpha^{(l)}}{\partial (\nabla^{(s)} \Gamma)}. \quad (40)$$

Now substituting Eq. (38) in Eq. (30), taking into account the relations (24) and (25), and equalizing the coefficients with the same degrees of  $\text{Kn}$ , we obtain integer equations of the generalized Chapman-Enskog method ( $A$  equation), valid for the  $k$  approximation ( $k=1, \dots$ ). In the dimensional form, these equations can be expressed as follows:

$$\sum_{l=0}^{k-1} \sum_{s=0}^{\infty} \nabla^{(s)} \Phi^{(k-l-1)} : \frac{\partial f_\alpha^{(l)}}{\partial (\nabla^{(s)} \Gamma)} + \mathbf{v}_\alpha \cdot \frac{\partial f_\alpha^{(k-1)}}{\partial \mathbf{r}} + \mathbf{F}_\alpha \cdot \frac{\partial f_\alpha^{(k-1)}}{\partial \mathbf{v}_\alpha} = f_\alpha^{(0)} \{ \mathcal{L}_\alpha[h^{(k)}] + \mathcal{P}_\alpha^{(k-1)} \}, \quad (41)$$

$\alpha=1, \dots, \mu$

where the following operators are introduced:

It is interesting to notice that if any process  $r$  belongs to the fast processes, then the last term on the right-hand side of relation (42) is equal to zero because of the state of chemical equilibrium for this  $r$  process. Therefore Eq. (41) has all features of interpolation between limit cases of kinetic theory of gases as mentioned in Sec. II when

the  $A$  equation was discussed from the physical point of view.

### III. RESOLUTION OF THE $A$ EQUATION

Suppose that  $\psi_\alpha^{(i)}$  ( $\alpha=1, \dots, \mu$ ) is a summational invariant for any gas. At least three invariants can be introduced

$$\psi_\alpha^{(1)} = m_\alpha, \quad \psi_\alpha^{(2)} = m_\alpha \mathbf{v}_\alpha, \quad \psi_\alpha^{(3)} = \frac{m_\alpha v_\alpha^2}{2} + \varepsilon_\alpha. \quad (46)$$

Multiplying Eq. (41) by  $\psi_\alpha^{(i)}$  and integrating throughout the velocity space, after the summation over  $\alpha$ , we obtain

$$\begin{aligned} & \sum_{l=0}^{k-1} \sum_{s=0}^{\infty} \nabla^{(s)} \Phi^{(k-l-1)} \cdot \frac{\partial}{\partial(\nabla^{(s)} \Gamma)} \sum_{\alpha=1}^{\mu} \int f_\alpha^{(l)} \psi_\alpha^{(i)} d\mathbf{v}_\alpha \\ & + \sum_{\alpha=1}^{\mu} \int \psi_\alpha^{(i)} \left[ \mathbf{v}_\alpha \cdot \frac{\partial f_\alpha^{(k-1)}}{\partial \mathbf{r}} + \mathbf{F}_\alpha \cdot \frac{\partial f_\alpha^{(k-1)}}{\partial \mathbf{v}_\alpha} \right] d\mathbf{v}_\alpha \\ & = \sum_{\alpha=1}^{\mu} \int f_\alpha^{(0)} \{ \mathcal{L}_\alpha[h^{(k)}] + \mathcal{P}_\alpha^{(k-1)} \} \psi_\alpha^{(i)} d\mathbf{v}_\alpha. \end{aligned} \quad (47)$$

As a consequence of the usual identification of  $n_\alpha, \bar{\mathbf{v}}_\alpha, T$  [7,22]

$$n_\alpha = \int f_\alpha d\mathbf{v}_\alpha, \quad (48)$$

$$\bar{\mathbf{v}}_\alpha = \frac{1}{n_\alpha} \int f_\alpha \mathbf{v}_\alpha d\mathbf{v}_\alpha, \quad (49)$$

$$\frac{3}{2} k_B T_\alpha = \int f_\alpha \frac{m_\alpha v_\alpha^2}{2} d\mathbf{v}_\alpha, \quad (50)$$

$$T = \frac{\sum n_\alpha T_\alpha}{n}, \quad (51)$$

we obtain an additional condition

$$\sum_{\alpha=1}^{\mu} \int f_\alpha^{(0)} h_\alpha^{(j)} \psi_\alpha^{(i)} d\mathbf{v}_\alpha = 0 \quad (j=1, 2, 3). \quad (52)$$

Equation (47) can be written using the relation (52) in the following form:

$$\begin{aligned} & \Phi^{(k-1)} \cdot \frac{\partial}{\partial \Gamma} \sum_{\beta=1}^{\mu} \int f_\beta^{(0)} \psi_\beta^{(i)} d\mathbf{v}_\beta \\ & = - \sum_{\beta=1}^{\mu} \int \psi_\beta^{(i)} \left[ \mathbf{v}_\beta \cdot \frac{\partial f_\beta^{(k-1)}}{\partial \mathbf{r}} + \mathbf{F}_\beta \cdot \frac{\partial f_\beta^{(k-1)}}{\partial \mathbf{v}_\beta} \right] d\mathbf{v}_\beta \\ & \quad + \sum_{\beta=1}^{\mu} \int f_\beta^{(0)} \{ \mathcal{L}_\beta[h^{(k)}] + \mathcal{P}_\beta^{(k-1)} \} \psi_\beta^{(i)} d\mathbf{v}_\beta. \end{aligned} \quad (53)$$

This relation (53) constitutes a linear algebraic system of equations for the determination of  $\Phi^{(k-1)}$  when the functions  $f_\alpha^{(0)}, f_\alpha^{(1)}, \dots, f_\alpha^{(k-1)}$  are known.

Now we assume that

$$\Phi^{(j)} = \Phi_N^{(j)} + \Phi_A^{(j)}, \quad (54)$$

leading to the following equations:

$$\begin{aligned} & \Phi_N^{(k-1)} \cdot \frac{\partial}{\partial \Gamma} \sum_{\beta=1}^{\mu} \int f_\beta^{(0)} \psi_\beta^{(i)} d\mathbf{v}_\beta \\ & = - \sum_{\beta=1}^{\mu} \int \psi_\beta^{(i)} \left[ \mathbf{v}_\beta \cdot \frac{\partial f_\beta^{(k-1)}}{\partial \mathbf{r}} + \mathbf{F}_\beta \cdot \frac{\partial f_\beta^{(k-1)}}{\partial \mathbf{v}_\beta} \right] d\mathbf{v}_\beta \\ & \quad + \sum_{\beta=1}^{\mu} \int f_\beta^{(0)} \mathcal{P}_\beta^{(k-1)} \psi_\beta^{(i)} d\mathbf{v}_\beta, \end{aligned} \quad (55)$$

$$\begin{aligned} & \Phi_A^{(k-1)} \cdot \frac{\partial}{\partial \Gamma} \sum_{\beta=1}^{\mu} \int f_\beta^{(0)} \psi_\beta^{(i)} d\mathbf{v}_\beta \\ & = \sum_{\beta=1}^{\mu} \int f_\beta^{(0)} \mathcal{L}_\beta[h^{(k)}] \psi_\beta^{(i)} d\mathbf{v}_\beta. \end{aligned} \quad (56)$$

Therefore  $\Phi_N^{(k-1)}$  depends on  $h^{(1)}, h^{(2)}, \dots, h^{(k-1)}$  and  $\Phi_A^{(k-1)}$  depends on  $h^{(k)}$ . Rewrite the  $A$  equation in the form

$$\mathbf{g}_\alpha^{(k-1)} = L_\alpha[h^{(k)}], \quad (57)$$

where

$$\begin{aligned} & f_\alpha^{(0)} \mathbf{g}_\alpha^{(k-1)} = \Phi_N^{(k-1)} \cdot \frac{\partial f_\alpha^{(0)}}{\partial \Gamma} \\ & \quad + (1 - \delta_{k1}) \sum_{l=1}^{k-1} \sum_{s=0}^{\infty} \nabla^{(s)} \Phi^{(k-l-1)} \cdot \frac{\partial f_\alpha^{(l)}}{\partial(\nabla^{(s)} \Gamma)} \\ & \quad + \mathbf{v}_\alpha \cdot \frac{\partial f_\alpha^{(k-1)}}{\partial \mathbf{r}} + \mathbf{F}_\alpha \cdot \frac{\partial f_\alpha^{(k-1)}}{\partial \mathbf{v}_\alpha} \\ & \quad - f_\alpha^{(0)} \mathcal{P}_\alpha^{(k-1)}, \quad k=1, 2, \dots \end{aligned} \quad (58)$$

$$L_\alpha[h^{(k)}] = \mathcal{L}_\alpha[h^{(k)}] - \frac{1}{f_\alpha^{(0)}} \Phi_A^{(k-1)} \cdot \frac{\partial f_\alpha^{(0)}}{\partial \Gamma}. \quad (59)$$

Now we state using the relations (52) and (58) that for an arbitrary invariant  $\psi_\alpha^{(i)}$ ,

$$\sum_{\beta=1}^{\mu} \int f_\beta^{(0)} \mathbf{g}_\beta^{(k-1)} \psi_\beta^{(i)} d\mathbf{v}_\beta = 0. \quad (60)$$

Suppose that  $h$  is any vector function; then the operator  $L_\alpha[h]$  is defined by Eq. (59) where  $\Phi_A^{(k-1)}$  must be determined using the set of equations (56). For  $L_\beta[h]$  we can state that

$$\sum_{\beta=1}^{\mu} \int f_\beta^{(0)} L_\beta[h] \psi_\beta^{(i)} d\mathbf{v}_\beta = 0. \quad (61)$$

In the following we prove that the relations (60) and (61) ensure the solubility of the  $A$  equation. The formal algorithm for the resolution of the  $A$  equation can be the following.

(i) Using a Maxwellian distribution function, we find from Eq. (55)  $\Phi_N^{(0)}$  for  $k=1$ .

(ii) Construct the  $A$  equation (57) for  $k=1$ ;  $\Phi_A^{(0)}$  is obtained formally from (56) for  $k=1$ .

(iii) Find the unique solution of this  $A$  equation by the method to be given in the following section.

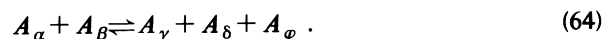
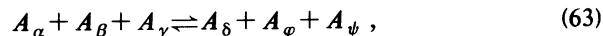
(iv) Using this solution we find  $\Phi^{(0)}$  with the help of (54).

(v) From (55) we find  $\Phi_N^{(1)}$  and go into item (ii) to obtain the  $A$  equation for  $k=2$  and so on.

This algorithm can be used with minimal changing in the case of ionized mixture of reacting gases with nonbimolecular reactions. Moreover this algorithm has a very important feature; it provides the solution of the integral  $A$  equation, which has a non-self-adjoint operator.

#### IV. KINETIC EQUATIONS FOR A MIXTURE OF REACTING GASES WITH TRIPLE COLLISIONS

We consider now a reacting system including both bimolecular and trimolecular reactions:



Then in the frame of a one-particle description we must write the next system of kinetic equations [7]:

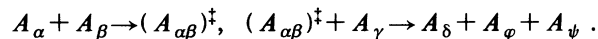
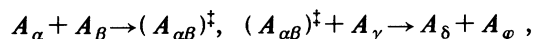
$$\begin{aligned} \frac{D\hat{f}_\alpha}{Dt} = & \sum_j \int [\hat{f}'_\alpha \hat{f}'_j - \hat{f}_\alpha \hat{f}_j] W_{\alpha j}^{\alpha j} d\mathbf{p}_j d\mathbf{p}'_j + \frac{1}{2} \sum_r \sum_{\beta, \gamma, \delta} \int [\hat{f}'_\gamma \hat{f}'_\delta {}^r W_{\gamma\delta}^{\alpha\beta} - \hat{f}_\alpha \hat{f}_\beta {}^r W_{\alpha\beta}^{\gamma\delta}] d\mathbf{p}_\beta d\mathbf{p}'_\gamma d\mathbf{p}'_\delta \\ & + \frac{1}{12} \sum_r \sum_{\beta, \gamma, \delta, \varphi, \psi} \int [\hat{f}'_\delta \hat{f}'_\varphi \hat{f}'_\psi {}^r W_{\delta\varphi\psi}^{\alpha\beta\gamma} - \hat{f}_\alpha \hat{f}_\beta \hat{f}_\gamma {}^r W_{\alpha\beta\gamma}^{\delta\varphi\psi}] d\mathbf{p}_\beta d\mathbf{p}'_\gamma d\mathbf{p}'_\delta d\mathbf{p}'_\varphi d\mathbf{p}'_\psi \\ & + \frac{1}{6} \sum_r \sum_{\beta, \gamma, \delta, \varphi} \int [\hat{f}'_\gamma \hat{f}'_\delta \hat{f}'_\varphi {}^r W_{\gamma\delta\varphi}^{\alpha\beta} - \hat{f}_\alpha \hat{f}_\beta {}^r W_{\alpha\beta}^{\gamma\delta\varphi}] d\mathbf{p}_\beta d\mathbf{p}'_\gamma d\mathbf{p}'_\delta d\mathbf{p}'_\varphi + \sum_r \sum_{\beta, \gamma} \int [\hat{f}'_\gamma {}^r W_{\gamma}^{\alpha\beta} - \hat{f}_\alpha \hat{f}_\beta {}^r W_{\alpha\beta}^{\gamma}] d\mathbf{p}_\beta d\mathbf{p}'_\gamma. \end{aligned} \quad (66)$$

The following remarks have to be made.

(i) In Eq. (66) we introduce the distribution function  $\hat{f}_\alpha$  ( $\alpha=1, \dots, \mu$ ) based on the momentum  $\mathbf{p}_\alpha$  of a molecule of the  $\alpha$  species and the probability of collision; for example,  ${}^r W_{\alpha\beta}^{\gamma\delta}$  denotes the process which would result in the chemical reaction (62) for four particles belonging to the elementary momentum interval  $d\mathbf{p}_\alpha, d\mathbf{p}_\beta, d\mathbf{p}'_\gamma, d\mathbf{p}'_\delta$ .

(ii) The formal factors are introduced under the summation sign in order to eliminate the unnecessary terms in the sum by a formal interchanging of indices, for example, in the computer calculations.

(iii) It is well known in chemical kinetics [23] that the reaction mechanism of the colliding particles  $A_\alpha$  and  $A_\beta$  leads to the creation of the activation complex  $(A_{\alpha\beta})^\ddagger$ , and the result of the collision of such a "quasiparticle"  $(A_{\alpha\beta})^\ddagger$  with the particle  $A_\gamma$  gives two or three particles  $A_\delta, A_\varphi$  or  $A_\delta, A_\varphi, A_\psi$ . Therefore we may write



If the lifetime  $t_{\alpha\beta}^\ddagger$  of the activation complex  $(A_{\alpha\beta})^\ddagger$  is less than or the same order as the mean free time  $\tau$  between collisions of  $A_\alpha, A_\beta, A_\gamma$  then the collision integrals should be written as they are expressed in the third and fourth terms of Eq. (66). If the lifetime  $t_{\alpha\beta}^\ddagger$  is greater than  $\tau_\alpha, \tau_\beta$  we should introduce the reaction (65) and the corresponding collision integral is given by the last term in Eq. (66). Thus we may state that in chemical kinetics of rarefied gases, triple collision reactions are realized as brute (effective) reactions through binary collisions. The inelastic collision operators mentioned above [Eq. (66)] were introduced for the first time by Ludwig and Heil [24]. However, in the transport theory of dense gases, for the first density correction the collision integrals should

be written as it is shown in the initiating works of Sengers [25].

The principle of microscopic reversibility needs several additional remarks. According to quantum theory for a gas composed of electrons and other Fermi-Dirac particles, the Pauli principle must be taken into account and therefore not more than  $s_\alpha d\mathbf{r} d\mathbf{p}_\alpha / h^3$ , the number of such particles, should be within an elementary volume  $d\mathbf{r} d\mathbf{p}_\alpha$  of six-dimensional phase space. This fact leads to the next relations corresponding to the principle of microscopic reversibility

$$s_\alpha s_\beta {}^r W_{\alpha\beta}^{\gamma\delta} = s_\gamma s_\delta {}^r W_{\gamma\delta}^{\alpha\beta}, \quad (67)$$

$$s_\alpha s_\beta s_\gamma {}^r W_{\alpha\beta\gamma}^{\delta\varphi\psi} = s_\delta s_\varphi s_\psi {}^r W_{\delta\varphi\psi}^{\alpha\beta\gamma}, \quad (68)$$

$$h^3 s_\alpha s_\beta {}^r W_{\alpha\beta}^{\gamma\delta\varphi} = s_\gamma s_\delta s_\varphi {}^r W_{\gamma\delta\varphi}^{\alpha\beta}, \quad (69)$$

$$h^3 s_\gamma {}^r W_{\gamma}^{\alpha\beta} = s_\alpha s_\beta {}^r W_{\alpha\beta}^{\gamma}. \quad (70)$$

The probabilities for binary and triple collisions  ${}^r W_{\alpha\beta}^{\gamma\delta}$  can be related to the effective cross-sections for the inelastic processes, for example,

$${}^r W_{\alpha\beta}^{\gamma\delta} (m_\gamma m_\delta)^3 d\mathbf{v}'_\gamma d\mathbf{v}'_\delta = g_{\alpha\beta} d(\sigma_{\alpha\beta}^{\gamma\delta}) \quad (71)$$

for elastic collisions

$$W_{\alpha i}^{\alpha i} (m_\alpha m_i)^3 d\mathbf{v}_\alpha d\mathbf{v}_i = g_{\alpha i} d\sigma_{\alpha i}, \quad (72)$$

and for triple collisions

$${}^r W_{\alpha\beta}^{\delta\varphi} (m_\gamma m_\delta m_\varphi)^3 d\mathbf{v}'_\gamma d\mathbf{v}'_\delta d\mathbf{v}'_\varphi = g_{\alpha\beta} d(\sigma_{\alpha\beta}^{\delta\varphi}), \quad (73)$$

where  $g_{\alpha\beta}$  is the usual relative velocity of  $\alpha$  and  $\beta$  particles.

Let us consider Eq. (67) from another point of view. Multiplying (67) by  $d\mathbf{p}_\alpha d\mathbf{p}_\beta d\mathbf{p}'_\gamma d\mathbf{p}'_\delta$  and using the definition (71), it follows that

$$s_{\alpha} s_{\beta} g_{\alpha\beta} d(\sigma_{\alpha\beta}^{\gamma\delta}) d\mathbf{p}_{\alpha} d\mathbf{p}_{\beta} = s_{\gamma} s_{\delta} g'_{\gamma\delta} d(\sigma_{\gamma\delta}^{\alpha\beta})' d\mathbf{p}'_{\gamma} d\mathbf{p}'_{\delta}. \quad (74)$$

This is another form of the principle of microscopic reversibility. Equation (74) could be rewritten in terms of the variables  $\mathbf{G}$  and  $\mathbf{g}_{\alpha\beta}$ , where

$$\mathbf{G} = \frac{m_{\alpha} \mathbf{v}_{\alpha} + m_{\beta} \mathbf{v}_{\beta}}{m_{\alpha} + m_{\beta}}, \quad (75)$$

$$\mathbf{g}_{\alpha\beta} = \mathbf{v}_{\alpha} - \mathbf{v}_{\beta}. \quad (76)$$

Noticing that  $d\mathbf{v}_{\alpha} d\mathbf{v}_{\beta} = d\mathbf{G} d\mathbf{g}_{\alpha\beta}$  and  $\mathbf{G} = \mathbf{G}'$ , we have

$$s_{\alpha} s_{\beta} d(\sigma_{\alpha\beta}^{\gamma\delta}) (m_{\alpha} m_{\beta})^3 d\mathbf{g}_{\alpha\beta} = s_{\gamma} s_{\delta} g'_{\gamma\delta} d(\sigma_{\gamma\delta}^{\alpha\beta})' (m_{\gamma} m_{\delta})^3 d\mathbf{g}'_{\gamma\delta}. \quad (77)$$

Introducing the spherical coordinates in the space of relative velocities  $\mathbf{g}_{\alpha\beta}$  and  $\mathbf{g}'_{\gamma\delta}$  we have

$$d\mathbf{g}_{\alpha\beta} = g_{\alpha\beta}^2 dg_{\alpha\beta} dw', \quad d\mathbf{g}'_{\gamma\delta} = g'_{\gamma\delta}{}^2 dg'_{\gamma\delta} dw' \quad (78)$$

and therefore

$$s_{\alpha} s_{\beta} g_{\alpha\beta}^3 (m_{\alpha} m_{\beta})^3 d(\sigma_{\alpha\beta}^{\gamma\delta}) dg_{\alpha\beta} dw' = s_{\gamma} s_{\delta} g'_{\gamma\delta}{}^3 (m_{\gamma} m_{\delta})^3 d(\sigma_{\gamma\delta}^{\alpha\beta})' dw'.$$

From the law of energy conservation

$$\mu_{\alpha\beta} \frac{g_{\alpha\beta}^2}{2} + \varepsilon_{\alpha} + \varepsilon_{\beta} = \mu_{\gamma\delta} \frac{g'_{\gamma\delta}{}^2}{2} + \varepsilon_{\gamma} + \varepsilon_{\delta}, \quad (79)$$

where  $\varepsilon_{\alpha}, \varepsilon_{\beta}, \varepsilon_{\gamma}, \varepsilon_{\delta}$  are the internal energies of the particles  $\alpha, \beta, \gamma$ , and  $\delta$ , we have

$$\mu_{\alpha\beta} g_{\alpha\beta} dg_{\alpha\beta} = \mu_{\gamma\delta} g'_{\gamma\delta} dg'_{\gamma\delta}. \quad (80)$$

The relation between cross sections for direct and reversal encounters has the form

$$s_{\alpha} s_{\beta} (\mu_{\alpha\beta} g_{\alpha\beta})^2 \frac{d(\sigma_{\alpha\beta}^{\gamma\delta})}{dw} = s_{\gamma} s_{\delta} (\mu_{\gamma\delta} g'_{\gamma\delta})^2 \frac{d(\sigma_{\gamma\delta}^{\alpha\beta})'}{dw'}. \quad (81)$$

In Eq. (81)  $d(\sigma_{\alpha\beta}^{\gamma\delta})/dw$  is the differential effective cross section for the reaction (62) and the relation (81) can also be obtained by the quantum-mechanical method.

Therefore the problem of the transport coefficient calculation leads finally to the problem of cross sections for complex chemical reactions. Strictly speaking we need explicit relations for the probabilities of inelastic transitions for every set of quantum wave functions. Of course such a demand is not realistic. However, experiments in chemistry usually provide data on the rate of reactions arranged in the typical Arrhenius form and related to the activation energy, the frequency of collision, and the steric factor (see, for example, [26]). From this point of view we do not intend to introduce any additional propositions about the population of the internal energetic levels of the molecules. So the transformation of the basic equations of the GCEM theory can be organized without any additional difficulty and with taking into account the above-mentioned propositions. One of the possible kinetic models for reactive collision leads to the affirmation that an inelastic collision can occur with a probability defined by the steric factor  $r_{\alpha\beta}^{\gamma\delta}$  if the relative velocity along the line of centers of encountered particles is higher

than a defined value which is connected with activation energy. This model corresponds to the principle of microscopic reversibility if the following relation holds [7]:

$$r_{\alpha\beta}^{\gamma\delta} \sigma_{\alpha\beta}^2 m_{\alpha} m_{\beta} = r_{\gamma\delta}^{\alpha\beta} \sigma_{\gamma\delta}^2 m_{\gamma} m_{\delta}. \quad (82)$$

## V. SOLUTION OF THE INTEGRAL EQUATIONS IN THE THEORY OF GCEM

In order to use the algorithm given in Sec. III, the set of macroparameters  $\Gamma$  has to be defined:

$$\Gamma = \{n_{\alpha}, (\alpha = 1, \dots, \mu), \mathbf{v}_0, T\}. \quad (83)$$

In the set (83) we use the usual notations, for example,  $\mathbf{v}_0$  for the hydrodynamic velocities of the reacting gas mixture

$$\mathbf{v}_0 = \frac{\sum m_{\alpha} \int f_{\alpha} \mathbf{v}_{\alpha} d\mathbf{v}_{\alpha}}{\sum m_{\alpha} n_{\alpha}}. \quad (84)$$

Using (40) and (55) and denoting  $k-1=j$  we can find from Eq. (55) for each  $\alpha$  species

$$\left[ \frac{\partial_j n_{\alpha}}{\partial t} \right]_N = - \int \left[ \mathbf{v}_{\alpha} \cdot \frac{\partial f_{\alpha}^{(j)}}{\partial \mathbf{r}} + \left\{ \mathbf{F}_{\alpha} + \frac{e_{\alpha}}{m_{\alpha}} \left[ \mathbf{E} + \frac{1}{c} \mathbf{v}_{\alpha} \times \mathbf{H} \right] \right\} \cdot \frac{\partial f_{\alpha}^{(j)}}{\partial \mathbf{v}_{\alpha}} \right] d\mathbf{v}_{\alpha} + \int f_{\alpha}^{(0)} \mathcal{P}_{\alpha}^{(j)} d\mathbf{v}_{\alpha}, \quad (85)$$

where  $e_{\alpha}$  is the charge of the particles of the  $\alpha$  species. In Eq. (85) the Lorentz force is introduced in the explicit form; therefore, the  $\mathbf{F}_{\alpha}$  are another kind of forces different from the magnetic  $\mathbf{H}$  and electrical  $\mathbf{E}$  fields. For peculiar velocity  $\mathbf{V}_{\alpha}$  we have  $\mathbf{V}_{\alpha} = \mathbf{v}_{\alpha} - \mathbf{v}_0$  and therefore

$$\int \mathbf{v}_{\alpha} \cdot \frac{\partial f_{\alpha}^{(j)}}{\partial \mathbf{r}} d\mathbf{v}_{\alpha} = \frac{\partial}{\partial \mathbf{r}} \cdot n_{\alpha} \bar{\mathbf{V}}_{\alpha}^{(j)} + \delta_{j0} \frac{\partial}{\partial \mathbf{r}} \cdot n_{\alpha} \mathbf{v}_0.$$

It is easy to prove that

$$\int \left\{ \mathbf{F}_{\alpha} + \frac{e_{\alpha}}{m_{\alpha}} \left[ \mathbf{E} + \frac{1}{c} \mathbf{v}_{\alpha} \times \mathbf{H} \right] \right\} \cdot \frac{\partial f_{\alpha}^{(j)}}{\partial \mathbf{v}_{\alpha}} d\mathbf{v}_{\alpha} = 0.$$

We obtain the equation of continuity for the  $\alpha$  species in the  $j$  approximation of the GCEM

$$\left[ \frac{\partial_j n_{\alpha}}{\partial t} \right]_N = -\delta_{j0} \frac{\partial}{\partial \mathbf{r}} \cdot n_{\alpha} \mathbf{v}_0 - \frac{\partial}{\partial \mathbf{r}} \cdot n_{\alpha} \bar{\mathbf{V}}_{\alpha}^{(j)} + \int f_{\alpha}^{(0)} \mathcal{P}_{\alpha}^{(j)} d\mathbf{v}_{\alpha}. \quad (86)$$

If we consider the collisional invariant  $m_{\beta} \mathbf{v}_{\beta}$ , we obtain for the left-hand side of Eq. (55) after the summation over  $\beta$  [see also (32)]



$$\xi = \left[ \frac{\partial_j \Gamma}{\partial t} \right]_N : \frac{\partial}{\partial \Gamma} \rho \mathbf{v}_0 = \rho \left[ \frac{\partial_j \mathbf{v}_0}{\partial t} \right]_N + \sum_{\beta} m_{\beta} \mathbf{v}_0 \left[ \frac{\partial_j n_{\beta}}{\partial t} \right]_N \quad (87)$$

and by using (86) the expression for  $\xi$  becomes

$$\xi = \rho \left[ \frac{\partial_j \mathbf{v}_0}{\partial t} \right]_N - \delta_{j0} \mathbf{v}_0 \cdot \frac{\partial}{\partial \mathbf{r}} \cdot \mathbf{v}_0 \quad (88)$$

because

$$\xi = - \sum_{\beta} \int m_{\beta} \mathbf{v}_{\beta} \left[ \mathbf{v}_{\beta} \cdot \frac{\partial}{\partial \mathbf{r}} f_{\beta} + \left\{ \mathbf{F}_{\beta} + \frac{e_{\beta}}{m_{\beta}} \left[ \mathbf{E} + \frac{1}{c} \mathbf{v}_{\beta} \times \mathbf{H} \right] \right\} \cdot \frac{\partial f_{\beta}^{(j)}}{\partial \mathbf{v}_{\beta}} \right] d\mathbf{v}_{\beta} . \quad (91)$$

The first term can be transformed as

$$\sum_{\beta} \int m_{\beta} \mathbf{v}_{\beta} \mathbf{v}_{\beta} \cdot \frac{\partial}{\partial \mathbf{r}} f_{\beta}^{(j)} d\mathbf{v}_{\beta} = \nabla \cdot \tilde{\mathbf{P}}^{(j)} + \delta_{j0} \frac{\partial}{\partial \mathbf{r}} \cdot \rho \mathbf{v}_0 \mathbf{v}_0 . \quad (92)$$

Here we introduce the tensor of pressure  $\tilde{\mathbf{P}}^{(j)}$  in the  $j$  approximation. The next term is transformed in

$$\begin{aligned} \sum_{\beta} \int m_{\beta} \mathbf{v}_{\beta} \left\{ \mathbf{F}_{\beta} + \frac{e_{\beta}}{m_{\beta}} \mathbf{E} \right\} \cdot \frac{\partial f_{\beta}}{\partial \mathbf{v}_{\beta}} d\mathbf{v}_{\beta} \\ = - \sum_{\beta} \delta_{j0} \rho_{\beta} \left[ \mathbf{F}_{\beta} + \frac{e_{\beta}}{m_{\beta}} \mathbf{E} \right] , \end{aligned} \quad (93)$$

$$\begin{aligned} \left\{ \sum_{\beta} \int \mathbf{v}_{\beta} \frac{e_{\beta}}{c} (\mathbf{v}_{\beta} \times \mathbf{H}) \cdot \frac{\partial f_{\beta}}{\partial \mathbf{v}_{\beta}} \right\}_k \\ = - \delta_{j0} \frac{Q}{c} (\mathbf{v}_0 \times \mathbf{H})_k - \frac{1}{c} (\mathcal{J}^{(j)} \times \mathbf{H})_k , \end{aligned} \quad (94)$$

where  $Q$  is the charge of the unit of volume and  $\mathcal{J}$  is the current density

$$Q = \sum_{\beta} e_{\beta} n_{\beta} , \quad (95)$$

$$\mathcal{J} = \sum_{\beta} e_{\beta} n_{\beta} \mathbf{V}_{\beta}^{(j)} . \quad (96)$$

Thus we obtain the following expression for the right-hand side of Eq. (91):

$$\begin{aligned} \xi = - \frac{\partial}{\partial \mathbf{r}} \cdot \tilde{\mathbf{P}}^{(j)} - \delta_{j0} \frac{\partial}{\partial \mathbf{r}} \cdot \rho \mathbf{v}_0 \mathbf{v}_0 \\ + \delta_{j0} \left\{ \sum_{\beta} \rho_{\beta} \mathbf{F}_{\beta} + Q \left[ \mathbf{E} + \frac{1}{c} (\mathbf{v}_0 \times \mathbf{H}) \right] \right\} \end{aligned} \quad (97)$$

and after equating the right-hand side of both Eq. (88) and (97), we obtain the  $N$  part of the hydrodynamic momentum equation

$$\sum_{\beta} \int m_{\beta} \mathbf{V}_{\beta} f_{\beta}^{(j)} d\mathbf{v}_{\beta} = 0 \quad (j=0, 1, \dots) \quad (89)$$

and

$$\sum_{\beta} \int f_{\beta}^{(0)} \mathcal{P}_{\beta}^{(j)} d\mathbf{v}_{\beta} = 0 . \quad (90)$$

Equation (90) is valid because of the microscopic reversibility principle and could be proved using the explicit form of the operator  $\mathcal{P}_{\beta}^{(j)}$ . Consider the right-hand side of Eq. (53):

$$\begin{aligned} \rho \left[ \frac{\partial_j \mathbf{v}_0}{\partial t} \right]_N = - \delta_{j0} \rho \mathbf{v}_0 \cdot \frac{\partial}{\partial \mathbf{r}} \mathbf{v}_0 \\ + \delta_{j0} \left\{ \sum_{\beta} \rho_{\beta} \mathbf{F}_{\beta} + Q \left[ \mathbf{E} + \frac{1}{c} (\mathbf{v}_0 \times \mathbf{H}) \right] \right\} \\ - \frac{\partial}{\partial \mathbf{r}} \cdot \tilde{\mathbf{P}}^{(j)} . \end{aligned} \quad (98)$$

The energy equation could be found with the help of the collisional invariant  $m_{\beta} v_{\beta}^2 / 2 + \varepsilon_{\beta}$ . The transformations we need are analogical to the ones operated for the continuity and momentum equations. Hence similarly it may be proved that

$$\begin{aligned} \frac{3}{2} k_B n \left[ \frac{\partial_j T}{\partial t} \right]_N = - \delta_{j0} \frac{3}{2} k_B n \mathbf{v}_0 \cdot \frac{\partial T}{\partial \mathbf{r}} - \frac{\partial}{\partial \mathbf{r}} \cdot \mathbf{q}^{(j)} \\ - \tilde{\mathbf{P}}^{(j)} : \frac{\partial}{\partial \mathbf{r}} \mathbf{v}_0 + \frac{3}{2} k_B T \sum_{\beta=1}^{\mu} \frac{\partial}{\partial \mathbf{r}} \cdot (n_{\beta} \bar{\mathbf{V}}_{\beta}^{(j)}) \\ + \sum_{\beta=1}^{\mu} \rho_{\beta} \mathbf{F}_{\beta} \cdot \bar{\mathbf{V}}_{\beta}^{(j)} - \sum_{\beta=1}^{\mu} \varepsilon_{\beta} k_{N_{\beta}}^{(j)} , \end{aligned} \quad (99)$$

where the following notations are introduced:

$$\bar{\mathbf{V}}_{\beta}^{(j)} = \frac{1}{n_{\beta}} \int \mathbf{v}_{\beta} f_{\beta}^{(j)} d\mathbf{v}_{\beta} \quad (100)$$

is the velocity of diffusion of the  $\beta$  species;

$$\tilde{\mathbf{P}}^{(j)} = \sum_{\beta=1}^{\mu} m_{\beta} \int \mathbf{v}_{\beta} \mathbf{v}_{\beta} f_{\beta}^{(j)} d\mathbf{v}_{\beta} \quad (101)$$

is the pressure tensor, which can represent the deviation of the pressure system from hydrostatic pressure  $p$ ;

$$\mathbf{q}^{(j)} = \sum_{\beta=1}^{\mu} \int \mathbf{v}_{\beta} (\frac{1}{2} m_{\beta} V_{\beta}^2 + \varepsilon_{\beta}) f_{\beta}^{(j)} d\mathbf{v}_{\beta} \quad (102)$$

is the total thermal flux and  $\varepsilon_{\beta}$  is the internal energy of  $\beta$  species; and

$$K_{N_{\alpha}}^{(j)} = \int f_{\alpha}^{(0)} \mathcal{P}_{\alpha}^{(j)} d\mathbf{v}_{\alpha} \quad (103)$$

is the production rate of  $\alpha$  species in the chemical reac-

tions. For example, in the zeroth approximation for the bimolecular reactions

$$f^{(0)}\mathcal{P}_\alpha^{(0)} = \frac{1}{2} \sum_r \sum_{\beta, \gamma, \delta} \int \left[ \frac{s_\alpha s_\beta}{s_\gamma s_\delta} f_\gamma^{(0)'} f_\delta^{(0)'} - f_\alpha^{(0)} f_\beta^{(0)} \right] \times g_{\alpha\beta} d(\sigma_{\alpha\beta}^{\gamma\delta}) d\mathbf{v}_\beta. \quad (104)$$

The  $A$  part of the derivatives  $(\partial_j n_\alpha / \partial t)_A$ ,  $(\partial_j \mathbf{v}_0 / \partial t)_A$ , and  $(\partial_j T / \partial t)_A$  are related to the subdivision of the operator  $\Phi^{(j)}$  in (54). It can be shown that

$$\left[ \frac{\partial_j n_\alpha}{\partial t} \right]_A = K_{A\alpha}^{(j)}, \quad (105)$$

$$\left[ \frac{\partial_j \mathbf{v}_0}{\partial t} \right]_A = 0, \quad (106)$$

$$\frac{3}{2} k_B n \left[ \frac{\partial_j T}{\partial t} \right]_A = - \sum_{\beta=1}^{\mu} \varepsilon_\beta K_{A\beta}^{(j)} \quad (j=0, 1, 2, \dots). \quad (107)$$

For the calculation of  $K_{A\alpha}^{(j)}$  we should obtain the solution of Eq. (57), since

$$K_{A\alpha}^{(j)} = \int f_\alpha^{(0)} \mathcal{L}[h^{(j+1)}] d\mathbf{v}_\alpha \quad (108)$$

and thus the sum  $K_{N\alpha}^{(j)} + K_{A\alpha}^{(j)}$  gives the production rate of the  $\alpha$  species in the  $j$  approximation of the GCEM. As usual in the zeroth-order approximation

$$\bar{\mathbf{V}}^{(0)} = \mathbf{0}, \quad \bar{\mathbf{P}}^{(0)} = p \bar{\mathbf{I}}, \quad \mathbf{q}^{(0)} = \mathbf{0}, \quad (109)$$

where  $\bar{\mathbf{I}}$  is the unit tensor.

The solution of the  $A$  equation in the first approximation requires us to find the function  $\Phi_N^{(0)}$  according to the algorithm given in Sec. III:

$$f^{(0)} g_\alpha^{(0)} = \Phi_N^{(0)}: \frac{\partial f_\alpha^{(0)}}{\partial \Gamma} + \mathbf{v}_\alpha \cdot \frac{\partial f_\alpha^{(0)}}{\partial \mathbf{r}} + \mathbf{F}_\alpha \cdot \frac{\partial f_\alpha^{(0)}}{\partial \mathbf{v}_\alpha} - f_\alpha^{(0)} \mathcal{P}_\alpha^{(0)}. \quad (110)$$

The calculation of the right-hand side of Eq. (110) is identical to the transformations used in [7] (pp. 139–141). We obtain the expression

$$g_\alpha^{(0)} = \frac{K_{N\alpha}^{(0)}}{n_\alpha} + (1 - \frac{2}{3} W_\alpha^2) \frac{1}{p} \sum_{\beta=1}^{\mu} \varepsilon_\beta K_{N\beta}^{(0)} - \mathcal{P}_\alpha^{(0)} + 2W_\alpha^0 \mathbf{W}_\alpha: \frac{\partial}{\partial \mathbf{r}} \mathbf{v}_0 + \mathbf{V}_\alpha \cdot \frac{\partial \ln T}{\partial \mathbf{r}} (W_\alpha^2 - \frac{5}{2}) + \frac{n}{n_\alpha} \mathbf{V}_\alpha \cdot \mathbf{d}_\alpha, \quad (111)$$

where

$$\mathbf{d}_\alpha = \frac{\partial}{\partial \mathbf{r}} \left[ \frac{n_\alpha}{n} \right] + \left[ \frac{n_\alpha}{n} - \frac{\rho_\alpha}{\rho} \right] \frac{\partial \ln p}{\partial \mathbf{r}} - \frac{\rho_\alpha}{\rho p} \left[ \rho \mathbf{F}_\alpha - \sum_{\beta} \rho_\beta \mathbf{F}_\beta \right], \quad (112)$$

$$\mathbf{W}_\alpha = \mathbf{V}_\alpha \left[ \frac{m_\alpha}{2k_B T} \right]^{1/2}.$$

Let us consider now the right-hand side of Eq. (57). With Eq. (37) and the system of hydrodynamic equations in the GCEM approximation we have

$$\frac{1}{f_\alpha^{(0)}} \Phi_A^{(j)}: \frac{\partial f_\alpha^{(0)}}{\partial \Gamma} = \frac{K_{A\alpha}^{(j)}}{n_\alpha} + (1 - \frac{2}{3} W_\alpha^2) \frac{1}{p} \sum_{\beta=1}^{\mu} \varepsilon_\beta K_{A\beta}^{(j)}. \quad (113)$$

Therefore the operator of the right-hand side of Eq. (57) has the form

$$L_\alpha[h^{(j)}] = \mathcal{L}_\alpha[h^{(j)}] - \frac{K_{A\alpha}^{(j-1)}}{n_\alpha} - \frac{1}{p} (1 - \frac{2}{3} W_\alpha^2) \sum_{\beta=1}^{\mu} \varepsilon_\beta K_{A\beta}^{(j-1)}, \quad (114)$$

or using (108)

$$L_\alpha[h] = \mathcal{L}_\alpha[h] - \frac{1}{n_\alpha} \int f_\alpha^{(0)} \mathcal{L}_\alpha[h] d\mathbf{v}_\alpha - \frac{1}{p} (1 - \frac{2}{3} W_\alpha^2) \sum_{\beta=1}^{\mu} \varepsilon_\beta \int f_\beta^{(0)} \mathcal{L}_\beta[h] d\mathbf{v}_\beta. \quad (115)$$

The structure on the left-hand side of Eq. (57) [see also (110) and in [7], pp. 142–148, 261–263] leads to the conclusion that the expression for  $h_\alpha^{(1)}$  could be written in the form

$$h_\alpha^{(1)} = t_\alpha(W_\alpha^2) - B_\alpha(W_\alpha^2) \mathbf{W}_\alpha^0 \mathbf{W}_\alpha: \frac{\partial}{\partial \mathbf{r}} \mathbf{v}_0 - A_\alpha(W_\alpha^2) \mathbf{W}_\alpha \cdot \frac{\partial \ln T}{\partial \mathbf{r}} + n \mathbf{W}_\alpha \cdot \sum_{\substack{h,k \\ h \neq k}} [C_\alpha^{(h)}(W_\alpha^2) - C_\alpha^{(k)}(W_\alpha^2)] \mathbf{d}_k. \quad (116)$$

Unknown functions  $t_\alpha, B_\alpha, A_\alpha, C_\alpha^{(h)}$  in (116) must be found as the result of the solution of the integral equations

$$\frac{K_{N\alpha}^{(0)}}{n_\alpha} + (1 - \frac{2}{3} W_\alpha^2) \frac{1}{p} \sum_{\beta=1}^{\mu} \varepsilon_\beta K_{N\beta}^{(0)} - \mathcal{P}_\alpha^{(0)} = L_\alpha(t), \quad (117)$$

$$-2W_\alpha^0 \mathbf{W}_\alpha = L_\alpha[B \mathbf{W}_\alpha^0 \mathbf{W}_\alpha], \quad (118)$$

$$\mathbf{V}_\alpha (\frac{5}{2} - W_\alpha^2) = L_\alpha[A \mathbf{W}], \quad (119)$$

$$\mathbf{V}_\alpha \frac{1}{n_\alpha} (\delta_{\alpha h} - \delta_{\alpha k}) = L_\alpha[(C^{(h)} - C^{(k)}) \mathbf{W}]. \quad (120)$$

As usual in GCEM we should identify the concentrations  $n_\alpha$ , the mean hydrodynamical velocity  $\mathbf{v}_0$ , and temperature  $T$ , with the help of the Maxwellian functions  $f_\alpha$ . This fact leads to the additional conditions

$$\int f_\alpha^{(j)} \psi_\alpha^{(1)} d\mathbf{v}_\alpha = 0, \quad j=1, 2, 3, \dots \quad (121)$$

$$\sum_\alpha \int f_\alpha^{(j)} \psi_\alpha^{(i)} d\mathbf{v}_\alpha = 0, \quad i=1, 2 \quad (122)$$

$$\psi_\alpha^{(1)} = m_\alpha, \quad \psi_\alpha^{(2)} = m_\alpha \mathbf{v}_\alpha, \quad \psi_\alpha^{(3)} = \frac{m_\alpha V_\alpha^2}{2}$$

and to the problem of solubility of Eqs. (117)–(120) taking into account relations (60) and (61). For Eq. (117) the additional conditions must be written in the form

$$\int f_{\alpha}^{(0)} t_{\alpha} d\mathbf{v}_{\alpha} = 0, \quad (123)$$

$$\sum_{\beta=1}^{\mu} \int t_{\beta} f_{\beta}^{(0)} m_{\beta} \mathbf{v}_{\beta} d\mathbf{v}_{\beta} = 0, \quad (124)$$

$$\sum_{\beta=1}^{\mu} \int t_{\beta} f_{\beta}^{(0)} m_{\beta} V_{\beta}^2 d\mathbf{v}_{\beta} = 0. \quad (125)$$

The integrand in (124) is the odd function and therefore the part of integral for which this integrand is positive cancels the part for which this integrand is negative; the integral is equal to zero and the additional condition (124) vanishes. Other relations which lead to  $\mu + 1$  conditions for other integral equations could be organized in an analogous manner; for example, it could be proved that additional conditions for Eq. (118) vanish.

As in the case of the additional condition (124) it is easy to prove that

$$\int f_{\alpha}^{(0)} \mathcal{L}_{\alpha} [B \mathbf{W}^{\circ} \mathbf{W}] d\mathbf{v}_{\alpha} = 0, \quad (126)$$

$$\int f_{\alpha}^{(0)} \mathcal{L}_{\alpha} [A \mathbf{W}] d\mathbf{v}_{\alpha} = 0, \quad (127)$$

$$\int f_{\alpha}^{(0)} \mathcal{L}_{\alpha} [(C^{(h)} - C^{(k)}) \mathbf{W}] d\mathbf{v}_{\alpha} = 0. \quad (128)$$

Therefore on the right-hand side of Eqs. (118)–(120) there are shorter operators [see also (115)]

$$-2\mathbf{W}_{\alpha}^{\circ} \mathbf{W}_{\alpha} = \mathcal{L}_{\alpha} [B \mathbf{W}^{\circ} \mathbf{W}], \quad (129)$$

$$(\frac{5}{2} - W_{\alpha}^2) \mathbf{V}_{\alpha} = \mathcal{L}_{\alpha} [A \mathbf{W}], \quad (130)$$

$$\mathbf{V}_{\alpha} \frac{1}{n_{\alpha}} (\delta_{ah} - \delta_{ak}) = \mathcal{L}_{\alpha} [(C^{(h)} - C^{(k)}) \mathbf{W}]. \quad (131)$$

## VI. TRANSPORT COEFFICIENTS FOR NONEQUILIBRIUM REACTING MIXTURE OF GASES

Equations (129)–(131) have the operator  $\mathcal{L}_{\alpha}$ , which was studied in [7,24]. Therefore the formal expressions for the velocity of diffusion  $\bar{\mathbf{V}}_{\alpha}$ , the tensor of pressure  $\bar{\mathbf{P}}$ , and the thermal flux can be expressed in the usual form:

$$\bar{\mathbf{V}}_{\alpha} = \frac{n^2}{\rho n_{\alpha}} \sum_{h=1}^{\mu} m_h D_{ah} \mathbf{d}_h - \frac{1}{\rho_{\alpha}} D_{\alpha}^T \frac{\partial \ln T}{\partial \mathbf{r}}, \quad (132)$$

$$\bar{\mathbf{P}} = p \bar{\mathbf{I}} - 2\eta \bar{\mathbf{S}}, \quad (133)$$

$$\mathbf{q} = \frac{5}{2} k_B T \sum_{j=1}^{\mu} n_j \bar{\mathbf{V}}_j - \lambda' \frac{\partial T}{\partial \mathbf{r}} - p \sum_{\alpha=1}^{\mu} \frac{1}{\rho_{\alpha}} D_{\alpha}^T \mathbf{d}_{\alpha}, \quad (134)$$

where the following coefficients are introduced: the diffusion and thermodiffusion coefficients

$$D_{ah} = \frac{\rho}{3m_h n} \left[ \frac{2k_B T}{m_{\alpha}} \right]^{1/2} \int [C_{\alpha}^{(h)} - C_{\alpha}^{(k)}] W_{\alpha}^2 f_{\alpha}^{(0)} d\mathbf{v}_{\alpha} \quad (h, k = 1, \dots, \mu) \quad (135)$$

$$D_{\alpha}^T = \frac{m_{\alpha}}{3} \left[ \frac{2k_B T}{m_{\alpha}} \right]^{1/2} \int A_{\alpha} W_{\alpha}^2 f_{\alpha}^{(0)} d\mathbf{v}_{\alpha}, \quad (136)$$

the coefficient of conduction

$$\lambda' = -\frac{\sqrt{2}}{3} k_B \sqrt{k_B T} \sum_{j=1}^{\mu} \frac{1}{\sqrt{m_j}} \int A_j (\frac{5}{2} - W_j^2) W_j^2 f_j^{(0)} d\mathbf{v}_j, \quad (137)$$

and the coefficient of viscosity

$$\eta = \frac{2k_B T}{15} \sum_{\beta=1}^{\mu} \int f_{\beta}^{(0)} B_{\beta} W_{\beta}^4 d\mathbf{v}_{\beta}. \quad (138)$$

The tensor  $\bar{\mathbf{S}}$  has the stress components

$$S_{ik} = \left[ \frac{\partial v_{0k}}{\partial x_i} - \frac{\partial v_{0i}}{\partial x_k} \right] - \frac{1}{3} \delta_{ik} \frac{\partial}{\partial \mathbf{r}} \cdot \mathbf{v}_0. \quad (139)$$

In order to obtain the explicit expressions for transport coefficients we should find the functions  $A_{\alpha}, B_{\alpha}, C_{\alpha}^{(h)}$  from integral Eqs. (129)–(131). For the approximation of the solution of integral equations (117) and (129)–(131) we use the well-known Bubnov-Galerkin method [27]. As test functions we use finite linear combinations of Sonine polynomials multiplied by tensor functions of velocity. For example, for the solution of Eq. (127) we suppose that the function  $A_{\alpha}$  can be expanded in a convergent series of the form

$$A_{\alpha} = \sum_{m'=0}^{\xi} a_{\alpha m'} S_{3/2}^{(m')} (W_{\alpha}^2). \quad (140)$$

The system of linear algebraic equations for the determination of the coefficients  $a_{\alpha m'}$  can be written as

$$\sum_{m'=0}^{\xi} \sum_{\beta=1}^{\mu} Q_{\alpha\beta}^{(m, m')} a_{\beta m'} = -\frac{15}{4} n_{\alpha} \left[ \frac{2k_B T}{m_{\alpha}} \right]^{1/2} \delta_{m1} \quad (m = 0, 1, \dots, \xi) \quad (141)$$

An additional condition (122), which has the following form should be added to this system:

$$\sum_{\beta=1}^{\mu} n_{\beta} \sqrt{m_{\beta}} a_{\beta 0} = 0. \quad (142)$$

In Eq. (141)

$$\begin{aligned} Q_{\alpha\beta}^{(m, m')} = & \sum_{l=1}^{\mu} (n_{\alpha} n_l \{ S_{\beta\alpha} [ \mathbf{W}_{\alpha} S_{3/2}^{(m)} (W_{\alpha}^2), \mathbf{W}_{\alpha} S_{3/2}^{(m')} (W_{\alpha}^2) ]_{\alpha l} + \delta_{\beta l} [ \mathbf{W}_{\alpha} S_{3/2}^{(m)} (W_{\alpha}^2), \mathbf{W}_l S_{3/2}^{(m')} (W_{\alpha}^2) ]_{\alpha l} \} \\ & + \frac{1}{2} \sum_r \sum_{\gamma \delta} \{ \delta_{\beta\alpha} [ \mathbf{W}_{\alpha} S_{3/2}^{(m)} (W_{\alpha}^2), \mathbf{W}_{\alpha} S_{3/2}^{(m')} (W_{\alpha}^2) ]_{\alpha l}^r + \delta_{\beta l} [ \mathbf{W}_{\alpha} S_{3/2}^{(m)} (W_{\alpha}^2), \mathbf{W}_l S_{3/2}^{(m')} (W_l^2) ]_{\alpha l}^r \\ & + \delta_{\beta\gamma} [ \mathbf{W}_{\alpha} S_{3/2}^{(m)} (W_{\alpha}^2), \mathbf{W}_{\gamma} S_{3/2}^{(m')} (W_{\gamma}^2) ]_{\alpha l}^r + \delta_{\beta\delta} [ \mathbf{W}_{\alpha} S_{3/2}^{(m)} (W_{\alpha}^2), \mathbf{W}_{\delta} S_{3/2}^{(m')} (W_{\delta}^2) ]_{\alpha l}^r \} ). \end{aligned} \quad (143)$$

Analogously for the function  $B_\alpha$ ,

$$B_\alpha = \sum_{m'=0}^{\xi} b_{\alpha m'} S_{5/2}^{(m')} (W_\alpha^2). \quad (144)$$

The system of linear algebraic equations for the determination of the coefficients  $b_{\alpha m'}$  becomes

$$\sum_{m'=0}^{\xi} \sum_{\beta=1}^{\mu} Q_{\alpha\beta}^{(m',m)} b_{\beta m'} = 5n_\alpha \delta_{m0}. \quad (145)$$

Here  $Q_{\alpha\beta}^{(m',m)}$  can be written in the form (143) in which we should change the complex  $\mathbf{W}_i S_{3/2}^{(p)} (W_i^2)$  into  $\mathbf{W}_i^{\mathbf{O}} \mathbf{W}_i S_{5/2}^{(p)} (W_i^2)$ . The values  $\mathbf{C}_\alpha^{(h)} - \mathbf{C}_\alpha^{(k)}$  are calculated by a similar method

$$\mathbf{C}_\alpha^{(h)} - \mathbf{C}_\alpha^{(k)} = \sum_{m'=0}^{\xi} c_{\alpha m'}^{(h,k)} S_{3/2}^{(m')} (W_\alpha^2), \quad (146)$$

where  $c_{\alpha m'}^{(h,k)}$  can be obtained from the system of algebraic equations

$$\sum_{m'=0}^{\xi} \sum_{\beta=1}^{\mu} Q_{\alpha\beta}^{(m',m')} c_{\beta m'}^{(h,k)} = -\frac{3}{2} \left( \frac{2k_B T}{m_\alpha} \right)^{1/2} (\delta_{ah} - \delta_{ak}) \delta_{m0}, \quad (147)$$

where  $Q_{\alpha\beta}^{(m',m')}$  are equal to corresponding values in Eq. (143).

We emphasize that the values  $Q_{\alpha\beta}^{(m',m')}$  contain bracket expressions for inelastic collisions. All these bracket expressions were calculated by Alexeev for bimolecular reactions and could be found in Ref. [7]. Bracket expressions for inelastic collisions contain integrals of inelastic collisions. As mentioned before, the simple (well known in chemistry) models of inelastic collisions could be used for evaluating these integrals denoted in [7] as  ${}^r \Omega_{\alpha\beta}^{\gamma\delta(h,k)}$ . If we introduce the energetic barrier, connected with the relative velocity along the line of centers of encountered particles (activation energy  $E$ ) and steric factor  $r_p$ , then all  ${}^r \Omega_{\alpha\beta}^{\gamma\delta(h,k)}$  are proportional to  $r_p \exp[-E/(k_B T)] f(E/k_B T)$ , where  $f(E/k_B T)$  is, generally speaking, the polynomial of high degree. It is the reason why we can obtain a significant deviation of the kinetic coefficient values in chemically reacting gases in comparison with the results obtained without considering the inelastic processes.

Now let us consider the problem of the chemical reaction rate calculation. Any chemical reaction rate is the consequence of the common theory of the GCEM and

TABLE I. Deviation from equilibrium of the reaction rate for the forward  $w_\xi$  and backward  $\xi_\xi$  reaction calculated for  $\xi$  Sonine approximation ( $\xi=1,2,3$ ) using the concentrations  $n_1=n_2=0.5n$  and  $n_3=n_4=0.45n$  and the steric factor  $p_{12}^3=0.05$ .

$T$	$w_1$	$w_2$	$w_3$	$\xi_1$	$\xi_2$	$\xi_3$
275	1.365	1.585	1.585	0.954	0.937	0.937
325	1.483	1.641	1.641	0.939	0.928	0.928
400	1.610	1.691	1.691	0.923	0.918	0.918
500	1.701	1.726	1.727	0.911	0.910	0.910
600	1.734	1.740	1.740	0.906	0.905	0.905

from this point of view it could be considered as a usual kinetic coefficient.

The corresponding value  $K_\alpha$  can be written in the following form:

$$K_\alpha = K_{N\alpha}^{(0)} + K_{A\alpha}^{(0)} + K_{N\alpha}^{(1)} + K_{A\alpha}^{(1)}, \quad (148)$$

where for bimolecular reactions

$$\begin{aligned} K_{N\alpha}^{(0)} &= \frac{1}{2} \sum_r \sum_{\beta, \gamma, \delta} \int [\xi_{\alpha\beta}^{\gamma\delta} f_\gamma^{(0)'} f_\delta^{(0)'} - f_\alpha^{(0)} f_\beta^{(0)}] \\ &\quad \times g_{\alpha\beta} d({}^r \sigma_{\alpha\beta}^{\gamma\delta}) d\mathbf{v}_\alpha d\mathbf{v}_\beta, \\ K_{A\alpha}^{(1)} &= \frac{1}{2} \sum_r \sum_{\beta, \gamma, \delta} \int [\xi_{\alpha\beta}^{\gamma\delta} f_\gamma^{(0)'} f_\delta^{(0)'} (t'_\gamma + t'_\delta) \\ &\quad - f_\alpha^{(0)} f_\beta^{(0)} (t_\alpha + t_\beta)] \\ &\quad \times g_{\alpha\beta} d({}^r \sigma_{\alpha\beta}^{\gamma\delta}) d\mathbf{v}_\alpha d\mathbf{v}_\beta. \end{aligned} \quad (149)$$

As a direct consequence of the existence of the non-self-adjoint operator in the proposed GCEM, only the expressions of  $K_{N\alpha}^{(1)}$  and  $K_{A\alpha}^{(2)}$  and no other transport coefficient involve part of the terms related to the second approximation. The explicit form for these values is written in [19], but usually the contribution of the higher approximation is small. For the calculations of the coefficients  $t_\alpha$  ( $\alpha=1, \dots, \mu$ ) we should use the solution of the system of linear algebraic equations which contain the bracket expressions with Sonine polynomials with index 1/2. All these bracket expressions were calculated and the table of these expressions could be found in [7]. The system of algebraic equations (see [7]) is  $\mu+1$  times linear dependent and for the resolution of this system we should add  $\mu+1$  relations [see (121) and (122)]:

$$t_{\alpha_0} = 0, \quad \alpha = 1, \dots, \mu; \quad \sum_{\beta=1}^{\mu} n_\beta t_{\beta 1} = 0. \quad (150)$$

Now we intend to consider several examples of the transport coefficient calculations. Let us consider the four component mixture of the reacting gases:



Let  $K_f^{(0)}$  and  $K_b^{(0)}$  denote the reaction rates calculated with the help of the Maxwellian distribution function, therefore in the frame of the Arrhenius chemical kinetics. We use the following values characterizing the process: the diameter of the molecules  $d_{\text{Cl}} = 2 \text{ \AA}$ ,  $d_{\text{H}_2} = 2.9 \text{ \AA}$ ,  $d_{\text{H}} = 1.45 \text{ \AA}$ ,  $d_{\text{HCl}} = 3.3 \text{ \AA}$ , the activation energy for the forward reaction  $\bar{E}_f = 2400/RT$  and the backward reaction  $\bar{E}_b = 2050/RT$ , where  $R = 1.986 \text{ cal/mol K}$  [28]. Using experimental data [26], the model of inelastic collision formulated above and the principal of microscopic reversibility, which could be written from this model as

$$s_\alpha s_\beta m_\alpha m_\beta {}^r p_{\alpha\beta}^{\gamma\delta} d_{\alpha\beta}^2 = s_\gamma s_\delta m_\gamma m_\delta {}^r p_{\gamma\delta}^{\alpha\beta} d_{\gamma\delta}^2 \quad (152)$$

for the temperature range 250–610 K, we obtain the estimate for the reaction Eq. (151) with the components

TABLE II. Ratio of the calculated kinetic coefficients to its value taking into account the influence of the inelastic collisions, ratios of the coefficients at 400 K for thermal diffusion  $x$ ; self-diffusion for Cl,  $y$ ; and mutual diffusion for Cl and  $H_2$ ,  $z$ .

$p_{Cl, H_2}^{H, HCl}$	$x$	$y$	$z$
0.05	0.0558	1.4410	1.2726
0.1	-0.8051	1.8568	1.5296

(Cl  $\equiv A_1$ ,  $H_2 \equiv A_2$ , H  $\equiv A_3$ , and HCl  $\equiv A_4$ ) [see Eq. (62)]

$$p_{12}^{34} \sim 0.1 - 0.2. \quad (153)$$

Equation (152) leads to the relation between steric factors

$$p_{34}^{12} \cong 2p_{12}^{34}. \quad (154)$$

Introduce the notation  $w_\xi = K_f/K_f^{(0)}$ ,  $\xi_\xi = K_b/K_b^{(0)}$ , and  $K_K/K_c = w_\xi/\xi_\xi$ , where  $K_c = K_f^{(0)}/K_b^{(0)}$ . Therefore  $w_\xi, \xi_\xi$ , and  $K_K/K_c$  are characterizing the deviation of the real rate coefficients of reactions and "kinetic constant" of equilibrium  $K_K$  from the corresponding values, which could be found in the frame of Arrhenius kinetics.

Table I contains values  $w_\xi$  and  $\xi_\xi$  calculated for the first, second, and third Sonine approximations. We use the following parameters: concentrations  $n_1/n = n_2/n = 0.5$ ,  $n_3/n = n_4/n = 0.45$ , and  $p_{12}^{34} = 0.05$ .

This table shows that even by a small relative share of inelastic collisions the influence of such collisions on the alternation of  $w_\xi, \xi_\xi, K_K$  could be very significant. Particularly, the "kinetic constant of chemical equilibrium"  $K_K$  could be twice as great as the thermodynamic one and fits the experimental data quite well [28].

Let us now consider the example of the possible influence of the inelastic collisions on other kinetic coefficients. Introduce the notations

$$\begin{aligned} x &= \frac{D_{Cl}^T(p_{Cl, H_2}^{H, HCl})}{D_{Cl}^T(0)}, \\ y &= \frac{D_{Cl, Cl}(p_{Cl, H_2}^{H, HCl})}{D_{Cl, Cl}(0)}, \\ z &= \frac{D_{Cl, H_2}(p_{Cl, H_2}^{H, HCl})}{D_{Cl, H_2}(0)}. \end{aligned} \quad (155)$$

TABLE III. Convergency of the Sonine approximation ( $\xi=1, 2, 3$ ) in the calculation of the thermal diffusion ratio  $x$  and self-diffusion for Cl,  $y$ .

	$x$	1	2	3
$x$ (with $p_{Cl, H_2}^{H, HCl} = 0.1$ )	-0.6321	-0.7729	-0.8051	
$y$ (with $p_{Cl, H_2}^{H, HCl} = 0.05$ )	1.4402	1.4409	1.4410	

The calculations of the values  $x, y, z$  in (155) are contained in Tables II and III (for  $T=400$  K). Several comments are to be made on Tables II and III. The symbol 0 in the parentheses of Eq. (155) means that the corresponding values are calculated without taking into account the influence of the inelastic processes on the transport coefficients.

From Tables II and III, it could be seen that the influence of inelastic collisions is very significant (for example, the coefficient of thermal diffusion changes sign) by the good convergency (Table III) of Sonine approximation.

## VII. TRIPLE COLLISIONS IN THE GCEM

Now let us consider the influence of triple collisions on the distribution function evolution in rarefied chemically reacting gases. For the hard-sphere model of molecules the frequency of binary collisions could be estimated as

$$\nu^{\text{bin}} \sim \bar{g} \pi d^2 \bar{n},$$

where  $d$  is the diameter of the particle. The total volume of such two spheres is  $\pi d^3/3$  and the volume calculated on one particle is  $\bar{n}^{-1}$ , where  $\bar{n}$  is the number density of the gas. Therefore the probability of an interaction between two encountered particles with the third particle is  $\sim \pi \bar{n} d^3/3$  and the frequency of triple collision  $\nu^{\text{tr}}$  can be estimated as

$$\nu^{\text{tr}} \sim \epsilon_0 \nu^{\text{bin}} \ll \nu^{\text{bin}}$$

because the density parameter  $\epsilon_0 = nd^3$  is small compared with unity. Hence we should state that triple inelastic collisions will not belong to fast processes. However, it is possible to show that triple collisions could be included in the scheme of the generalized Chapman-Enskog method without any difficulty.

The Boltzmann equation including triple collisions can be written in the form

$$\begin{aligned} \frac{\partial f_\alpha}{\partial t} + \mathbf{v}_\alpha \cdot \frac{\partial f_\alpha}{\partial \mathbf{r}} + \mathbf{F}_\alpha \cdot \frac{\partial f_\alpha}{\partial \mathbf{v}_\alpha} &= \sum_{j=1}^{\mu} I_{\alpha j}(f, f) + \frac{1}{2} \sum_r \sum_{\beta, \gamma, \delta} \int \left[ \frac{s_\alpha s_\beta}{s_\gamma s_\delta} \left( \frac{m_\alpha m_\beta}{m_\gamma m_\delta} \right)^3 f'_\gamma f'_\delta - f_\alpha f_\beta \right] d(\tau \sigma_{\alpha\beta}^{\gamma\delta}) d\mathbf{v}_\beta \\ &+ \frac{1}{6} \sum_r \sum_{\beta, \gamma, \delta} \int \left[ \frac{s_\alpha s_\beta s_\gamma^3}{s_\gamma s_\delta s_\varphi} \left( \frac{m_\alpha m_\beta}{m_\gamma m_\delta m_\varphi} \right)^3 f'_\gamma f'_\delta f'_\varphi - f_\alpha f_\beta \right] W_{\alpha\beta}^{\gamma\delta\varphi} (m_\gamma m_\delta m_\varphi)^3 d\mathbf{v}_\beta d\mathbf{v}'_\gamma d\mathbf{v}'_\delta d\mathbf{v}'_\varphi. \end{aligned} \quad (156)$$

The reactions of the type (63) are neglected because in aerothermochemistry its mechanism could be considered as an intermediate step or an activation complex in reactions (64) and (65).

Consequently the linearized collision integral could be written in the form [analogously to Eq. (42)],

$$f_\alpha^{(0)} \mathcal{L}_\alpha[h] = f_\alpha^{(0)} \left\{ \sum_{j=1}^{\mu} \mathcal{L}_{\alpha j}[h] + \frac{1}{2} \sum_r \sum_{\beta, \gamma, \delta} \mathcal{L}_{\alpha\beta}^{\gamma\delta}[h] + \frac{1}{6} \sum_r \sum_{\beta, \gamma, \delta, \varphi} {}^r \mathcal{L}_{\alpha\beta}^{\gamma\delta\varphi}[h] \right\}. \quad (157)$$

Analogously

$$\mathcal{P}_\alpha^{(k-1)} = \sum_j \mathcal{P}_{\alpha j}^{(k-1)} + \frac{1}{2} \sum_r \sum_{\beta, \gamma, \delta} {}^r \mathcal{P}_{\alpha\beta}^{\gamma\delta(k-1)} + \frac{1}{6} \sum_r \sum_{\beta, \gamma, \delta, \varphi} {}^r \mathcal{P}_{\alpha\beta}^{\gamma\delta\varphi(k-1)}. \quad (158)$$

The first terms on the right-hand sides of Eqs. (156)–(158) are related to the elastic collisions. In explicit form we have

$$f_\alpha^{(0)} {}^r \mathcal{L}_{\alpha\beta}^{\gamma\delta\varphi}[h] = \int \left[ \frac{s_\alpha s_\beta h^3}{s_\gamma s_\delta s_\varphi} \left[ \frac{m_\alpha m_\beta}{m_\gamma m_\delta m_\varphi} \right]^3 f_\gamma^{(0)'} f_\delta^{(0)'} f_\varphi^{(0)'} (h'_\gamma + h'_\delta + h'_\varphi) - f_\alpha^{(0)} f_\beta^{(0)} (h_\alpha + h_\beta) \right] \\ \times {}^r \mathcal{W}_{\alpha\beta}^{\gamma\delta\varphi} (m_\gamma m_\delta m_\varphi)^3 d\mathbf{v}_\beta d\mathbf{v}'_\gamma d\mathbf{v}'_\delta d\mathbf{v}'_\varphi, \quad (159)$$

$$f_\alpha^{(0)} {}^r \mathcal{P}_{\alpha\beta}^{\gamma\delta\varphi(0)} = \int \left[ \frac{s_\alpha s_\beta h^3}{s_\gamma s_\delta s_\varphi} \left[ \frac{m_\alpha m_\beta}{m_\gamma m_\delta m_\varphi} \right]^3 f_\gamma^{(0)'} f_\delta^{(0)'} f_\varphi^{(0)'} - f_\alpha^{(0)} f_\beta^{(0)} \right] {}^r \mathcal{W}_{\alpha\beta}^{\gamma\delta\varphi} (m_\gamma m_\delta m_\varphi) d\mathbf{v}_\beta d\mathbf{v}'_\gamma d\mathbf{v}'_\delta d\mathbf{v}'_\varphi. \quad (160)$$

Reactions (159) and (160) can be written in a more simple form using the relations between the Maxwellian functions:

$$\frac{\xi_{\alpha\beta}^{\gamma\delta} f_\gamma^{(0)'} f_\delta^{(0)'}}{f_\alpha^{(0)} f_\beta^{(0)}} \equiv \xi_{\alpha\beta}^{\gamma\delta} = \frac{n_\gamma n_\delta}{n_\alpha n_\beta} \left[ \frac{m_\alpha m_\beta}{m_\gamma m_\delta} \right]^{3/2} \frac{s_\alpha s_\beta}{s_\gamma s_\delta} \exp \left[ \frac{\varepsilon_\gamma + \varepsilon_\delta - \varepsilon_\alpha - \varepsilon_\beta}{k_B T} \right], \quad (161)$$

$$\frac{s_\delta s_\varphi h^3}{s_\alpha s_\beta s_\delta} \left[ \frac{m_\delta m_\varphi}{m_\alpha m_\beta m_\delta} \right]^3 \frac{f_\alpha^{(0)} f_\beta^{(0)} f_\gamma^{(0)'}}{f_\delta^{(0)'} f_\gamma^{(0)'}} \\ \equiv \xi_{\delta\varphi}^{\alpha\beta\gamma} = \frac{n_\alpha n_\beta n_\gamma}{n_\delta n_\varphi} \left[ \frac{m_\delta m_\varphi}{m_\alpha m_\beta m_\gamma} \frac{h^2}{2\pi k_B T} \right]^{3/2} \frac{s_\delta s_\varphi}{s_\alpha s_\beta s_\gamma} \exp \frac{\varepsilon_\alpha + \varepsilon_\beta + \varepsilon_\gamma - \varepsilon_\delta - \varepsilon_\varphi}{k_B T}. \quad (162)$$

Using (161) and (162) we can write the  $A$  equation involving triple collisions and in the first approximation

$$2\mathbf{W}_\alpha^0 \mathbf{W}_\alpha : \nabla \mathbf{v}_0 - S_{3/2}^{(1)} (\mathbf{W}_\alpha^2) \mathbf{V}_\alpha \cdot \frac{\partial}{\partial \mathbf{r}} \ln T + \frac{n}{n_\alpha} \mathbf{V}_\alpha \cdot \mathbf{d}_\alpha \\ + \left\{ \frac{1}{n_\alpha} \int f_\alpha^{(0)} \mathcal{P}_\alpha^{(0)} d\mathbf{v}_\alpha + \frac{2}{3} S_{1/2}^{(1)} (\mathbf{W}_\alpha^2) \sum_{\beta=1}^{\mu} \int f_\alpha^{(0)} \mathcal{P}_\beta^{(0)} S_{1/2}^{(1)} (\mathbf{W}_\beta^2) d\mathbf{v}_\beta - \mathcal{P}_\alpha^{(0)} \right\} = L_\alpha[h^{(1)}], \quad (163)$$

where

$$L_\alpha[h] = \mathcal{L}_\alpha[h] - \frac{1}{n_\alpha} \int f_\alpha^{(0)} \mathcal{L}_\alpha[h] d\mathbf{v}_\alpha - \frac{2}{3n_\alpha} S_{1/2}^{(1)} (\mathbf{W}_\alpha^2) \sum_{\beta=1}^{\mu} \int f_\beta^{(0)} \mathcal{L}_\beta[h] S_{1/2}^{(1)} (\mathbf{W}_\beta^2) d\mathbf{v}_\beta. \quad (164)$$

The operator  $\mathcal{L}_\alpha[h]$  is defined by Eq. (157) and the separate terms in (157) can be written as

$$f_\alpha^{(0)} \mathcal{L}_{\alpha j}[h] = \int f_\alpha^{(0)} f_j^{(0)} (h'_\alpha + h'_j - h_\alpha - h_j) g_{\alpha j} \mathcal{P}_{\alpha j}^{aj} b db d\varepsilon d\mathbf{v}_j, \quad (165)$$

$$f_\alpha^{(0)} {}^r \mathcal{L}_{\alpha\beta}^{\gamma\delta}[h] = \int [\xi_{\alpha\beta}^{\gamma\delta} (h'_\gamma + h'_\delta) - (h_\alpha + h_\beta)] f_\alpha^{(0)} f_\beta^{(0)} g_{\alpha\beta} d({}^r \sigma_{\alpha\beta}^{\gamma\delta}) d\mathbf{v}_\beta, \quad (166)$$

$$f_\alpha^{(0)} {}^r \mathcal{P}_{\alpha\beta}^{\gamma\delta\varphi(0)} = (\xi_{\alpha\beta}^{\gamma\delta\varphi} - 1) (m_\gamma m_\delta m_\varphi)^3 \int f_\alpha^{(0)} f_\beta^{(0)} {}^r \mathcal{W}_{\alpha\beta}^{\gamma\delta\varphi} d\mathbf{v}_\beta d\mathbf{v}'_\gamma d\mathbf{v}'_\delta d\mathbf{v}'_\varphi, \quad (167)$$

$$f_\alpha^{(0)} {}^r \mathcal{L}_{\alpha\beta}^{\gamma\delta\varphi}[h] = (m_\gamma m_\delta m_\varphi)^3 \int [\xi_{\alpha\beta}^{\gamma\delta\varphi} (h'_\gamma + h'_\delta + h'_\varphi) - (h_\alpha + h_\beta)] f_\alpha^{(0)} f_\beta^{(0)} {}^r \mathcal{W}_{\alpha\beta}^{\gamma\delta\varphi} d\mathbf{v}_\beta d\mathbf{v}'_\gamma d\mathbf{v}'_\delta d\mathbf{v}'_\varphi. \quad (168)$$

We only need to indicate the form of the operator  $\mathcal{P}_\alpha^{(0)}$  on the left-hand side of Eq. (163)

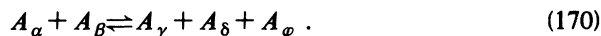
$$f_\alpha^{(0)} \mathcal{P}_\alpha^{(0)} = \frac{1}{2} \sum_r \sum_{\beta, \gamma, \delta} (\xi_{\alpha\beta}^{\gamma\delta} - 1) \int f_\alpha^{(0)} f_\beta^{(0)} g_{\alpha\beta} d({}^r \sigma_{\alpha\beta}^{\gamma\delta}) d\mathbf{v}_\beta \\ + \frac{1}{6} \sum_r \sum_{\beta, \gamma, \delta, \varphi} (\xi_{\alpha\beta}^{\gamma\delta\varphi} - 1) (m_\gamma m_\delta m_\varphi)^3 \int f_\alpha^{(0)} f_\beta^{(0)} {}^r \mathcal{W}_{\alpha\beta}^{\gamma\delta\varphi} d\mathbf{v}_\beta d\mathbf{v}'_\gamma d\mathbf{v}'_\delta d\mathbf{v}'_\varphi. \quad (169)$$

Writing Eqs. (167)–(169) we realize that the main idea is to avoid an explicit description of triple collisions with the help of the principle of microscopic reversibility, which connects in this case binary and triple collisions. However, we have to calculate the resulting bracket expressions.

Let us consider as an example the bracket expressions arising in the description of triple recombination processes:

$$[\mathbf{W}'_\gamma S'_{3/2}(W'^2_\gamma), \mathbf{W}'_\alpha S'_{3/2}(W'^2_\alpha)]_{\alpha\beta}^{\gamma\delta\varphi, r}$$

and corresponding to the reaction



For such a process we write the following conservation laws for energy

$$\begin{aligned} \frac{m_\alpha V_\alpha^2}{2} + \frac{m_\beta V_\beta^2}{2} + \varepsilon_\alpha + \varepsilon_\beta \\ = \frac{m_\gamma V_\gamma'^2}{2} + \frac{m_\delta V_\delta'^2}{2} + \frac{m_\varphi V_\varphi'^2}{2} + \varepsilon_\gamma + \varepsilon_\delta + \varepsilon_\varphi, \end{aligned} \quad (171)$$

momentum

$$m_\alpha \mathbf{V}_\alpha + m_\beta \mathbf{V}_\beta = m_\gamma \mathbf{V}'_\gamma + m_\delta \mathbf{V}'_\delta + m_\varphi \mathbf{V}'_\varphi, \quad (172)$$

and mass

$$m_\alpha + m_\beta = m_\gamma + m_\delta + m_\varphi. \quad (173)$$

Introducing the Jacobi variables, and considering the particles  $A_\delta$  and  $A_\varphi$  as a formal subsystem of the whole system

$$\mathbf{g}'_{\delta\varphi} = \mathbf{V}'_\delta - \mathbf{V}'_\varphi, \quad (174)$$

$$\mathbf{g}'_{\gamma} = \mathbf{V}'_\gamma - \frac{m_\delta \mathbf{V}'_\delta + m_\varphi \mathbf{V}'_\varphi}{m_\delta + m_\varphi}, \quad (175)$$

$$\mathbf{G}_0 = \frac{m_\gamma \mathbf{V}'_\gamma + m_\delta \mathbf{V}'_\delta + m_\varphi \mathbf{V}'_\varphi}{m_\gamma + m_\delta + m_\varphi}. \quad (176)$$

Then after the collision we have

$$\mathbf{V}'_\gamma = \mathbf{G}'_0 + \frac{m_\delta + m_\varphi}{m_\gamma + m_\delta + m_\varphi} \mathbf{g}'_{\gamma}{}^{\delta\varphi}, \quad (177)$$

$$[\mathbf{W}'_\gamma S'_{3/2}(W'^2_\gamma), \mathbf{W}'_\alpha S'_{3/2}(W'^2_\alpha)]_{\alpha\beta}^{\gamma\delta\varphi, r}$$

$$= -\frac{n_\alpha n_\beta}{\pi^3} \frac{3}{16\pi^2} \int \mathbf{W}'_\gamma \cdot \mathbf{W}'_\alpha \exp(-\tilde{G}_0^2 - \tilde{g}_{\alpha\beta}^2) S'_{3/2}(W'^2_\alpha) g_{\alpha\beta} \hat{\sigma}_{\alpha\beta}^{\gamma\delta\varphi} \tilde{g}_{\gamma}{}^{\delta\varphi/2} (\tilde{g}_{\alpha\beta}^2 - \tilde{\varepsilon}) d\tilde{g}_{\gamma}{}^{\delta\varphi} d\mathbf{m} d\mathbf{n} d\tilde{g}_{\alpha\beta} d\tilde{G}_0, \quad (186)$$

where

$$\tilde{\varepsilon} = \frac{\varepsilon}{k_B T}, \quad \tilde{G}_0 = \left[ \frac{m_\alpha + m_\beta}{2k_B T} \right]^{1/2} G_0, \quad \tilde{g}_{\alpha\beta} = \left[ \frac{\mu_{\alpha\beta}}{2k_B T} \right]^{1/2} g_{\alpha\beta}, \quad \tilde{g}_{\gamma}{}^{\delta\varphi} = \left[ \frac{\mu_{\gamma}{}^{\delta\varphi}}{2k_B T} \right]^{1/2} g_{\gamma}{}^{\delta\varphi}.$$

The bracket integral on the right-hand side of Eq. (186) is the coefficient by  $s^p t^q$  in expanding the following expression in an infinite series of  $s$  and  $t$ :

$$\mathbf{V}'_\delta = \mathbf{G}'_0 - \frac{m_\gamma}{m_\gamma + m_\delta + m_\varphi} \mathbf{g}'_{\gamma}{}^{\delta\varphi} + \frac{m_\delta}{m_\delta + m_\varphi} \mathbf{g}'_{\delta\varphi}, \quad (178)$$

$$\mathbf{V}'_\varphi = \mathbf{G}'_0 - \frac{m_\gamma}{m_\gamma + m_\delta + m_\varphi} \mathbf{g}'_{\gamma}{}^{\delta\varphi} - \frac{m_\delta}{m_\delta + m_\varphi} \mathbf{g}'_{\delta\varphi}. \quad (179)$$

Using the energy equation we have

$$\mathbf{g}'_{\delta\varphi} = \mu_{\delta\varphi}^{-1/2} [(\mu_{\alpha\beta} g_{\alpha\beta}^2 - 2\varepsilon) - \mu_{\gamma}{}^{\delta\varphi} g_{\gamma}{}^{\delta\varphi/2}]^{1/2} \quad (180)$$

and then

$$0 \leq g_{\gamma}{}^{\delta\varphi} \leq (\mu_{\gamma}{}^{\delta\varphi})^{-1/2} [\mu_{\alpha\beta} g_{\alpha\beta}^2 - 2\varepsilon]^{1/2}, \quad (181)$$

where

$$\mu_{\gamma}{}^{\delta\varphi} = m_\gamma (m_\delta + m_\varphi) / (m_\gamma + m_\delta + m_\varphi), \quad (182)$$

$$\mu_{\delta\varphi} = m_\delta m_\varphi / (m_\delta + m_\varphi). \quad (183)$$

Let us introduce the cross section  $\hat{\sigma}_{\alpha\beta}^{\gamma\delta\varphi}(g_{\alpha\beta}, g_{\gamma}{}^{\delta\varphi}, \mathbf{m}, \mathbf{n})$ , where  $\mathbf{m} = \mathbf{g}'_{\delta\varphi} / g_{\gamma}{}^{\delta\varphi}$  and  $\mathbf{n} = \mathbf{g}'_{\delta\varphi} / g_{\delta\varphi}$ . The relationship between the previous and present form of the cross section can be written as

$$d(\hat{\sigma}_{\alpha\beta}^{\gamma\delta\varphi}) = \frac{\hat{\sigma}_{\alpha\beta}^{\gamma\delta\varphi}(g_{\alpha\beta}, g_{\gamma}{}^{\delta\varphi}, \mathbf{m}, \mathbf{n})}{\frac{16\pi^2}{3} \left[ \frac{\mu_{\alpha\beta} g_{\alpha\beta}^2 - 2\varepsilon}{\mu_{\gamma}{}^{\delta\varphi}} \right]^{3/2} g_{\gamma}{}^{\delta\varphi/2} dg_{\gamma}{}^{\delta\varphi} d\mathbf{m} d\mathbf{n}}. \quad (184)$$

We have already mentioned the lack of data in theoretical chemistry about the cross section of reactions. Therefore we should introduce any model of inelastic processes. In correspondence with one of these models the reaction may occur with a probability defined by the steric factor  $p_{\alpha\beta}^{\gamma\delta\varphi}$  if the energy of the translational motion of the particles  $\alpha$  and  $\beta$  along the line of centers is higher than the activation energy. However, in all cases we need the deflection angle of the particle path. For the reasonable hypothesis of an isotropic deflection angles for the arising particles, the total cross section is identical to  $\hat{\sigma}_{\alpha\beta}^{\gamma\delta\varphi}(g_{\alpha\beta})$ ,

$$\int d(\hat{\sigma}_{\alpha\beta}^{\gamma\delta\varphi}) = \hat{\sigma}_{\alpha\beta}^{\gamma\delta\varphi}(g_{\alpha\beta}). \quad (185)$$

The bracket expression

$$[\mathbf{W}'_\gamma S'_{3/2}(W'^2_\gamma), \mathbf{W}'_\alpha S'_{3/2}(W'^2_\alpha)]_{\alpha\beta}^{\gamma\delta\varphi, r}$$

can be written in the following form:

$$N = -\frac{n_\alpha n_\beta}{\pi^3} \frac{3}{16\pi^2} [(1-s)(1-t)]^{-5/2} \int \mathbf{W}'_\gamma \cdot \mathbf{W}_\alpha \exp \left[ -(\tilde{G}_0^2 + \tilde{g}_{\alpha\beta}^2) - W_\gamma'^2 \frac{s}{1-s} - W_\alpha'^2 \frac{t}{1-t} \right] g_{\alpha\beta} \times \hat{\sigma}_{\alpha\beta}^{\gamma\delta\varphi} \tilde{g}_\gamma^{\delta\varphi'2} (\tilde{g}_{\alpha\beta}^2 - \bar{\epsilon})^{-3/2} d\tilde{g}_\gamma^{\delta\varphi'} d\mathbf{m} d\mathbf{n} d\tilde{g}_{\alpha\beta} d\tilde{G}_0 \tag{187}$$

and after integration we obtain

$$N = -\frac{n_\alpha n_\beta}{\pi^3} \frac{3}{4\pi} (A_1 B_1 + C_1)^{1/2} Q_1^{-5/2} \int_0^\infty g_{\alpha\beta} \tilde{g}_{\alpha\beta}^2 e^{-g_{\alpha\beta}^2} \int_0^{(\tilde{g}_{\alpha\beta}^2 - \bar{\epsilon})^{1/2}} \tilde{g}_\gamma^{\delta\varphi'2} d\tilde{g}_\gamma^{\delta\varphi'} \times \int d\mathbf{m} d\mathbf{n} \frac{\hat{\sigma}_{\alpha\beta}^{\gamma\delta\varphi}(\mathbf{g}_{\alpha\beta}, \mathbf{g}_\gamma^{\delta\varphi'}, \mathbf{m}, \mathbf{n})}{(\tilde{g}_{\alpha\beta}^2 - \bar{\epsilon})^{3/2}} \left\{ \frac{3}{2} - \frac{(1-A_1s)B_1t}{Q_1} \tilde{g}_{\alpha\beta}^2 - \frac{A_1s(1-B_1t)}{Q_1} \tilde{g}_\gamma^{\delta\varphi'2} + D_1 \left[ 1 + \frac{2(A_1B_1 + C_1)st}{Q_1} \right] \tilde{g}_\gamma^{\delta\varphi'} \tilde{g}_{\alpha\beta} \cos\theta \right\} \times \exp \left\{ -\frac{(1-A_1s)B_1t}{Q_1} \tilde{g}_{\alpha\beta}^2 + \frac{A_1s(B_1t-1)}{Q_1} \tilde{g}_\gamma^{\delta\varphi'2} + D_1 \frac{2(A_1B_1 + C_1)st}{Q_1} \tilde{g}_\gamma^{\delta\varphi'} \tilde{g}_{\alpha\beta} \cos\theta \right\}, \tag{188}$$

where

$$d\mathbf{m} = \sin\theta d\theta d\psi, \quad \tilde{g}_\gamma^{\delta\varphi'} \cdot \tilde{g}_{\alpha\beta} = \tilde{g}_\gamma^{\delta\varphi'} \tilde{g}_{\alpha\beta} \cos\theta, \quad A_1 = M_\delta + M_\varphi, \\ B_1 = M_\beta, \quad C_1 = M_\gamma - M_\beta, \quad D_1 = \left( \frac{A_1 B_1}{A_1 B_1 + C_1} \right)^{1/2}, \quad Q_1 = 1 - (A_1 s + B_1 t + C_1 st),$$

with the usual notation for dimensionless masses

$$M_\alpha = m_\alpha / (m_\alpha + m_\beta), \quad M_\beta = m_\beta / (m_\alpha + m_\beta), \dots$$

Analyzing Eq. (188), we remark that the bracket expression for triple collisions could be written as a function of the following collision integrals:

$$r\Omega_{\alpha\beta}^{\gamma\delta\varphi(m,n)}(k,l) = \frac{3}{32\pi^{5/2}} \int_0^\infty g_{\alpha\beta} \tilde{g}_{\alpha\beta}^{2+2k+m} e^{-g_{\alpha\beta}^2} d\tilde{g}_{\alpha\beta} \times \int_0^{(\tilde{g}_{\alpha\beta}^2 - \bar{\epsilon})^{1/2}} \tilde{g}_\gamma^{\delta\varphi'2+2l+m+n} (\tilde{g}_{\alpha\beta}^2 - \tilde{g}_\gamma^{\delta\varphi'2} - \bar{\epsilon})^{n/2} d\tilde{g}_\gamma^{\delta\varphi'} \times \int \cos^m\theta \sin\theta d\theta d\psi \int \cos^n\theta \hat{\sigma}_{\alpha\beta}^{\gamma\delta\varphi}(\mathbf{g}_{\alpha\beta}, \mathbf{g}_\gamma^{\delta\varphi'}, \mathbf{m}, \mathbf{n}) \sin\theta d\theta d\varphi, \tag{189}$$

where  $d\mathbf{n} = \sin\theta d\theta d\varphi$ . Then we obtain

$$[\mathbf{W}'_\gamma S_{3/2}^{(p)}(W_\gamma'^2), \mathbf{W}_\alpha S_{3/2}^{(q)}(W_\alpha'^2)]_{\alpha\beta}^{\gamma\delta\varphi,r} = \sum_{m=0}^{\min\left\{ \begin{matrix} p \\ q \end{matrix} \right\} + 1} \sum_{k=0}^{q-m+1} \sum_{l=0}^{p-m+1} A_{klm}^{pq} r\Omega_{\alpha\beta}^{\gamma\delta\varphi(m,0)}, \tag{190} \\ A_{klm}^{pq} = -8n_\alpha n_\beta \frac{(-1)^{k+l} 2^m}{k! l! m!} (A_1 B_1 + C_1)^{(m+1)/2} (A_1 B_1)^{m/2} \times [(\frac{3}{2} + k + l + m)\theta_c(p-m-l)\theta_c(q-m-k)F_{klm}^{pq}(A_1, B_1, C_1)] + \frac{m}{2(A_1 B_1 + C_1)} F_{kl(m-1)}^{pq}(A_1, B_1, C_1), \tag{191}$$

where

$$F_{klm}^{pq}(A_1, B_1, C_1) = \sum_{j=\max\left\{ \begin{matrix} 0 \\ p-k-l-m \end{matrix} \right\}}^{p-l-m} \sum_{n=k+m}^{\min\left\{ \begin{matrix} q \\ k+l+m \end{matrix} \right\}} \frac{k! l! (-1)^{p-j+n-k-l} A_1^{p-j-m}}{(p-j-l-m)!(n-k-m)!} \times \frac{B_1^{n-m}}{(k+l+m-p+j)!(k+l+m-n)!} \sum_{j=\max\left\{ \begin{matrix} j \\ q-n \end{matrix} \right\}}^{j+q-n} \frac{(k+l+m+\frac{\epsilon}{2})_i A_1^{i-q+n} B_1^{i-j} C_1^{j+q-n-i}}{(i-q+n)!(i-j)!(j+q-n-i)!}$$



and  $\theta_c$  is the "cutting function"

$$\theta_c = \begin{cases} 0 & \text{if } n < 0 \\ 1 & \text{if } n \geq 0 \end{cases}$$

All the bracket expressions obtained this way can be handled easily using a computer for any  $p, q$ .

The calculation of the transport coefficients with triple collisions will be presented and discussed in future work. We will give as an example the case of partially ionized chemical reacting gas mixture.

### VIII. CONCLUSION

In chemical reacting mixtures of gases, the inelastic collisions can lead to a significant change in the transport properties. The usual evaluation  $\sim \exp(-E/k_B T)$  of such an influence is not valid because in the strict theory this exponential term should be multiplied by a polynomial in  $\bar{E}$  ( $\bar{E} = E/k_B T$ ). If the steric factor is not too small, which is the case for inelastic collisions between an atom and a molecule, the range where we can expect the most significant influence of inelastic collisions is  $\bar{E} \in [3, 7]$ . If for all reactions  $\gamma_p \ll 1$  and  $\bar{E} \gg 1$ , all results received with the help of the generalized Chapman-

Enskog method coincides with the classical results of the theory of Chapman and Enskog. The simplest means to introduce the correction of the classical theory is to use the approximation of Prigogine [7]. For a small value of  $\bar{E}$  it is impossible to use this approximation. In this connection it is interesting to notice that the above-mentioned classical Prigogine problem concerning the perturbation of the Maxwellian function in the model reaction if  $\bar{E} \rightarrow 0$  does not lead to the upper effect of the influence of inelastic collisions on the Maxwellian distribution function. Moreover if  $E = 0$  for this type of reaction, the perturbation of the Maxwellian distribution function practically vanishes [7]. We believe that the calculations for practical use should be based on the GCEM because the physical system may undergo a set of qualitatively different chemical states during the processes. Therefore the investigation of limit cases only leads to many difficulties for practical use. The basic equation of the GCEM is the  $A$  equation obtained by Alexeev. It is a qualitatively linear integral equation in the Boltzmann theory because this equation contains a collision integral considered as an anomalous term in the previous theory of the non-self-adjoint integral operator. This fact has led in the past to a variety of solution methods of this equation. The method given here appears to be more efficient from a practical point of view.

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