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THE KINETIC PHENOMENA IN NONISOTHERMAL MOTION OF A BINARY GAS MIXTURE THROUGH A PLANE CHANNEL

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Abstract—Based on a linearized kinetic equation (the McCormack model), the theory of motion of binary gas mixtures in a plane channel owing to the temperature, concentration and pressure gradients is established. As a result, the relationships are obtained showing the dependence of the thermal, diffusional and numerical mean fluxes on the Knudsen number and concentration of the components. The calculations are carried out for the mixtures He–Ar, He–Ne, Ne–Ar with the use of three models of intermolecular potential: 'solid spheres', 'Maxwell molecules', Lennard–Jones (6–12)-potential. Based on the Prigogine theorem, the effects characteristic of gas mixtures (thermal diffusion and pressure diffusion separation of mixtures, diffusional baroeffect, thermomolecular pressure difference) are considered. The theory is compared with experiment.

NOMENCLATURE

f_i	distribution function of ith species molecules
J_i	diffusional mass flux of ith species
m_i	mass of ith species molecule
n_i	number density of ith species
p	mixture pressure
P_{ixz}	shear stress tensor of ith species
q_i	heat flux of ith species
Q	heat flux in a mixture determined relative to the numerical mean velocity U
T	mixture temperature
U	numerical mean velocity of mixture
U_i	mean velocity of ith species
$\mathbf{v}_i$	velocity vector of i molecules
y_i	molar concentration of ith species.

Greek symbols

α_T	thermal diffusion factor
α_p	pressure diffusion factor
γ_{ij}	frequency of collisions between molecules of ith and jth species
δ_i	gas rarefaction parameter inversely proportional to the Knudsen number
σ	entropy production.

INTRODUCTION

IN THE majority of works dealing with the theory of motion of gas mixtures in channels the results obtained are restricted to small Knudsen numbers [1–5]. Therefore, the discussions of results were virtually reduced to the analysis of hydrodynamic-type equations, diffusional slip and pressure diffusion factor. Few attempts to describe the isothermal motion of binary gas mixtures in a cylindrical channel at arbitrary Knudsen numbers were based on the use of the kinetic equation involving the Hamel model of the collision integral [6–8]. As pointed out in ref. [4], the Hamel model equation does not incorporate a sufficient set of free parameters, and, therefore, on proceeding to the hydrodynamic limit does not give an adequate description of the mixture diffusion and viscosity. Moreover, this equation cannot be used to describe nonisothermal gas motion, since it does not, in principle, account for thermal diffusion.

The present work deals with the study of binary gas mixture motion in a plane channel owing to the temperature, concentration and pressure gradients at arbitrary Knudsen numbers. The calculation is based on the approximating third-order kinetic equation [9] providing an accurate description of transport processes in proceeding to the hydrodynamic limit and admitting the use of an arbitrary intermolecular interaction potential. It is shown that numerical mean, diffusional and heat fluxes are determined by nine kinetic coefficients, with the cross coefficients being connected by the Onsager reciprocity relations at any Knudsen numbers. Applying the Prigogine theorem on the stationary states [10], the diffusional pressure effect, thermal and pressure diffusion separation of the mixture, and thermomolecular pressure are considered. The theory is compared with experiment.

INTEGRAL-MOMENT EQUATIONS

Consider a binary gas mixture between infinite parallel planes located in $X = \pm d/2$ (d is the distance between the plates). The gas is excited by the longitudinal gradients of temperature T, molar concentration of the ith species y_i and of pressure p, all directed along the Z-axis. It is assumed that the gradients are small and the temperatures of the mixture components at any fixed channel section are the same. Then the distribution functions of each of the components differ little from the equilibrium functions and can be written as

$$f_i = f_{i0}\left[1+\frac{Z}{p}\frac{\mathrm{d}p}{\mathrm{d}Z}+\frac{Z}{y_i}\frac{\mathrm{d}y_i}{\mathrm{d}Z} + \left(c_i^2-\frac{5}{2}\right)\frac{Z}{T}\frac{\mathrm{d}T}{\mathrm{d}Z}+h_i(X,\mathbf{c}_i)\right], \quad (1)$$

where

$$f_{i0} = n_{i0}\left(\frac{m_i}{2\pi kT_0}\right)^{3/2}\exp(-c_i^2), \quad \mathbf{c}_i = \left(\frac{m_i}{2kT_0}\right)^{1/2}\mathbf{v}_i,$$

n_{i0}, m_i are the mean density and mass of the ith kind molecules, T_0 is the mean gas temperature, and $\mathbf{v}_i$ is the velocity vector of the ith component molecules.

The perturbation function h_i of the ith component is the solution of the system of approximating kinetic equations [9], which in dimensionless form are written as

$$\begin{aligned}
&c_{ix}\frac{\partial h_i}{\partial x}+c_{iz}\left[\nu+\mu_i+\left(c_i^2-\frac{5}{2}\right)\tau\right]\\
&=\delta_i\left\{-h_i+2c_{iz}\left[u_i+\varphi_{ij}^{(1)}\left(u_i-\left(\frac{m_i}{m_j}\right)^{1/2}u_j\right)\right.\right.\\
&\qquad\left.-\varphi_{ij}^{(2)}\left(H_i-\left(\frac{m_i}{m_j}\right)^{3/2}H_j\right)\right]\\
&\qquad+4c_{ix}c_{iz}[(\gamma_{ij}^{*}-\varphi_{ij}^{(3)})p_{ixz}+\varphi_{ij}^{(4)}p_{jxz}]\\
&\qquad+\frac{8}{5}c_{iz}\left(c_i^2-\frac{5}{2}\right)\left[(1-\varphi_{ii}^{(5)}+\varphi_{ii}^{(6)}-\varphi_{ij}^{(5)})H_i+\varphi_{ij}^{(6)}H_j\right.\\
&\qquad\left.\left.-\frac{5}{8}\varphi_{ij}^{(2)}\left(u_i-\left(\frac{m_i}{m_j}\right)^{1/2}u_j\right)\right]\right\},
\end{aligned}$$

$$(i,j) = 1,2; \quad i \neq j. \tag{2}$$

Here, the following notation is used

$$u_i = \left(\frac{m_i}{2kT_0}\right)^{1/2}U_i = \pi^{-3/2}\int c_{iz}\exp(-c_i^2)h_i\,\mathrm{d}\mathbf{c}_i,$$

$$p_{ixz} = \frac{P_{ixz}}{2p_i} = \pi^{-3/2}\int c_{ix}c_{iz}\exp(-c_i^2)h_i\,\mathrm{d}\mathbf{c}_i,$$

$$H_i = \left(\frac{m_i}{2kT_0}\right)^{1/2}\frac{1}{2p_i}\left(q_i-\frac{5}{2}\frac{kT_0}{m_i}J_i\right)$$

$$= \frac{1}{2}\pi^{-3/2}\int c_{iz}\left(c_i^2-\frac{5}{2}\right)\exp(-c_i^2)h_i\,\mathrm{d}\mathbf{c}_i,$$

$$x = \frac{X}{d}, \quad \delta_i = (\gamma_{ii}+\gamma_{ij})\left(\frac{m_i}{2kT_0}\right)^{1/2}d,$$

$$\nu = \frac{\mathrm{d}\ln p}{\mathrm{d}(Z/d)}, \quad \tau = \frac{\mathrm{d}\ln T}{\mathrm{d}(Z/d)}, \quad \mu_i = \frac{\mathrm{d}\ln y_i}{\mathrm{d}(Z/d)},$$

$$\gamma_{ij}^{*} = \frac{\gamma_{ij}}{\gamma_{ij}+\gamma_{ii}}, \quad \varphi_{ij}^{(n)} = \frac{\nu_{ij}^{(n)}}{\gamma_{ii}+\gamma_{ij}}, \quad \varphi_{ii}^{(n)} = \frac{\nu_{ii}^{(n)}}{\gamma_{ii}+\gamma_{ij}}, \tag{3}$$

where U_i is the macroscopic velocity of the ith component; p_i, p_{ixz} are the partial pressure and shear stress tensor, respectively; q_i, J_i are the thermal and mass diffusional fluxes of the ith component, respectively; γ_{ii}, γ_{ij} are the frequencies of collisions between similar and dissimilar molecules; δ_i is the rarefaction gas parameter inversely proportional to the Knudsen number; the values of $\nu_{ij}^{(n)}$ depending on concentrations, molecular weights of the components and Chapman–Cowling integrals are given in ref. [9].

The frequency of collisions between similar molecules is governed by the expression

$$\gamma_{ii} = \frac{8}{5}n_{i0}\Omega_{ii}^{(2,2)}, \tag{4}$$

while the frequency of collisions between dissimilar molecules, γ_{ij} $(i \neq j)$, has been chosen following the recommendations given in ref. [9].

That the boundary conditions for equation (2) could be adopted, it is necessary to account for the discontinuous nature of the distribution function in the domain of velocities

$$h_i = \frac{1}{2}[(1+\operatorname{sign}c_{ix})h_i^{+}+(1-\operatorname{sign}c_{ix})h_i^{-}], \tag{5}$$

where $\operatorname{sign}(t) = \pm 1$ at $t \gtrless 0$.

The representation of the distribution function in the form of equation (5) is convenient because it allows the distinction between the distribution functions of the incident and reflected molecules on the bounding surfaces.

It is assumed that the molecules that have arrived at the boundary surface experience complete accommodation and scatter in a diffuse manner. The molecules emitted from the surface are distributed according to Maxwell's law. Then for each surface, bounding the gas, the following boundary conditions can be written as

$$h_i\left(x = -\frac{1}{2}\operatorname{sign}c_{ix}, \mathbf{c}_i\right) = 0. \tag{6}$$

With equations (5) and (6) taken into account, the kinetic equation (2) can be written in integral form. Substituting the expression obtained for h_i into the definitions of macroscopic quantities (3), it is not difficult to obtain a system of integral-moment equations of the form

$$\begin{aligned}
u_i = &-\frac{1}{2\sqrt{\pi}}\int_{-1/2}^{1/2}\left[(\nu+\mu_i)I_{-1}+\tau\left(I_1-\frac{1}{2}I_{-1}\right)\right]\mathrm{d}x'\\
&+\frac{\delta_i}{\sqrt{\pi}}\int_{-1/2}^{1/2}\left\{\left[(1-\varphi_{ij}^{(1)})I_{-1}\right.\right.\\
&\left.-\frac{1}{2}\varphi_{ij}^{(2)}\left(I_1-\frac{1}{2}I_{-1}\right)\right]u_i\\
&+\left(\frac{m_i}{m_j}\right)^{1/2}\left[\varphi_{ij}^{(1)}I_{-1}+\frac{1}{2}\varphi_{ij}^{(2)}\left(I_1-\frac{1}{2}I_{-1}\right)\right]u_j\\
&+2\operatorname{sign}(x-x')[(\gamma_{ij}^{*}-\varphi_{ij}^{(3)})p_{ixz}+\varphi_{ij}^{(4)}p_{jxz}]I_0\\
&-\left[\varphi_{ij}^{(2)}I_{-1}-\frac{4}{5}(1-\varphi_{ii}^{(5)}+\varphi_{ii}^{(6)}\right.\\
&\left.-\varphi_{ij}^{(5)})\left(I_1-\frac{1}{2}I_{-1}\right)\right]H_i+\left[\varphi_{ij}^{(2)}\left(\frac{m_i}{m_j}\right)^{3/2}I_{-1}\right.\\
&\left.\left.+\frac{4}{5}\varphi_{ij}^{(6)}\left(I_1-\frac{1}{2}I_{-1}\right)\right]H_j\right\}\mathrm{d}x',
\end{aligned}$$

$$
\begin{aligned}
p_{ixz} = &-\frac{1}{2\sqrt{\pi}}\int_{-1/2}^{1/2}\left[(\nu+\mu_i)I_0+\tau\left(I_2-\frac{1}{2}I_0\right)\right] \\
&\times \operatorname{sign}(x-x')\,\mathrm{d}x'+\frac{\delta_i}{\sqrt{\pi}}\int_{-1/2}^{1/2}\left\{\left[(1-\varphi_{ij}^{(1)})I_0\right.\right. \\
&\left.-\frac{1}{2}\varphi_{ij}^{(2)}\left(I_2-\frac{1}{2}I_0\right)\right]u_i+\left(\frac{m_i}{m_j}\right)^{1/2}\left[\varphi_{ij}^{(1)}I_0\right. \\
&\left.+\frac{1}{2}\varphi_{ij}^{(2)}\left(I_2-\frac{1}{2}I_0\right)\right]u_j+2\operatorname{sign}(x-x') \\
&\times[(\gamma_{ij}^{*}-\varphi_{ij}^{(3)})p_{ixz}+\varphi_{ij}^{(4)}p_{jxz}]I_1-\left[\varphi_{ij}^{(2)}I_0\right. \\
&\left.-\frac{4}{5}(1-\varphi_{ii}^{(5)}+\varphi_{ii}^{(6)}-\varphi_{ij}^{(5)})\left(I_2-\frac{1}{2}I_0\right)\right]H_i \\
&\left.+\left[\left(\frac{m_i}{m_j}\right)^{3/2}\varphi_{ij}^{(2)}I_0+\frac{4}{5}\varphi_{ij}^{(6)}\left(I_2-\frac{1}{2}I_0\right)\right]H_j\right\} \\
&\times \operatorname{sign}(x-x')\,\mathrm{d}x', \\
H_i = &-\frac{1}{4\sqrt{\pi}}\int_{-1/2}^{1/2}\left[(\nu+\mu_i)\left(I_1-\frac{1}{2}I_{-1}\right)\right. \\
&\left.+\tau\left(I_3-I_1+\frac{9}{4}I_{-1}\right)\right]\mathrm{d}x'+\frac{\delta_i}{2\sqrt{\pi}} \\
&\times\int_{-1/2}^{1/2}\left\{\left[(1-\varphi_{ij}^{(1)})\left(I_1-\frac{1}{2}I_{-1}\right)\right.\right. \\
&\left.-\frac{1}{2}\varphi_{ij}^{(2)}\left(I_3-I_1+\frac{9}{4}I_{-1}\right)\right]u_i+\left(\frac{m_i}{m_j}\right)^{1/2} \\
&\times\left[\varphi_{ij}^{(1)}\left(I_1-\frac{1}{2}I_{-1}\right)+\frac{1}{2}\varphi_{ij}^{(2)}\left(I_3-I_1+\frac{9}{4}I_{-1}\right)\right]u_j \\
&+2\operatorname{sign}(x-x')[(\gamma_{ij}^{*}-\varphi_{ij}^{(3)})p_{ixz} \\
&+\varphi_{ij}^{(4)}p_{jxz}]\left(I_2-\frac{1}{2}I_0\right)-\left[\varphi_{ij}^{(2)}\left(I_1-\frac{1}{2}I_{-1}\right)\right. \\
&\left.-\frac{4}{5}(1-\varphi_{ii}^{(5)}+\varphi_{ii}^{(6)}-\varphi_{ij}^{(5)})\left(I_3-I_1+\frac{9}{4}I_{-1}\right)\right]H_i \\
&+\left[\left(\frac{m_i}{m_j}\right)^{3/2}\varphi_{ij}^{(2)}\left(I_1-\frac{1}{2}I_{-1}\right)+\frac{4}{5}\varphi_{ij}^{(6)}\right. \\
&\left.\left.\times\left(I_3-I_1+\frac{9}{4}I_{-1}\right)\right]H_j\right\}\mathrm{d}x'; \\
I_n(t) = &\int_0^{\infty}c^n\exp\left(-c^2-\frac{t}{c}\right)\mathrm{d}c,\quad i\neq j. \qquad (7)
\end{aligned}
$$

The argument of the function I_n is $\delta_i|x-x'|$.

From the structure of the absolute terms of the linear integral equations (7), it follows that the solution of the system is

$$
\begin{aligned}
u_i &= u_i^{(p)}\nu+u_i^{(c)}\mu_i+u_i^{(T)}\tau, \\
p_{ixz} &= p_{ixz}^{(p)}\nu+p_{ixz}^{(c)}\mu_i+p_{ixz}^{(T)}\tau, \\
H_i &= H_i^{(p)}\nu+H_i^{(c)}\mu_i+H_i^{(T)}\tau. \qquad (8)
\end{aligned}
$$

Substitution of expressions (8) into equations (7) and equation of terms in identical gradients lead to the splitting of system (7) into three independent systems of integral equations for the quantities $u_i^{(k)}$, $p_{ixz}^{(k)}$, $H_i^{(k)}$ $(k = p, c, T)$.

KINETIC COEFFICIENTS

The integral-moment equations (7) involve the local values of macroparameters. However, the following quantities, averaged over the channel cross-section, are virtually of practical interest: the heat flux Q (determined relative to the coordinate system moving with numerical mean mixture velocity), diffusional flux and numerical mean mixture velocity U. It is not difficult to show that the following relations will be valid

$$
\begin{aligned}
\langle Q\rangle &= p\left(\frac{2kT_0}{m_1}\right)^{1/2} \\
&\quad\times\left(l_{11}\frac{\mathrm{d}\ln T}{\mathrm{d}Z}+l_{12}\frac{\mathrm{d}y}{\mathrm{d}Z}+l_{13}\frac{\mathrm{d}\ln p}{\mathrm{d}Z}\right), \\
\langle U_1-U_2\rangle &= \left(\frac{2kT_0}{m_1}\right)^{1/2} \\
&\quad\times\left(l_{21}\frac{\mathrm{d}\ln T}{\mathrm{d}Z}+l_{22}\frac{\mathrm{d}y}{\mathrm{d}Z}+l_{23}\frac{\mathrm{d}\ln p}{\mathrm{d}Z}\right), \\
\langle U\rangle &= y\langle U_1\rangle+(1-y)\langle U_2\rangle \\
&= \left(\frac{2kT_0}{m_1}\right)^{1/2}\left(l_{31}\frac{\mathrm{d}\ln T}{\mathrm{d}Z}+l_{32}\frac{\mathrm{d}y}{\mathrm{d}Z}+l_{33}\frac{\mathrm{d}\ln p}{\mathrm{d}Z}\right),
\end{aligned}
\qquad (9)
$$

where the kinetic coefficients have the form

$$
\begin{aligned}
l_{11} &= 2\left[y\langle H_1^{(T)}\rangle+(1-y)\left(\frac{m_1}{m_2}\right)^{1/2}\langle H_2^{(T)}\rangle\right], \\
l_{12} &= 2\left[\langle H_1^{(c)}\rangle-\left(\frac{m_1}{m_2}\right)^{1/2}\langle H_2^{(c)}\rangle\right], \\
l_{13} &= 2\left[y\langle H_1^{(p)}\rangle+(1-y)\left(\frac{m_1}{m_2}\right)^{1/2}\langle H_2^{(p)}\rangle\right], \\
l_{21} &= \langle u_1^{(T)}\rangle-\left(\frac{m_1}{m_2}\right)^{1/2}\langle u_2^{(T)}\rangle, \\
l_{22} &= \frac{1}{y}\langle u_1^{(c)}\rangle+\frac{1}{1-y}\left(\frac{m_1}{m_2}\right)^{1/2}\langle u_2^{(c)}\rangle, \\
l_{23} &= \langle u_1^{(p)}\rangle-\left(\frac{m_1}{m_2}\right)^{1/2}\langle u_2^{(p)}\rangle, \\
l_{31} &= y\langle u_1^{(T)}\rangle+(1-y)\left(\frac{m_1}{m_2}\right)^{1/2}\langle u_2^{(T)}\rangle, \\
l_{32} &= \langle u_1^{(c)}\rangle-\left(\frac{m_1}{m_2}\right)^{1/2}\cdot\langle u_2^{(c)}\rangle, \\
l_{33} &= y\langle u_1^{(p)}\rangle+(1-y)\left(\frac{m_1}{m_2}\right)^{1/2}\langle u_2^{(p)}\rangle, \\
y &= y_1 = 1-y_2. \qquad (10)
\end{aligned}
$$

The angular brackets mean averaging over the channel height.

The coefficient l_{11} characterizes the heat flux in a gas at rest and is due to the temperature gradient; l_{12} is the diffusional thermoeffect; l_{13} is the convective heat transfer together with a moving gas under the action of the pressure gradient; the coefficients l_{21}, l_{22}, l_{23} characterize thermal diffusion, ordinary diffusion in a binary gas mixture owing to the concentration gradient and barodiffusion; the coefficients l_{31}, l_{32}, l_{33} characterize the thermal creep, numerical mean gas flow owing to the concentration gradient and the Poiseuille binary gas flow.

It should be noted that for the explanation of the physical meaning of some kinetic coefficients, the terminology was used which is adopted in the Chapman–Enskog theory for an infinite gas. In the present case the coefficients (10) depend not only on the law of mutual interaction of molecules but also on their interaction with the bounding surface, and also on the geometrical form of the channel. The two latter factors are the determining ones at intermediate and large Knudsen numbers. Therefore, the diffusional thermoeffect in the present problem can be interpreted, for example, as an ordinary Dufour effect only in the limit of small Knudsen numbers ($\delta_i \to \infty$).

The basic task of the theory is the evaluation of the kinetic coefficients (10). For this, it is necessary to solve a system of integral-moment equations (7).

METHOD OF SOLUTION

In choosing an approximate method for the solution of the system of linear Fredholm-type second-order integral equations (7), it is necessary to take into account the fact that the kinetic equations (10), averaged over the channel cross-section, are eventually of interest rather than the profiles of gas flows moving in the channel. From this it follows that the approximate method should converge in the mean. The requirement is satisfied by the Galerkin method which has proved a good means of describing one-component gas motion [11]. For its realization, it is necessary to specify a system of base functions. The problem symmetry and the behaviour of the unknown quantities in the hydrodynamic limit ($\delta_i \gg 1$) show that in the N-approximation the following approximation can be chosen

$$u_i^{(k)} = \sum_{l=0}^{N} A_{il}^{(k)} x^{2l}, \quad p_{ixz}^{(k)} = \sum_{l=1}^{N} B_{il}^{(k)} x^{2l-1},$$
$$H_i^{(k)} = \sum_{l=1}^{N} C_{il}^{(k)} x^{2l-2}; \quad i = 1,2; \quad k = p, c, T. \tag{11}$$

That the expansion coefficients could be determined, it is necessary to substitute expressions (11) into equations (7) and to require the orthogonality of the resulting expressions in each of the base functions. In this case, the scalar product of any two functions f and g has the form

$$(f, g) = \int_{-1/2}^{1/2} f(x)g(x)\,\mathrm{d}x.$$

As a result, we obtain three independent systems, each including $2(3N+1)$ linear algebraic equations for the determination of the coefficients $A_{il}^{(k)}$, $B_{il}^{(k)}$, $C_{il}^{(k)}$.

It was shown for the case of a one-component gas [11] that in the first approximation ($N = 1$) the results obtained by the Galerkin method have an accuracy not lower than 1.5%. This very rapid convergence of the method may apparently be also expected for gas mixtures. In fact, at $N = 1$ the approximations (11) give an exact description of the flow profiles at small Knudsen numbers ($\delta_i \gg 1$), while the motion of gas at large Knudsen numbers ($\delta_i \ll 1$) is fully described by the absolute terms of the integral-moment equations (7).

In the present work, only the first approximation from the system (11) has been considered. The formalism of the Galerkin method for this case is given in detail in ref. [11]. Full expressions for the kinetic coefficients (10) have a cumbersome form and are not given here.

DISCUSSION OF RESULTS

The asymptotic analysis has shown that in the case of a nearly free-molecular regime ($\delta_i \ll 1$) the solution has a simple form

$$\langle H_i^{(T)} \rangle = -\frac{9}{2}\langle H_i^{(p)} \rangle = -\frac{9}{2}\langle H_i^{(c)} \rangle = -\frac{9}{16\sqrt{\pi}} \ln \delta_i,$$
$$\langle u_i^{(T)} \rangle = -\frac{1}{2}\langle u_i^{(p)} \rangle = -\frac{1}{2}\langle u_i^{(c)} \rangle = \frac{1}{4\sqrt{\pi}} \ln \delta_i. \tag{12}$$

Thus, at $\delta_i \to 0$ the absolute value of all the kinetic coefficients (10) increases by logarithmic law. This is explained by the degeneracy of the channel geometry.

In the diffusional regime ($\delta_i \gg 1$), the results can be presented in the form of the ratio between the eighth-order determinants the elements of which involve the Chapman–Cowling integrals. At $\delta_i \to \infty$, the quantity l_{33}, which characterizes the Poiseuille flow, increases proportionally to δ_i, while the values of the remaining kinetic coefficients decrease generally as δ_i^{-1}.

The calculations were carried out for the three pairs of gases (He–Ar, He–Ne, Ne–Ar) on a BESM-6 computer with an accuracy not lower than 0.1%. Three model potentials of the intermolecular interaction were used: solid spheres, Maxwell molecules and Lennard–Jones (6–12)-potential. The potential parameters for pure gases were taken from experiments on the measurement of viscosity coefficients [12], while for the binary mixtures they were calculated from the combination rule. It was also assumed that the gas temperature was equal to 300 K. The respective values of the Chapman–Cowling integrals are given in ref. [12].

As a result of calculations, the dependence of the kinetic coefficients on the rarefaction parameter δ_i, concentration y and on the form of intermolecular potential was investigated. It has been established that at any values of the variable parameters the Onsager reciprocity relations are fulfilled, i.e. $l_{\alpha\beta} = l_{\beta\alpha}$ at $\alpha \neq \beta$. This agrees with the basic implications of the irreversible thermodynamics for discontinuous systems [10].

The dependence of the value of kinetic coefficients on the form of the intermolecular potential makes itself felt most appreciably in the diffusion regime ($\delta_i \gg 1$). Particular sensitivity to the form of the potential is exhibited by the coefficients $l_{21} = l_{12}$ responsible for thermal diffusion and diffusional thermoeffect. The maximum divergence between the results, obtained for the solid spheres and Lennard–Jones (6–12)-potentials for $l_{21} = l_{12}$ is up to 50%, while for the remaining coefficients it does not exceed 20%.

Figure 1 shows the dependence of the kinetic coefficients on the rarefaction parameter δ_i and concentration y of the light component for the He–Ar mixture.

At any fixed value of concentration, the dependence of the Poiseuille flow (l_{33}) on the rarefaction parameter δ_1 has a characteristic minimum known in the kinetic theory of gases as the Knudsen paradox. The remaining kinetic coefficients decrease monotonously with an increase of the parameter δ_1. It is interesting to note that in the diffusional regime ($\delta_1 \gg 1$), the values of thermal diffusion (l_{21}) and diffusional thermoeffect ($l_{12} = l_{21}$) for a mixture of Maxwell molecules decrease, with an increasing δ_1, as δ_1^{-2}, while for any other intermolecular potential, as δ_1^{-1}. This result agrees with the conclusions of the Chapman–Enskog theory [12].

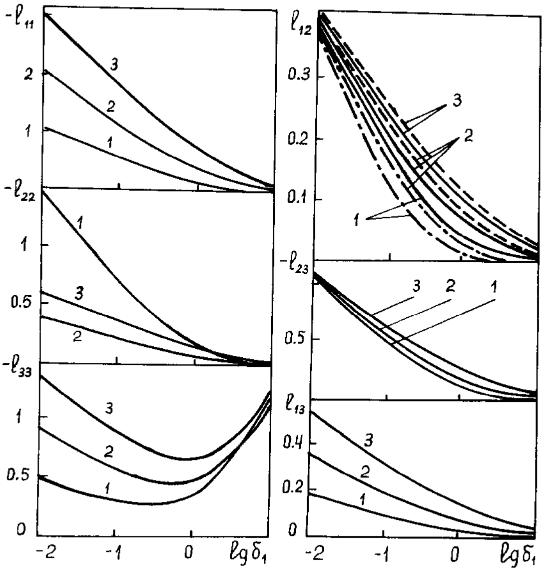

FIG. 1. The dependence of the kinetic coefficients on the rarefaction parameter δ_1 for the pair of gases He–Ar; ——, the Lennard–Jones (6–12)-potential; – – – –, 'solid spheres'; —·—·-, 'Maxwell molecules'; (1) $y = 0.1$; (2) $y = 0.5$; (3) $y = 0.9$.

At any fixed value of the rarefaction parameter δ_1, the values of the kinetic coefficients $l_{11}, l_{12} = l_{21}, l_{13} = l_{31}$ and $l_{23} = l_{32}$ increase monotonously with an increasing concentration y of the light component. It is evident that an increase of the fraction of light, and consequently more volatile, molecules leads to an increase of the heat flux. The coefficient l_{22} as a function of concentration has a pronounced minimum. As shown by calculations, depending on the concentration of He–Ne and He–Ar, the coefficient l_{33} has the minimum at $\delta_1 > 5$ (for Ne–Ar the dependence is monotonous). The authors failed to give a physical explanation of this dependence of the Poiseuille flow on concentration.

When the kinetic coefficients are known, then on the basis of the theorems of the irreversible thermodynamics for discontinuous systems [10] one can study all the kinetic phenomena which may take place when gas mixtures move through the channel. Below, the most typical phenomena are considered.

For a binary gas mixture the entropy production has the form [10]

$$\sigma = \langle Q \rangle X_1 + \langle U_1 - U_2 \rangle p X_2 + \langle U \rangle X_3, \tag{13}$$

where

$$X_1 = \frac{1}{T^2}\frac{dT}{dZ}, \quad X_2 = \frac{1}{T}\frac{dy}{dZ}, \quad X_3 = \frac{1}{T}\frac{dp}{dZ}. \tag{14}$$

The flows, conjugate of the thermodynamic forces (14), are written down as

$$\begin{aligned} \langle Q \rangle &= L_{11}X_1 + L_{12}X_2 + L_{13}X_3, \\ \langle U_1 - U_2 \rangle p &= L_{21}X_1 + L_{22}X_2 + L_{33}X_3, \\ \langle U \rangle &= L_{31}X_1 + L_{32}X_2 + L_{33}X_3. \end{aligned} \tag{15}$$

The comparison of expressions (15) and (9) yields

$$\begin{aligned} &L_{11} = apTl_{11}, \quad L_{12} = apTl_{12}, \quad L_{13} = aTl_{13}, \\ &L_{21} = apTl_{21}, \quad L_{22} = apTl_{22}, \quad L_{23} = aTl_{23}, \\ &L_{31} = aTl_{31}, \quad L_{32} = aTl_{32}, \quad L_{33} = a\frac{T}{p}l_{33}, \\ &a = \left(\frac{2kT_0}{m_1}\right)^{1/2}. \end{aligned} \tag{16}$$

The Onsager reciprocity relations are fulfilled

$$L_{\alpha\beta} = L_{\beta\alpha} \quad \text{or} \quad l_{\alpha\beta} = l_{\beta\alpha} \quad \text{at} \quad \alpha \neq \beta.$$

All subsequent considerations will be based on the Prigogine theorem on the stationary states [10]. The essence of the theorem is that if in the system with the minimal entropy production there are N thermodynamic forces K of which are fixed, then the fluxes, which are conjugate of the remainder $N - K$ forces, are equal to zero.

Below, we will consider some specific cases.

(1) The pressure along the channel does not change ($X_3 = 0$) and the temperature gradient is fixed

($X_1 = \text{const.}$). Then according to the Prigogine theorem

$$\langle U_1 - U_2 \rangle p = L_{21}X_1 + L_{22}X_2 = 0.$$

From this, taking equations (14) and (16) into account, it follows that

$$\frac{\mathrm{d}y}{\mathrm{d}Z} = -\frac{l_{21}}{l_{22}}\frac{\mathrm{d}\ln T}{\mathrm{d}Z}. \tag{17}$$

Thus, the ratio of the kinetic coefficients l_{21}/l_{22} describes the thermodiffusional mixture separation at arbitrary Knudsen numbers. In the hydrodynamic limit ($\delta_1 \to \infty$), the value of l_{21}/l_{22} does not depend on the Knudsen number

$$\lim_{\delta_i \to \infty} \frac{l_{21}}{l_{22}} = -y(1-y)\alpha_T.$$

The value of the thermodiffusion factor α_T, calculated for the Lennard–Jones (6–12)-potential, agrees satisfactorily with the experimental data [13] at any concentrations. The maximum deviation of the theory from the experiment does not exceed 7% for all of the pairs of gases investigated.

(2) The pressure gradient is zero ($X_3 = 0$) and the concentration gradient is fixed ($X_2 = \text{const.}$). By the Prigogine theorem

$$\langle Q \rangle = L_{11}X_1 + L_{12}X_2 = 0.$$

Whence

$$\frac{\mathrm{d}\ln T}{\mathrm{d}Z} = -\frac{l_{12}}{l_{11}}\frac{\mathrm{d}y}{\mathrm{d}Z}, \tag{18}$$

i.e. at constant pressure the concentration gradient induces the temperature gradient along the channel. The dependence of the temperature gradient magnitude on the Knudsen number is determined by the ratio of kinetic coefficients l_{12}/l_{11}.

(3) The temperature gradient is zero ($X_1 = 0$) and the pressure gradient is fixed ($X_3 = \text{const.}$). Then

$$\langle U_1 - U_2 \rangle p = L_{22}X_2 + L_{23}X_3 = 0.$$

Whence

$$\frac{\mathrm{d}y}{\mathrm{d}Z} = -\frac{l_{23}}{l_{22}}\frac{\mathrm{d}\ln p}{\mathrm{d}Z}. \tag{19}$$

Hence, the pressure diffusional separation of mixture is determined by the ratio l_{23}/l_{22}. The quantity α_p, defined as

$$\alpha_p = \frac{1}{y(1-y)} \lim_{\delta_i \to \infty} \frac{l_{23}}{l_{22}},$$

is called the pressure diffusional factor. The difference between the calculated and measured [14] values of α_p for the pair He–Ar at any concentrations does not exceed 1.5%.

(4) The temperature along the channel does not change ($X_1 = 0$) and the concentration gradient is fixed ($X_2 = \text{const.}$). By the Prigogine theorem

$$\langle U \rangle = L_{32}X_2 + L_{33}X_3 = 0.$$

Whence

$$\frac{\mathrm{d}\ln p}{\mathrm{d}Z} = -\frac{l_{32}}{l_{33}}\frac{\mathrm{d}y}{\mathrm{d}Z}. \tag{20}$$

The effect of pressure gradient origination in the presence of a concentration gradient in a mixture is called the diffusional baroeffect. In real conditions the concentration gradient is not kept constant, but varies slowly with time as a result of mixing of components. At the initial time the magnitude of the pressure gradient increases, but after some time the concentration gradient starts to decrease as a result of mixing of the components and this leads to a decrease in the pressure gradient. Thus, depending on the time, the diffusional baroeffect has a maximum. The effect of mixing of components can easily be taken into account with the aid of the conservation equations [2, 7].

Figure 2 shows the dependence of the maximum pressure difference Δp on the mean pressure in the system for the pair He–Ar; a comparison is also given of the theory with the experiment [15]. The measurements were carried out in the pressure range 10^4 N m^{-2} $\leqslant p \leqslant 10^5$ N m^{-2} corresponding to the following range of the rarefaction parameter: $8 \leqslant \delta_1 \leqslant 80$. The difference between the theory and experiment is at a maximum at $\delta_1 < 15$, but does not exceed an experimental error.

(5) Only the temperature gradient is fixed ($X_1 = \text{const.}$). Then, according to the Prigogine theorem

$$\langle U_1 - U_2 \rangle p = L_{21}X_1 + L_{22}X_2 + L_{23}X_3 = 0,$$

$$\langle U \rangle = L_{31}X_1 + L_{32}X_2 + L_{33}X_3 = 0.$$

Solving these equations for X_2 and X_3, it is not difficult to obtain the following relationships

$$\frac{\mathrm{d}y}{\mathrm{d}Z} = A\frac{\mathrm{d}\ln T}{\mathrm{d}Z}, \quad A = \frac{l_{23}l_{31} - l_{33}l_{21}}{l_{33}l_{22} - l_{23}l_{32}}; \tag{21}$$

$$\frac{\mathrm{d}\ln p}{\mathrm{d}Z} = B\frac{\mathrm{d}\ln T}{\mathrm{d}Z}, \quad B = \frac{l_{32}l_{21} - l_{22}l_{31}}{l_{33}l_{22} - l_{23}l_{32}}. \tag{22}$$

Thus, the temperature gradient in the mixture causes simultaneously the thermodiffusional separation of the components (21) and thermomolecular pressure difference (22).

It follows from equations (10) and (12) that in a free

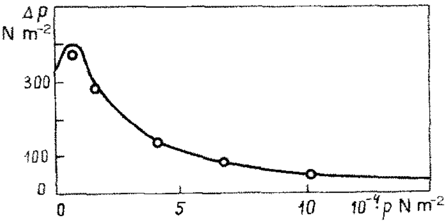

FIG. 2. The dependence of the baroeffect on the mean pressure for the He–Ar mixture. Comparison between theory and experiment [15].

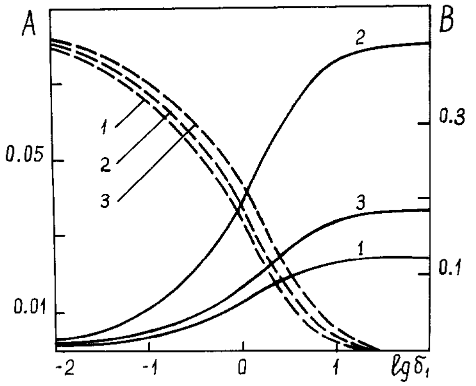

FIG. 3. The dependence of the thermal diffusion separation (——) and thermomolecular pressure (– – – –) on the parameter δ_1 for the He–Ne mixture: (1) $y = 0.1$; (2) $y = 0.5$; (3) $y = 0.9$.

molecular regime ($\delta_i \to 0$)

$$A = 0, \quad B = \frac{1}{2}.$$

In the hydrodynamic limit ($\delta_i \to \infty$)

$$A = y(1-y)\alpha_T, \quad B = 0.$$

The dependence of the coefficients A and B on the rarefaction parameter at different concentrations of a light component for the pair He–Ne is given in Fig. 3.

It should be noted in conclusion that the results of the present work can be used in planning the experiments on the measurement of transfer coefficients in gas mixtures. In practice, they might be of use for the optimization of the processes of gas cleaning and drying, for the calculation of vacuum systems.

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LES PHENOMENES CINETIQUES DANS UN MOUVEMENT NON ISOTHERME D'UN MELANGE BINAIRE DE GAZ A TRAVERS UN CANAL PLAN

Résumé—A partir d'une équation cinétique linéarisée (le modèle de MacCormack), on établit la théorie du mouvement de mélanges binaires de gaz dans un canal plan en considérant les gradients de température, de concentration et de pression. On obtient des formules donnant la dépendance des flux moyens thermiques, diffusionnels et numériques vis-à-vis du nombre de Knudsen et de la concentration des composants. Les calculs sont conduits pour les mélanges He–Ar, He–Ne, Ne–Ar en utilisant les trois modèles de potentiel intermoléculaire : sphères solides, molécules de Maxwell, potentiel de Lennard–Jones (6–12). Avec le théorème de Prigogine, les effets caractéristiques des mélanges de gaz sont considérés (diffusion thermique et diffusion de pression, baro-effet diffusionnel, différence de pression thermomoléculaire). La théorie est comparée à l'expérience.

DIE KINETISCHEN VORGÄNGE BEI NICHTISOTHERMER STRÖMUNG EINES BINÄREN GASGEMISCHES IN EINEM EBENEN KANAL

Zusammenfassung—Auf der Grundlage einer linearisierten kinetischen Gleichung (dem McCormack-Modell) wird die Theorie der Strömung eines binären Gasgemisches in einem ebenen Kanal aufgrund von Temperatur-, Konzentrations- und Druckgradienten aufgestellt. Die erhaltenen Beziehungen zeigen die Abhängigkeit der mittleren thermischen, numerischen und Diffusionsströme von der Knudsen-Zahl und der Konzentration der Komponenten. Die Berechnungen werden für die Gemische He–Ar, He–Ne, Ne–Ar für drei Modelle des intermolekularen Potentials durchgeführt: 'Vollkugel', 'Maxwell-Moleküle' und das Lennard-Jones (6-12)-Potential. Auf der Grundlage des Prigogine-Theorems werden die charakteristischen Effekte in Gasgemischen (Thermodiffusion und Druckdiffusionstrennung von Gemischen, Diffusionsbaroeffekt und thermomolekulare Druckdifferenz) behandelt. Die theoretischen Ergebnisse werden mit experimentellen Daten verglichen.

КИНЕТИЧЕСКИЕ ЯВЛЕНИЯ ПРИ НЕИЗОТЕРМИЧЕСКОМ ДВИЖЕНИИ БИНАРНОЙ ГАЗОВОЙ СМЕСИ В ПЛОСКОМ КАНАЛЕ

Аннотация—На основе линеаризованного кинетического уравнения (модель Маккормака) строится теория движения бинарных газовых смесей в плоском канале под действием градиентов температуры, концентрации и давления. В результате получены зависимости теплового, диффузионного и среднечислового потоков от числа Кнудсена и от концентрации компонентов. Расчеты проводятся для смесей He–Ar, He–Ne, Ne–Ar с использованием трех моделей межмолекулярного потенциала: "твердые сферы", "максвелловские молекулы", (6–12) Леннарда–Джонса. На основе теоремы Пригожина рассматриваются характерные для газовых смесей эффекты (термо- и бародиффузионное разделение смеси, диффузионный бароэффект, термомолекулярная разность давлений). Проводится сравнение теории с экспериментом.