NONSTEADY HEAT TRANSFER IN DIFFUSING SYSTEMS

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By the methods of the thermodynamics of irreversible processes and molecular-kinetic theory, it is shown that the effective thermal conductivities of mixtures measured by steady and nonsteady methods are not equal, which is confirmed by experimental data.

A nonsteady heat-transfer process in diffusing systems is understood to entail specific experimental conditions, in which a pressure gradient $\nabla p \sim \nabla T$ of sufficiently large relaxation time appears in measuring cells of small dimension; a density gradient arises in the shock tube, and the pressure remains practically constant in the course of the experiment.

In the first case, the effective thermal conductivity includes contributions due to the concentration and pressure gradients, and in the second case, due to the concentration and density gradients.

Conductive heat transfer in diffusing systems is characterized by three different forms of the thermal conductivity: the thermal conductivity of a homogeneously mixed mixture λ_0, the effective thermal conductivity in the steady state λ^∞, and the effective thermal conductivity in the nonsteady state λ^N. An expression is found for the effective thermal conductivity of a mixture in the nonsteady state, regardless of the method adopted for its measurement. This involves the consideration of two methods of describing the nonsteady conductive heat transfer, based on the formalisms of molecular—kinetic theory and the thermodynamics of irreversible processes.

The conductive heat transfer in gas mixtures is characterized by the relation [1]

$$\vec{J}_q' = -\lambda_0 \nabla T - p \sum_{i=1}^{\nu} \frac{D_i^{\mathrm{T}}}{n_j m_j} \vec{d}_j,$$

which for binary mixtures takes the form

$$\vec{J}_q' = -\lambda_0 \nabla T - \frac{p \rho D_i^{\mathrm{T}}}{n_i n_j m_i m_j} \vec{d}_j = -\lambda^{\mathrm{N}} \nabla T, \tag{1}$$

where

$$\vec{d}_j = \frac{\rho}{n^2 m_i m_j D_{ij}} \vec{J}_i + \frac{\tilde{k}_{\mathrm{T}}}{T} \nabla T, \ \tilde{k}_{\mathrm{T}} = \frac{\rho D_i^{\mathrm{T}}}{n^2 m_i m_j D_{ij}}. \tag{2}$$

According to Eq. (2), the form of the expression for the mass flux λ^N in the steady state must be known in order to determine J_i; use is made of the concept of the thermodiffusional ratio in the nonsteady state [2] $-s_{\mathrm{T}_i} = T\partial x_i/\partial T|_{\nabla p \neq 0}$ by analogy with the steady state $-\tilde{k}_{\mathrm{T}_i} = T\partial x_i/\partial T|_{\nabla p = 0}$.

Before passing to the different forms of the expression for the mass flux $\vec{J}_i$ used in molecular—kinetic theory and the thermodynamics of irreversible processes, an expression is found for s_T, assuming for the sake of simplicity that the mixture is ideal.

For the system of the mean-mass velocity (equation of state $c_1 p = \rho_1 AT$), the following relation is valid:

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$$p\nabla c_1 + c_1\nabla p = AT\nabla\rho_1 + A\rho_1\nabla T,$$

and hence

$$\frac{\partial \ln c_1}{\partial \ln T} + c_1\frac{\partial \ln p}{\partial \ln T} = c_1\left(\frac{\partial \ln \rho_1}{\partial \ln T} + 1\right).$$

Taking into account that

$$T\cdot\frac{\partial c_1}{\partial T}\bigg|_{\nabla p\neq 0} = -\bar{s}_T,\ c_1\left(1+\frac{\partial \ln \rho_1}{\partial \ln T}\right) = -\overline{\tilde{k}}_T,$$

where $T(\partial c_1/\partial T)_{\nabla p=0} = -\tilde{k}_T$.

$$\bar{s}_T = \overline{\tilde{k}}_T + c_1\frac{\partial \ln p}{\partial \ln T}, \tag{3a}$$

and analogously for the system of the mean-numerical velocity

$$s_T = \tilde{k}_T + x_1\frac{\partial \ln p}{\partial \ln T}. \tag{3b}$$

The description of the process of nonsteady thermodiffusion in the thermodynamics of irreversible processes is associated both with the thermodynamic force $\vec{\Lambda}_i^*$, which is determined by the expression $\vec{\Lambda}_i^* = \nabla x_i + x_i\nabla \ln p$, for the mean-numerical-velocity system, and the thermodynamic force $\vec{Y} = \nabla T$, so that

$$\tilde{k}_T = -T\frac{\vec{\Lambda}_i^*}{\vec{Y}} = s_T - x_i\frac{\nabla \ln p}{\nabla \ln T},$$

and for the mean-mass velocity system

$$\overline{\tilde{k}}_T = -T\frac{\vec{\Lambda}_i^*}{\vec{Y}} = s_T - c_i\frac{\nabla \ln p}{\nabla \ln T}.$$

The description of the process of nonsteady thermodiffusion in terms of molecular-kinetic theory is associated with the concentration-gradient vector $\vec{d}_i$, which is expressed in terms of the thermodynamic force Λ_i as follows:

$$\vec{d}_i^* = \vec{\Lambda}_i^* - \frac{\rho_i}{\rho}\nabla \ln p \text{ and } \vec{d}_i = \vec{\Lambda}_i - \frac{\rho_i}{\rho}\nabla \ln p,$$

where $\vec{\Lambda}_i = \frac{n_i m_i}{\rho}\vec{\Lambda}_i^*$, so that

$$\tilde{k}_T = -T\frac{\vec{d}_i^*}{\vec{Y}} = s_T - \left(x_i - \frac{\rho_i}{\rho}\right)\frac{\nabla \ln p}{\nabla \ln T}.$$

Hence, it is evident that the thermodiffusional ratio is determined by the ratio between two vectors: the concentration gradient and the temperature gradient. The latter expression may be used to write the relation

$$s_T = \tilde{k}_T + \left(x_i - \frac{\rho_i}{\rho}\right)\frac{\nabla \ln p}{\nabla \ln T}. \tag{4}$$

Equation (4) defines the thermodiffusional ratio in the nonsteady state, written in terms of molecular-kinetic theory.

Passing now to the different forms of the expression for the mass flux (number of particles), it will first be shown that the numerical flux of particles, defined as $nD_{12}(\nabla x_1 + \tilde{k}_T\nabla \ln T)$, is $nD_{12}x_1\nabla \ln p$, i.e., that

$$\frac{\nabla \ln x_1}{\nabla \ln p} + \frac{\tilde{k}_T}{x_1} \frac{\nabla \ln T}{\nabla \ln p} = -1. \quad (5)$$

Since $\nabla \ln x_1 = \nabla \ln (p_1/p)$, it follows that

$$\frac{\nabla \ln x_1}{\nabla \ln p} = \frac{\nabla \ln p_1}{\nabla \ln p} - 1 = \frac{\nabla \ln p_1}{\nabla \ln T} \frac{\nabla \ln T}{\nabla \ln p} - 1 = \left(1 + \frac{\partial \ln n_1}{\partial \ln T}\right) \frac{\nabla \ln T}{\nabla \ln p} - 1 = -\frac{\tilde{k}_T}{x_1} \frac{\nabla \ln T}{\nabla \ln p} - 1,$$

from which Eq. (5) follows.

Adopting the notation $nD_{12}(\nabla x_1 + \tilde{k}_T \nabla \ln T) = \vec{I}_1'$, it is found that

$$\vec{I}_1 = \vec{I}_1' + nD_{12} x_1 \nabla \ln p = 0, \quad (6a)$$

$$\vec{J}_1 = \vec{J}_1' + \rho D_{12} c_1 \nabla \ln p = 0, \quad (6b)$$

where $\vec{J}_1 = -\rho D_{12} (\nabla c_1 + \tilde{k}_T \nabla \ln T)$. Equations (6) follow from the relations

$$\vec{\Lambda}_1^* + \frac{\tilde{k}_T}{T} \vec{Y} = 0, \quad \vec{\vec{\Lambda}}_1^* + \frac{\tilde{\tilde{k}}_T}{T} \vec{Y} = 0, \quad \vec{d}_i^* + \frac{\tilde{k}_T}{T} \vec{Y} = 0,$$

and leads to the identity

$$\vec{J}_1 = \frac{n^2 m_1 m_2}{\rho} D_{12} [\nabla x_1 + \tilde{k}_T \nabla \ln T + (x_1 - \rho_1/\rho) \nabla \ln p] = 0. \quad (7)$$

Using Eq. (7), Eq. (2) takes the form

$$\lambda^N = \lambda_0 + \frac{pD_{12}}{T} \alpha_T \tilde{k}_T = \lambda_0 + \lambda_{D^T} = \lambda_\infty ,$$

i.e., the description of nonsteady conductive heat transfer in terms of molecular-kinetic theory completely coincides with the description of steady conductive heat transfer. In connection with this, it is necessary, in the experimental determination of the thermal conductivity by a nonsteady method, to create conditions such that the mass flux $\vec{J}_i = 0$, i.e., to create a "countervaling" pressure gradient.

Determining the nonsteady conductive heat transfer by the methods of the thermodynamics of irreversible processes, the following expressions are written [3]:

$$\vec{J}_q' = -\lambda_0 \nabla T - \rho c_1 D_1^T T \vec{\Lambda}_1; \; \vec{J}_1 = -\rho c_1 c_2 D_1^T - \rho c_1 D_{12} \vec{\Lambda}_1, \quad (8)$$

and in general form for an ideal mixture

$$\vec{\Lambda}_1 = AT \left(\frac{1}{c_1} \nabla c_1 + \nabla \ln p \right) = \frac{p}{\rho_1} (\nabla c_1 + c_1 \nabla \ln p). \quad (9)$$

Taking account of Eq. (9), the system in Eq. (8) takes the form

$$\begin{aligned} \vec{J}_q' &= -\lambda_0 \nabla T - \frac{pD_{12}}{T} \alpha_T (T \nabla c_1 + T c_1 \nabla \ln p), \\ \vec{J}_1 &= -\rho c_1 c_2 D_1^T \nabla \ln T - \rho D_{12} (\nabla c_1 + c_1 \nabla \ln p), \end{aligned} \quad (10)$$

where $\alpha_T = D_1^T / D_{12}$.

The first relation in Eq. (10) may be written in the form

$$\vec{J}_q' = -\lambda_0 \nabla T - \frac{pD_{12}}{T} \alpha_T (T \nabla c_1 + T c_1 \nabla \ln p) = -\lambda^N \nabla T,$$

where

$$\lambda^N = \left[\lambda_0 + \frac{pD_{12}}{T} \alpha_T \left(T \frac{\nabla c_1}{\nabla T} + c_1 \frac{\nabla \ln p}{\nabla \ln T} \right) \right]. \quad (11)$$

Since $T\frac{\nabla c_1}{\nabla T}\Big|_{\nabla p\neq 0} = -s_T$, $s_T = \tilde{k}_T + c_1\frac{\nabla \ln p}{\nabla \ln T}$. Eq. (11) reduces to the form $N = \lambda_0 - \frac{pD_{12}}{T}\alpha_T\tilde{k}_T = \lambda_\infty$.

Thus, in the case when the total mass flux $\vec{J}_i$ (or the thermodynamic force $\vec{\Lambda}_i$) is used to describe transfer processes, the effective thermal conductivity characterizing the nonsteady conductive heat transfer λ^N is equal to the effective thermal conductivity λ_∞.

The process of nonsteady conductive heat transfer will be considered using the reduced mass flux $\vec{J}_i$ (which corresponds to the thermodynamic force $\bar{\mu}_{11}^c = \vec{\Lambda}_1' = \left(\frac{\partial \bar{\mu}_1}{\partial c_1}\right)_{T,p}$, [2]).

For an ideal mixture

$$\vec{J}_q' = -\lambda_0\nabla T - \rho\bar{\mu}_{11}^c T D_1^T \nabla c_1 = -\lambda^N \nabla T,$$

where

$$\lambda^N = \lambda_0 + AT\alpha_T\cdot T\frac{\nabla c_1}{\nabla T} = \lambda_0 - AT\alpha_T s_T = \lambda_\infty - \lambda_{DT}\frac{c_1}{\tilde{k}_T}\frac{\nabla \ln p}{\nabla \ln T}.$$

Thus, when nonsteady transfer processes are described using the reduced mass flux (or the thermodynamic force $\vec{\Lambda}_i'$), the thermal conductivities λ^N and λ_∞ are related as follows:

$$\lambda^N = \lambda_\infty - c_1\lambda_{DT}\tilde{k}_T^{-1}\frac{\nabla \ln p}{\nabla \ln T}; \quad \lambda_{DT} = \frac{pD_{12}}{T}\alpha_T\tilde{k}_T. \tag{12}$$

For a nonideal mixture

$$\bar{\mu}_{ii}^c = AT\left(1 + \frac{\partial \ln f_i}{\partial \ln c_i}\right)_{T,p} = AT\left(1 + \frac{\partial \ln f_i}{\partial T}\frac{\partial T}{\partial \ln c_i}\right)_{T,p} = p\left(1 + \frac{H_i}{RT}\frac{c_i}{s_{T_i}}\right)_{T,p},$$

where $H_i = -RT^2\partial \ln f_i/\partial T$. Taking this into account, for a nonideal mixture

$$\lambda^N = \lambda_0 - \frac{pD_{12}}{T}\alpha_T\left(s_{T_1} + \frac{H_1}{RT}x_1\right).$$

Using the method of molecular–kinetic theory, it is found that

$$\lambda^N = \lambda_0 - \frac{pD_{12}}{T}\alpha_T\left(s_{T_1} + \frac{H_1}{RT}x_1\right), \tag{13}$$

since

$$s_{T_1} = \tilde{k}_T + [n_1(v_1^0 + v_1^M) - \rho_1/\rho]\frac{\partial \ln p}{\partial \ln T} - \frac{H_1x_1}{RT}, \tag{14}$$

where

$$v_1^M = RT\frac{\partial \ln f_1}{\partial p}, \quad v_1^0 = \frac{\partial \mu_1^0}{\partial p}.$$

Using Eq. (14), Eq. (13) takes the form

$$\lambda^N = \lambda_\infty - \lambda_{DT}k_{T_1}^{-1}[x_1(1 + v_1^M n) - \rho_1/\rho]\frac{\nabla \ln p}{\nabla \ln T}. \tag{15}$$

Equations (12) and (15) define the effective thermal conductivity of systems in the nonsteady state when their volume is practically unchanged. If the volume of the system is changed in the nonsteady process, while the pressure remains constant, the expression for the effective coefficient λ^N takes a form analogous in form to Eq. (12)

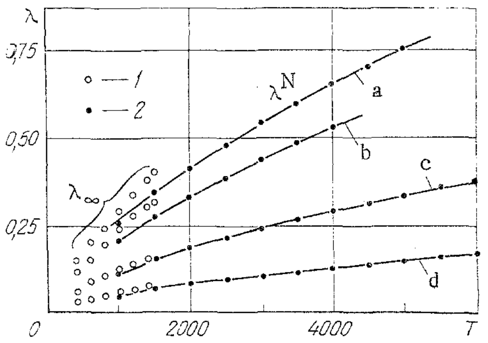

Fig. 1. Dependence of the thermal conductivity of a helium–argon mixture on the temperature: 1) measurement of the thermal conductivity by the steady heated-wire method [4]; 2) by the nonsteady shock-tube method [5]; a) 0.6 He–0.1 Ar; b) 0.8 He–0.2 Ar; c) 0.5 He–0.5 Ar; d) 0.1 He–0.9 Ar.

$$\lambda^N = \lambda_\infty - c_1 \lambda_{D^T} \tilde{k}_T^{-1} \frac{\nabla \ln \rho}{\nabla \ln T} . \tag{16}$$

Calculation of λ^N by Eq. (16) shows that for a mixture of helium and argon with T = 1500°K, λ_∞ = 0.159 W/m•°K [4], $x_1 = 0.5$ $(c_1 = 0.091)$, $\tilde{k}_T = -0.0924$ (calculation of [6]), $\nabla \ln \rho / \nabla \ln T = -1$, $c_1 \lambda_{D^T} \tilde{k}_T^{-1} \frac{\nabla \ln \rho}{\nabla \ln T} = 0.004$, and λ^N = 0.155 W/m•°K. Experimental determination of the thermal conductivity of this mixture in a shock tube shows that λ^N = 0.154 W/m•°K [5].

A comparison of the experimental data on the effective thermal conductivity of a helium–argon mixture measured by the steady heated-wire method [4] and the nonsteady shock-tube method [5] is shown in Fig. 1. As in the case of single-component gases, the data obtained by the steady method (λ_∞) are larger than the data obtained by the nonsteady method (λ^N).

Thus, the discrepancy between the experimental data on the thermal conductivity of the helium–argon mixture obtained by the steady and nonsteady methods, as in the case of single-component gases, is associated with the contribution of the density gradient to the nonsteady heat-transfer process [7].

NOTATION

λ_0, thermal conductivity of a homogeneous mixture; λ^N, effective thermal conductivity of the mixture measured by a nonsteady method; λ_∞, effective thermal conductivity of the mixture measured by a steady method; D_i^T, thermodiffusion coefficient; S_T, k_T, thermodiffusional ratio; D_{ij}, mutual diffusion coefficient; T, temperature; ρ, mixture density; ρ_i, density of the i-th component; p, pressure; n, numerical density; m, mass; x_i, molar fraction of the i-th component; $\vec{J}_i$, mass flux; $\vec{I}_j$, flux of the number of particles; $\vec{J}'_q$, reduced heat flux; A, gas constant; v_i^M, mixing volume; μ_i, chemical potential; f_i, activity coefficient of the i-th component; H_i, heat of mixing of the i-th component.

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CONSTRUCTING A SINGLE EQUATION OF STATE FOR GAS AND LIQUID BY THE METHOD OF MINIMIZING THE SUM OF SQUARES OF THE RELATIVE DEVIATIONS

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The use of the sum of squares of the relative deviations as the minimization criterion in the scheme of the least-squares method is proposed for the construction of a single thermal equation of state.

A typological scheme for the comparison of tables of thermodynamical properties from experimental data must precede the stage of constructing the thermal equation of state on the basis of statistical treatment of compatible measurements and the subsequent calculation of thermodynamic functions from the resulting equation. Two approaches are possible [1]:

1. Only experimental P, v, T data are used to determine the constants of the thermal equation of state. Information on the other properties is taken into account indirectly in choosing the version of the equation of state optimal from the viewpoint of the simultaneous description of the thermal, caloric, and acoustic properties.

2. The empirical constants of the equation are determined on the basis of combined analysis of the various kinds of experimental data.

In both cases, the problem of determining the constants of the empirical equation of state reduces to the application of the generalized least-squares method. From a mathematical viewpoint, the problem consists in minimization of the quadratic functional

$$S=\sum_{q=1}^{Q}\sum_{k=1}^{n_q} w_k\,(x_{qk}-x_q(\omega_k,\ \theta_k,\ \bar{b}))^2. \tag{1}$$

In the first case, Q = 1, x = z. In the second, $x_q=\{z,\ h,\ c_v,\ \ldots\}$.

The least-squares method (LSM) in Eq. (1) consists in minimizing the sum of squares of the absolute deviations. In general form, for

$$\bar{Y}=X\bar{b}+\bar{\varepsilon} \tag{2}$$

the problem reduces to minimization of the quantity

$$\bar{\varepsilon}'\,\bar{\varepsilon}=(\bar{Y}-X\bar{b})'(\bar{Y}-X\bar{b}). \tag{3}$$

However, the quality criterion of the equation obtained by the method is not absolute, as a rule, but the relative mean-square deviation

$$\delta_{\mathrm{m.\,sq}}=\sqrt{\sum_{i=1}^{N}((y_{\exp_i}-y\ \mathrm{calc}_i)/y_{\exp_i})^2/(N-M-1)}. \tag{4}$$

The values of the coefficients giving a minimum of the functional of the absolute and relative deviations do not necessarily coincide here [2]. In connection with this, the possibility of using the sum of squares of the relative deviations as the minimization criteria in the LSM scheme is investigated in the present work. In matrix form, the relative-devia-

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