ON TRANSPORT PHENOMENA IN REACTING MIXTURES OF GASES

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Abstract

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ON TRANSPORT PHENOMENA IN REACTING MIXTURES OF GASES

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At the present time the theory of transport phenomena in nonreacting mixtures of gases whose molecules may be regarded as point centers of forces has been developed in detail ([1],[2]). The transport coefficients in reacting media can be obtained from the usual formulas of the rigorous kinetic theory of gases in the case when $e^{\varepsilon^*/kT} \gg 1$, where ε^* is the activation energy of the chemical reaction. However, at high temperatures or in the case of sufficiently low activation energies, the number of inelastic collisions of molecules leading to chemical reactions may become comparable in order of magnitude with the number of elastic collisions. In the present work transport phenomena in reacting media are considered. The system of notation used is made as close as possible to the corresponding notation system of the book ([2]). All new notation will be introduced in the text.

Let, in a gas mixture consisting of μ components, there occur l bimolecular homogeneous reactions of the form

$$\sum_{\alpha=1}^{\mu} \nu_{\alpha r} A_\alpha + \sum_{\beta=1}^{\mu} \nu_{\beta r} A_\beta \to \sum_{\gamma=1}^{\mu} \nu_{\gamma r} A_\gamma + \sum_{\delta=1}^{\mu} \nu_{\delta r} A_\delta \quad (r = 1, \dots, l); \tag{1}$$

$\nu_{\alpha r}, \nu_{\beta r}, \nu_{\gamma r}, \nu_{\delta r}$ are stoichiometric coefficients taking the values 0, 1. Components $A_\alpha, A_\beta, A_\gamma, A_\delta$, having the same chemical nature, are regarded as distinct if they have different internal energies $\varepsilon_\alpha, \varepsilon_\beta, \varepsilon_\gamma, \varepsilon_\delta$. The Boltzmann equation can be written in the form

$$\frac{\partial f_\alpha}{\partial t} + \mathbf{v}_\alpha \cdot \frac{\partial f_\alpha}{\partial \mathbf{r}} + \mathbf{F}_\alpha \cdot \frac{\partial f_\alpha}{\partial \mathbf{v}_\alpha} = \left(\frac{\partial_e f_\alpha}{\partial t}\right)_{el} + \left(\frac{\partial_e f_\alpha}{\partial t}\right)_r, \tag{2}$$

where

$$\left(\frac{\partial_e f_\alpha}{\partial t}\right)_{el} = \sum_{j=1}^{\mu} \iiint \left(f'_\alpha f'_j - f_\alpha f_j\right) g_{\alpha j} P_{\alpha j}^{aj} b \, db \, d\varepsilon \, d\mathbf{v}_j, \tag{3}$$

$$\left(\frac{\partial_e f_\alpha}{\partial t}\right)_r = \frac{1}{2}\sum_{r=1}^{l}\sum_{\beta,\gamma,\delta}\iiiint\int\int \left(f'_\gamma f'_\delta - f_\alpha f_\beta\right) g_{\alpha\beta} P_{\alpha\beta}^{\gamma\delta} \sin\theta\, b\, d\theta\, d\varphi\, db\, d\varepsilon\, d\mathbf{v}_\beta. \tag{4}$$

$P_{\alpha\beta}^{r\,\gamma\delta}$ is the probability of the transformation of molecules of species α and β into molecules of species γ, δ in the reaction whose number is r.

Consider a certain hypothetical problem for which the two collision terms on the right-hand side of the Boltzmann equation have the form

$$\frac{\partial f_\alpha}{\partial t} + \mathbf{v}_\alpha \cdot \frac{\partial f_\alpha}{\partial \mathbf{r}} + \mathbf{F}_\alpha \cdot \frac{\partial f_\alpha}{\partial \mathbf{v}_\alpha} = \frac{1}{\varepsilon}\left(\frac{\partial_e f_\alpha}{\partial t}\right)_{el} + \frac{1}{\delta}\left(\frac{\partial_e f_\alpha}{\partial t}\right)_r, \tag{5}$$

where $1/\varepsilon$, $1/\delta$ are, respectively, measures of the frequency of elastic and inelastic collisions. Let $1/\varepsilon \sim 1/\delta$. Represent the distribution function f_α in the form

$$f_\alpha = \sum_{k=0}^{\infty} \varepsilon^k f_\alpha^{(k)}, \quad \alpha = 1, \dots, \mu.$$

The Boltzmann equation in the first approximation has the form

$$f_\alpha^{(0)}\left\{\mathbf{V}_\alpha \cdot \left(W_\alpha^2 - \frac{5}{2}\right)\frac{\partial \ln T}{\partial r} + \frac{n}{n_\alpha}\mathbf{V}_\alpha \cdot \mathbf{d}_\alpha + 2\mathbf{W}_\alpha^0 \mathbf{W}_\alpha : \frac{\partial}{\partial r}\mathbf{v}_0\right\} =$$

$$= \sum_{j=1}^{\mu}\iiint f_\alpha^{(0)} f_j^{(0)}\left(\Phi'_\alpha + \Phi'_j - \Phi_\alpha - \Phi_j\right) g_{\alpha j} P_{\alpha j}^{aj} b\, db\, d\varepsilon\, d\mathbf{v}_j + \tag{6}$$

$$+\frac{1}{2}\sum_{r=1}^{l}\sum_{\beta,\gamma,\delta}\iiint\iiint f_\alpha^{(0)} f_\beta^{(0)}\left(\Phi'_\gamma + \Phi'_\delta - \Phi_\alpha - \Phi_\beta\right) g_{\alpha\beta} P_{\alpha\beta}^{\gamma\delta} \sin\theta\, b\, d\theta\, d\varphi\, d\varepsilon\, d\mathbf{v}_\beta\, db.$$

The supplementary conditions are written in the usual way. The general solution of the system of linear integral equations (6) can be found in the form

$$\Phi_\alpha = -\left(\mathbf{A} \cdot \frac{\partial \ln T}{\partial r}\right) - B_\alpha : \frac{\partial}{\partial r}\mathbf{v}_0 + n\sum_{j=1}^{\mu}\mathbf{C}_\alpha^{(j)} \cdot \mathbf{d}_j. \tag{7}$$

It can be shown that the following variational principle is valid:

$$\{T^{(h,k)}, T^{(h,k)}\} + \frac{1}{2}\{T^{(h,k)}, T^{(h,k)}\}^r \geq \{t^{(h,k)}, t^{(h,k)}\} + \frac{1}{2}\{t^{(h,k)}, t^{(h,k)}\} \geq 0, \tag{8}$$

where

$$\{T^{(h,k)}, T^{(h,k)}\}^r = -\sum_r \sum_{\alpha,\beta,\gamma,\delta} \iiint\iiint \left(T_\alpha^{(h,k)} + T_\beta^{(h,k)}\right) : \left(T_\gamma'^{(h,k)} + T_\delta'^{(h,k)} - T_\alpha^{(h,k)} - T_\beta^{(h,k)}\right) g_{\alpha\beta} P_{\alpha\beta}^{\gamma\delta} f_\alpha^{(0)} f_\beta^{(0)} \sin$$

Here $T_\alpha^{(h,k)}$ is one of the unknown functions $\mathbf{A}_\alpha$, $\mathbf{C}_\alpha^{(h)} - \mathbf{C}_\alpha^{(k)}$, B_α, and $t^{(h,k)}$ are trial functions.

Let us introduce the following bracket expressions for inelastic collisions:

$$[P_\alpha, P_\alpha]_{\alpha\beta}^r = \iiint\iiint P_\alpha : P_\alpha f_\alpha^{(0)} f_\beta^{(0)} P_{\alpha\beta}^{\gamma\delta} g_{\alpha\beta} b \sin\theta \, d\theta \, d\varphi \, d\varepsilon \, db \, d\mathbf{v}_\alpha \, d\mathbf{v}_\beta; \quad (9)$$

$$[P_\alpha, P_\beta]_{\alpha\beta}^r = \iiint\iiint P_\alpha : P_\beta f_\alpha^{(0)} f_\beta^{(0)} P_{\alpha\beta}^{\gamma\delta} g_{\alpha\beta} b \sin\theta \, d\theta \, d\varphi \, d\varepsilon \, db \, d\mathbf{v}_\alpha \, d\mathbf{v}_\beta; \quad (10)$$

$$[P_\alpha, P_\gamma']_{\alpha\beta}^r = -\iiint\iiint P_\alpha : P_\gamma' f_\alpha^{(0)} f_\beta^{(0)} P_{\alpha\beta}^{\gamma\delta} g_{\alpha\beta} b \sin\theta \, d\theta \, d\varphi \, d\varepsilon \, db \, d\mathbf{v}_\alpha \, d\mathbf{v}_\beta. \quad (11)$$

As trial functions we use finite combinations of Sonine polynomials

$$t_\alpha^{(h,k)} = W_\alpha \sum_{m=0}^{\zeta-1} t_{\alpha m}^{(h,k)} S_n^{(m)}(W_\alpha^2).$$

Finding the expansion coefficients $t_{\beta m'}$ reduces to solving the algebraic system of equations

$$\sum_{\beta=1}^{\mu} \sum_{m'=0}^{\zeta-1} Q_{\alpha\beta}^{(m,m')} t_{\beta m'}^{(h,k)} = -R_{\alpha m}^{(h,k)}, \quad (12)$$

where

$$\sum_l \Big(n_\alpha n_l \left\{ \delta_{\alpha\beta} [W_\alpha S_n^{(m)},\, W_\alpha S_n^{(m')}]_{\alpha l} + \delta_{\beta l} [W_\alpha S_n^{(m)},\, W_l S_n^{(m')}]_{\alpha l} \right\} +$$

$$+ \frac{1}{2} \sum_{\gamma,\delta} \sum_r \Big\{ \delta_{\alpha\beta} [W_\alpha S_n^{(m)},\, W_\alpha S_n^{(m')}]_{\alpha l}^r + \delta_{\beta l} [W_\alpha S_n^{(m)},\, W_l S_n^{(m')}]_{\alpha l}^r +$$

$$+2\delta_{\beta\gamma}[W_\alpha S_n^{(m)} W_\alpha S_n^{(m)},\, W'_\gamma S_n^{(m')}]^r_{\alpha l}\Big\}\Big) = Q^{(m,m')}_{\alpha\beta}. \quad (13)$$

It can be shown that the phenomenological relations for the transport coefficients remain the same as in a nonreacting gas mixture; however, the elements of the corresponding determinants change and must be calculated from formulas (13). The bracket expressions of all ···

types. For example, the bracket expression $[\mathbf{W}^0_\alpha \mathbf{W}_\alpha, \mathbf{W}'_\gamma{}^0 \mathbf{W}'_\gamma]^r_{\alpha\beta}$, needed for calculating the viscosity in the first approximation, has the form:

$$[\mathbf{W}^0_\alpha \mathbf{W}_\alpha, \mathbf{W}'_\gamma{}^0 \mathbf{W}'_\gamma]_{\alpha\beta} = -8 n_\alpha n_\beta M_\alpha M_\gamma \Bigg[{}^5/_2\, \Omega^{r\gamma\delta(0)}_{\alpha\beta}(0) + {}^1/_3 \frac{M_\beta M_\delta}{M_\alpha M_\gamma} \varepsilon \Omega^{r\gamma\delta(0)}_{\alpha\beta}(1) - {}^1/_3 \frac{M_\beta M_\delta}{M_\alpha M_\gamma} \Omega^{r\gamma\delta(0)}_{\alpha\beta}(2) - {}^{10}/_3 \sqrt{\frac{M_\beta M_\delta}{M_\alpha M_\gamma}}\, \Omega^{r\gamma\delta(1)}_{\alpha\beta}(0) + \frac{M_\beta M_\delta}{M_\alpha M_\gamma} \Omega^{r\gamma\delta(2)}_{\alpha\beta}(0)\Bigg]; \quad (14)$$

$$\varepsilon = (\varepsilon_\gamma + \varepsilon_\delta - \varepsilon_\alpha - \varepsilon_\beta)/kT$$

is the heat of reaction.

To find the transport coefficients one must calculate collision integrals of three types:

1. $$\Omega^{(l)}_{ij}(r) = \sqrt{\pi} \int e^{-g_{ij}{}^2} g_{ij}^{2r+2} \Phi^{(l)}_{ij}\, dg_{ij}, \quad \Phi^{(l)}_{ij} = \int (1 - \cos^l \chi) D^{ij}_{ij} g_{ij} b\, db.$$

2. $$\Omega^{r\gamma\delta}_{\alpha\beta}(r) = \sqrt{\pi} \int e^{-g_{\alpha\beta}{}^2} g_{\alpha\beta}^{2r+2} \Phi^{r\gamma\delta}_{\alpha\beta}\, dg_{\alpha\beta}, \quad \Phi^{r\gamma\delta}_{\alpha\beta} = \iiint P^{r\gamma\delta}_{\alpha\beta} g_{\alpha\beta} \sin\theta\, b\, db\, d\theta\, d\varphi.$$

3. $$\Omega^{r\gamma\delta(f)}_{\alpha\beta}(h) = \sqrt{\pi} \int e^{-g_{\alpha\beta}{}^2} g_{\alpha\beta}^{2h+f+2} (g^2_{\alpha\beta} - \varepsilon)^{f/2} \Phi^{r\gamma\delta(f)}_{\alpha\beta}\, dg_{\alpha\beta},$$
$$\Phi^{r\gamma\delta(f)}_{\alpha\beta} = \iiint P^{r\gamma\delta}_{\alpha\beta} \times \cos^f \chi\, g_{\alpha\beta} \sin\theta\, b\, db\, d\theta\, d\varphi.$$

The collision integrals were found for two cases. The first theory: the probability of an inelastic collision $P^{r\gamma\delta}_{\alpha\beta}$ is equal to a constant value $p^{r\gamma\delta}_{\alpha\beta}$ when the total translational energy of the relative motion of molecules α and β is greater than ε^*, and $p^{r\gamma\delta}_{\alpha\beta} = 0$ in the opposite case. According to the second theory, the probability of an inelastic collision is assumed to be equal to a constant value when the translational energy of the relative motion of the molecules along the line of centers is greater than $\tilde{\varepsilon}^*$. For example,

$$\Omega_{\alpha\beta}^{r\gamma\delta}(3) = \pi\sqrt{\frac{2\pi kT}{\mu}}\, p_{\alpha\beta}^{r\gamma\delta}\sigma_{\alpha\beta}^2 e^{-g_{\alpha\beta}{}^{*2}} \left(g_{\alpha\beta}^{*8} + 4g_{\alpha\beta}^{*6} + 12g_{\alpha\beta}^{*4} + 24g_{\alpha\beta}^{*2} + 24\right)$$

according to the first theory, and according to the second theory

$$\Omega_{\alpha\beta}^{r\gamma\delta}(3) = \pi\sqrt{\frac{2\pi kT}{\mu}}\, p_{\alpha\beta}^{r\gamma\delta}\sigma_{\alpha\beta}^2 e^{-g_{\alpha\beta}{}^{*2}} \left(g_{\alpha\beta}^{*6} + 6g_{\alpha\beta}^{*4} + 18g_{\alpha\beta}^{*2} + 24\right),$$

where $g_{\alpha\beta}^{*2} = \tilde{\varepsilon}^*/kT$.

Let us consider an example. Suppose that in a gas consisting of molecules N and O_2 the reaction

$$N + O_2 \to NO + O$$

begins to proceed in such a way that, at the initial moment, the concentrations of NO and O may be neglected. Let us find the viscosity of such a mixture. We assume that the concentrations $n_N/n = n_{O_2}/n = 0.5$, $T = 5000;\ 8000°$K. It is known ([3]) that the activation energy of the reaction $NO + O \to N + O_2$ is 40.5 kcal/mole, and the heat of reaction is -32.5 kcal/mole; $p_{NO,O}^{N,O_2} \sim 0.1 \div 1$. Further, we assume that $p_{N,O_2}^{N,O_2} = p_{N,O_2}^{NO,O} = 1$. Then at $T = 5000°$K, according to the classical theory (hard-sphere model), we have $\eta = 0.8559 \cdot 10^{-3}$ g/cm $\cdot$ sec, while with account of inelastic collisions according to the first theory $\eta_1 = 1.4989 \cdot 10^{-3}$ g/cm $\cdot$ sec, and according to the second theory $\eta_2 = 1.3077 \cdot 10^{-3}$ g/cm $\cdot$ sec. Correspondingly, at $T = 8000°$K,

$$\eta = 1.0825 \cdot 10^{-3} \text{ g/cm}\cdot\text{sec}, \quad \eta_1 = 1.8450 \cdot 10^{-3} \text{ g/cm}\cdot\text{sec}, \quad \eta_2 = 1.7755 \cdot 10^{-3} \text{ g/cm}\cdot\text{sec}.$$

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Note: Figure translations are in progress. See original paper for figures.