

duced. The influence of negative reflexivities of the upper and lower bases on the quantity δ is shown in Fig. 3d for adiabatic side walls. The maximum error is observed for absolutely black surfaces of the bases.

The method proposed and the computation results are recommended for utilization to estimate the error in the plane layer approximation when modeling radiation heat transfer in rectangular chambers.

NOTATION

T, absolute temperature; q, radiation flux density; Q, resultant radiation flux; σ , Stefan-Boltzmann constant; r, surface reflexivity; k, linear attenuation factor; γ , ratio of scattering to attenuation coefficients; $\bar{\mu}$, effective mean cosine of the scattering angle in an elementary scattering act; D, transmission function; l , ray pathlength; a, channel width; b, channel height; x, y, coordinates. Subscripts: e, effective radiation; c, intrinsic radiation; 1, lower base of channel cross section; 2, side walls; 3, upper base.

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PROBLEM OF THE NONSTATIONARY STATE OF HEAT- AND MASS-TRANSFER PROCESSES IN BINARY GASEOUS MIXTURES

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Nonstationary heat- and mass-transfer processes in gaseous mixtures are considered, and expressions are obtained for the heat-diffusion ratio and for the contribution of diffusion thermal conduction in conductive heat transfer.

Molecular heat- and mass-transfer processes in gaseous mixtures are characterized by effective values of the thermal conductivity and thermal diffusion ratio, and these two (effective) characteristics (transfer processes) are mutually related and may differ in value in the stationary and nonstationary states.

Despite the large number of papers published on the subject, the mechanism of the phenomenon of thermal diffusion in gaseous mixtures is still unclear even in the case of mixtures of monotonic gases. Experimental methods of determining the thermal diffusion constant of gaseous mixtures are usually stationary, since at the present time there is not even a theory which describes the nonstationary state of thermal diffusion.

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A study of the mechanism of thermal diffusion and refinement of the theoretical model of this process in order to improve existing experimental methods of investigating thermal conduction in gaseous mixtures are of independent interest.

In the stationary state the expression for the flow of a mass of binary gaseous mixture, e.g., within the framework of the rigorous molecular-kinetic theory, has the form [1]

$$\mathbf{J}_1(\mathbf{r}) = \frac{n^2(\mathbf{r}) m_1 m_2 D_{12}}{\rho} [\nabla x_1(\mathbf{r}) + \kappa_T \nabla \ln T(\mathbf{r})],$$

and the thermal-diffusion ratio is defined as

$$\frac{\partial x_1(\mathbf{r})}{\partial T} = -\frac{\kappa_{T_1}}{T(\mathbf{r})}, \quad (1)$$

where

$$\kappa_{T_1} = -\kappa_{T_2} = \kappa_T = \frac{\rho D_{12}^T}{n^2 m_1 m_2 D_{12}}.$$

In the nonstationary state

$$\mathbf{J}_1(\mathbf{r}, t) = -\frac{n^2(\mathbf{r}, t) m_1 m_2 D_{12}}{\rho} [\nabla x_1(\mathbf{r}, t) + (x_1(\mathbf{r}, t) - c_1(\mathbf{r}, t)) \nabla \ln \rho(\mathbf{r}, t) + \kappa_T \nabla \ln T(\mathbf{r}, t)],$$

and the thermal-diffusion ratio is defined as

$$\frac{\partial x_1(\mathbf{r}, t)}{\partial T} = -\frac{s_{T_1}}{T(\mathbf{r}, t)}, \quad (2)$$

so that $s_{T_1} = -s_{T_2} = s_T$.

Then, for mixtures of ideal gases

$$\mathbf{J}_1(\mathbf{r}, t) = \frac{n^2(\mathbf{r}, t) m_1 m_2 D_{12}}{\rho} \left[(s_T - \kappa_T) - (x_1(\mathbf{r}, t) - c_1(\mathbf{r}, t)) \frac{\nabla \ln \rho(\mathbf{r}, t)}{\nabla \ln T(\mathbf{r}, t)} \right] \nabla \ln T(\mathbf{r}, t), \quad (3)$$

and for mixtures of real gases

$$\begin{aligned} \mathbf{J}_1(\mathbf{r}, t) = & \frac{n^2(\mathbf{r}, t) m_1 m_2 D_{12}}{\rho} \left\{ \left[\frac{n(\mathbf{r}, t) kT(\mathbf{r}, t)}{p(\mathbf{r}, t)} \left(1 + \frac{\partial \ln f_2}{\partial \ln x_1} \right) s_T - \kappa_T \right] + \right. \\ & \left. + \left[x_2(\mathbf{r}, t) \frac{n(\mathbf{r}, t) kT(\mathbf{r}, t) (1 + \ln f_2)}{p(\mathbf{r}, t)} - c_2(\mathbf{r}, t) \right] \frac{\nabla \ln \rho(\mathbf{r}, t)}{\nabla \ln T(\mathbf{r}, t)} \right\} \nabla \ln T(\mathbf{r}, t). \end{aligned}$$

In the nonstationary state $\nabla p \neq 0$, and according to the equation of state of an ideal gas,*

$$\nabla p = \frac{p}{T} \left(1 + \frac{T}{n} \frac{\partial n}{\partial T} \right) \nabla T = \frac{p}{T} \left[\left(1 + \frac{T}{n_1} \frac{\partial n_1}{\partial T} \right) - \frac{T}{x_1} \frac{\partial x_1}{\partial T} \right] \nabla T \quad (4)$$

or

$$\nabla \ln \rho(\mathbf{r}, t) = \frac{s_T - \kappa_T^*}{x_1(\mathbf{r}, t)} \nabla \ln T(\mathbf{r}, t). \quad (5)$$

Here

$$\kappa_T^* = -x_1(\mathbf{r}, t) \left[1 + \frac{\partial \ln n_1(\mathbf{r}, t)}{\partial \ln T} \right].$$

Using (5) we obtain

*A similar discussion can be carried out for a nonideal gas.

$$s_T = -\frac{\partial x_1(\mathbf{r}, t)}{\partial \ln T} = \kappa_T^* + x_1(\mathbf{r}, t) \frac{\nabla \ln p(\mathbf{r}, t)}{\nabla \ln T(\mathbf{r}, t)}, \quad (6)$$

whence it follows that in the stationary case

$$s_T = \kappa_T = -x_1(\mathbf{r}) \left[1 + \frac{\partial \ln n_1(\mathbf{r})}{\partial \ln T} \right],$$

in the case of a single-component gas $s_T = 0$.

In the stationary state the reduce flow of heat (in a system of coordinates moving with the mean-mass velocity) is described by the relation

$$\mathbf{J}'_q(\mathbf{r}) = -\lambda_\infty \nabla T(\mathbf{r}), \quad (7)$$

and in the nonstationary state [1]

$$\mathbf{J}'_q(\mathbf{r}, t) = -\lambda_\infty \nabla T(\mathbf{r}, t) + p(\mathbf{r}, t) \kappa_T [\bar{\mathbf{V}}_1(\mathbf{r}, t) - \bar{\mathbf{V}}_2(\mathbf{r}, t)] = -\lambda^n \nabla T(\mathbf{r}, t). \quad (8)$$

Since

$$\bar{\mathbf{V}}_1 - \bar{\mathbf{V}}_2 = -\frac{n^2 \mathcal{D}_{12}}{n_1 n_2} \left[(\kappa_T - s_T) + (x_1 - c_1) \frac{\nabla \ln p}{\nabla \ln T} \right] \nabla T,$$

the expression for the thermal conductivity, measured by the nonstationary method, has the form

$$\lambda^n = \lambda_\infty + \lambda_{DT}^\infty \left[\left(1 - \frac{s_T}{\kappa_T} \right) + \frac{x_1 - c_1}{\kappa_T} \frac{\nabla \ln p}{\nabla \ln T} \right], \quad (9)$$

where λ_{DT}^∞ is the contribution of diffusion thermal conduction in the stationary state

$$\lambda_{DT}^\infty = \lambda_0 - \lambda_\infty = \frac{p D_{12}}{T} \alpha_T \kappa_T.$$

In the case of complete heat flow (system of coordinates moving with the mean numerical velocity) the thermal conductivity is

$$\lambda^n = \lambda_\infty + \lambda_{DT}^\infty \left(1 + \frac{n}{\rho} \frac{h_1 m_2 - h_2 m_1}{kT} \frac{1}{\alpha_T} \right) \left[\left(1 - \frac{s_T}{\kappa_T} \right) + \frac{x_1 - c_1}{\kappa_T} \frac{\nabla \ln p}{\nabla \ln T} \right].$$

According to (9), the contribution of diffusion thermal conduction in the nonstationary state for the case of a reduced flow of heat

$$\lambda_{DT}^n = \lambda_0 - \lambda^n = \lambda_{DT}^\infty \left(\frac{s_T}{\kappa_T} - \frac{x_1 - c_1}{\kappa_T} \frac{\nabla \ln p}{\nabla \ln T} \right) \quad (10)$$

and

$$\lambda^n = \lambda_\infty + (\lambda_{DT}^\infty - \lambda_{DT}^n)^* \quad (11)$$

As a rule, the thermal conductivity in the nonstationary state is defined in the form [2, 3]

$$\lambda^n = \lambda_\infty + \lambda_{DT}^\infty \exp(-t/\tau), \quad (12)$$

where τ is the buildup time of the stationary state. According to (9), in relation (12)

the term $\left[\left(1 - \frac{s_T}{\kappa_T} \right) + \frac{x_1 - c_1}{\kappa_T} \frac{\nabla \ln p}{\nabla \ln T} \right]$ is replaced by $\exp(-t/\tau)$.

When solving a number of applied problems connected with the problem of heat transfer at high temperatures, it is often necessary, when investigating the processes occurring in the stationary state, to use experimental data of the properties of the transfer obtained in nonstationary measuring systems. For example [4], when determining the effective state of a

*It can be shown that $\lambda_{DT}^\infty = \lambda_{DT}^n$ and $\lambda^n = \lambda_\infty$.

gaseous medium for filling incandescent lamps, when optimizing the mode of operation of the gas-filled lamps in the stationary state experimental data are necessary on the thermal conductivity of gaseous mixtures at temperatures of 2500-3500°K, which can only be obtained using the nonstationary shock-tube method [5].

We will make an approximate estimate of the value of k_T compared with s_T , for which we will consider the linearized problem and obtain an expression for the thermal-diffusion ratio in the nonstationary state. We will write the system of equations of conservation of energy and of the number of particles in the form

$$\rho c_p \frac{dT}{dt} = -\nabla \cdot \mathbf{J}_q, \text{ where } \mathbf{J}_q = -\lambda^n \nabla T,$$

$$\rho \frac{dc_1}{dt} = -\nabla \cdot \mathbf{J}_1, \text{ where } \mathbf{J}_1 = -D_1^T \left[\left(1 - \frac{s_T}{\kappa_T}\right) + \frac{x_1 - c_1}{\kappa_T} \frac{\nabla \ln p}{\nabla \ln T} \right] \nabla \ln T = -\bar{D}_1^T \nabla T. \quad (13)$$

For simplicity we will confine ourselves to the one-dimensional case

$$\rho c_p \left(\frac{\partial T}{\partial t} + v \frac{\partial T}{\partial x} \right) = \lambda \frac{\partial^2 T}{\partial x^2} + \frac{\partial \lambda}{\partial T} \left(\frac{\partial T}{\partial x} \right)^2,$$

$$\rho \left(\frac{\partial c_1}{\partial t} + v \frac{\partial c_1}{\partial x} \right) = \bar{D}_1^T \frac{\partial^2 T}{\partial x^2} + \frac{\partial \bar{D}_1^T}{\partial T} \left(\frac{\partial T}{\partial x} \right)^2. \quad (14)$$

The thermal properties of the materials can be approximated by the power relationship

$$\lambda^n = b(T/T_0)^n, \quad \bar{D}_1^T = c(T/T_0)^m, \quad (15)$$

where $b, c = \text{const.}$

Taking (15) into account, system (14) has the form

$$\frac{1}{a} \left(\frac{\partial T}{\partial t} + v \frac{\partial T}{\partial x} \right) = \frac{n}{T} \left(\frac{\partial T}{\partial x} \right)^2 + \frac{\partial^2 T}{\partial x^2},$$

$$\rho \left(\frac{\partial c_1}{\partial t} + v \frac{\partial c_1}{\partial x} \right) = \frac{m}{T} \left(\frac{\partial T}{\partial x} \right)^2 + \frac{\partial^2 T}{\partial x^2}. \quad (16)$$

Since the temperature dependences of the thermal conductivity and thermal-diffusion constant are characterized by the same form of behavior, we will assume that $m \approx n$. Then, according to (16)

$$\frac{1}{a} \left(\frac{\partial T}{\partial t} + v \frac{\partial T}{\partial x} \right) = \frac{\rho}{\bar{D}_1^T} \left(\frac{\partial c_1}{\partial t} + v \frac{\partial c_1}{\partial x} \right),$$

whence

$$\left(\frac{\partial T}{\partial t} + v \frac{\partial T}{\partial x} \right) \left(\frac{1}{a} - \frac{\rho}{\bar{D}_1^T} \frac{\partial c_1}{\partial T} \right) = 0. \quad (17)$$

The last relation holds if

$$\frac{\partial c_1}{\partial T} \approx \frac{\text{Le}^T}{T} \left[\left(1 - \frac{s_T}{\kappa_T}\right) + \frac{x_1 - c_1}{\kappa_T} \frac{\nabla \ln p}{\nabla \ln T} \right], \quad \text{Le}^T = \frac{D_1^T c_p}{\rho}, \quad (18)$$

or

$$\frac{\partial x_1}{\partial T} \approx \frac{\text{Le}}{T} \left[(\kappa_T - s_T) + (x_1 - c_1) \frac{\nabla \ln p}{\nabla \ln T} \right], \quad \text{Le} = \frac{\mathcal{D}_{12}}{a}, \quad (19)$$

and finally

*The ratio of the characteristic diffusion time to the thermal relaxation time is defined by the quantity $|\nabla p| = \rho g$, which for the majority of gaseous mixtures is approximately equal to 1-10.

$$s_T \approx \frac{Le}{Le-1} \left[\kappa_T + (x_1 - c_1) \frac{\nabla \ln p}{\nabla \ln T} \right]. \quad (20)$$

Assuming in (20) that $|\nabla p| = \rho g$, the expression for s_T becomes

$$s_T \approx \frac{Le}{Le-1} \left(\kappa_T + \frac{M_2 - M_1}{R} \frac{g x_1 x_2}{|\nabla T|} \right).$$

The value of s_T was estimated for an equimolar mixture of He and Ar at a temperature of 326°K: $\rho = 0.78 \text{ kg}\cdot\text{m}^{-3}$, $\mathcal{D}_{12} = 0.87 \cdot 10^{-4} \text{ m}^2 \cdot \text{sec}^{-1}$, $\kappa_T = 0.0927$, $\lambda_\infty = 0.05700 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$, $\lambda_{DT}^\infty = 0.00080 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$, $Le = 3.40$, giving $s_T = 0.1313$.

NOTATION

α , thermal diffusivity; c_p , specific heat capacity at constant pressure; \mathcal{D}_{12} , interdiffusion coefficient of a binary gaseous mixture; D_T , thermal diffusion coefficient; f_i , activity coefficient of the i -th component; g , acceleration due to the gravity; h_i , enthalpy per molecule of the i -th sort; J , mass flow; J'_q , reduced heat flux; k , Boltzmann's constant; κ_T , thermal diffusion ratio in the stationary state; s_T , thermal diffusion ratio in the nonstationary state; M_i and m_i , molecular weight and mass of the molecule of the i -th component, respectively; n , number density of the molecules; p , pressure; T , temperature; R , universal gas constant; t , time; x , coordinate; r , radius vector; x_i and c_i , molecular and mass concentration of the i -th component of the mixture, respectively; v , velocity; V , diffusion velocity; λ , thermal conductivity; λ_0 , thermal conductivity of the uniform mixture; ρ , mass density. The indices are: ∞ , stationary state; n , nonstationary state.

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