THERMAL CONDUCTIVITY OF A MULTICOMPONENT GAS MIXTURE IN THE PRESENCE OF EQUILIBRIUM CHEMICAL REACTIONS

M. I. Verba and V. D. Portnov

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Using methods of the thermodynamics of irreversible processes, an expression is obtained for the thermal conductivity of multicomponent gas mixtures.

When chemical reactions take place between the components of a gas mixture, it is expedient to investigate heat and mass transfer by introducing the transformed mass and energy fluxes [1]

$$J_i = K_i - x_i \sum_{k=1}^{f} K_k \quad (i = 1, 2, 3, \ldots, f), \tag{1}$$

$$J_q = -h \sum_{i=1}^{f} K_i. \tag{2}$$

In the absence of external forces, the phenomenological equation connected with transfer of mass and energy may be written in the form

$$K_i = -\sum_{k=1}^{f} a_{ik} \cdot \operatorname{grad} \psi_k \quad (i = 1, 2, 3, \ldots, f). \tag{3}$$

Relations (1)–(3) were used by De Groot [2, 3] to determine the thermal conductivity, concentration gradients, and temperatures relating to the special case of a chemically reacting binary mixture. In our paper, as an example of a three-component mixture reacting according to the scheme A ⇌ B + C, we examine the general case of thermal conductivity of a multicomponent mixture. A relation is established between the ordinary phenomenological coefficients L_{uu}, L_{uj}, L_{ij} and the phenomenological coefficients a. For the chemically reacting binary gas mixture we find that such a relation is not mandatory, since in this very simple case we may obtain expressions which allow the values of a to be determined directly from the values λ, D_{ij} and D_i^T, without establishing a general relation between a and L_{uu}, L_{uj}, L_{ij}, as De Groot did.

Allowing for the assumptions made in [2] and [3], the expression for the effective thermal conductivity may be written in the form

$$\lambda_{\text{eff}} = \frac{h^2}{T^2 [(x_2^*)^2 + (x_3^*)^2]}, \tag{4}$$

where

$$x_2^* = x_1 Q_{12} + x_2 Q_{22} + x_3 Q_{32}, \tag{5}$$

$$x_3^* = x_1 Q_{13} + x_2 Q_{23} + x_3 Q_{33}, \tag{6}$$

and the elements of the transformation matrix Q are determined by the equations

$$Q_{i1} = \sum_{k=1}^{f} \nu_{k1} D_{ik} / |a| \sqrt{Sp\,|a^{-1}b|} \quad (i = 2, 3), \tag{7}$$

$$Q_{3i} = \sqrt{(D_{33} - Q_{31}^2 |a|)/2|a|} \quad (i = 2, 3), \tag{8}$$

$$Q_{23} = (a^* + \sqrt{(a^*)^2 - 2b^*})/2, \tag{9}$$

$$Q_{22} = -Q_{23} + a^*, \tag{10}$$

$$Q_{1i} = -(Q_{2i}\nu_{21} + Q_{3i}\nu_{31})/\nu_{11} \quad (i = 2, 3). \tag{11}$$

Here $a^* = (D_{32} - Q_{21} \cdot Q_{31} |a|)/|a| Q_{32}$; $b^* = a^{*2} - D_{22}/a + Q_{21}^2$.

In order to determine the effective thermal conductivity from (4), besides the enthalpy h and temperature T, we need to know the reduced concentrations x_2^* and x_3^*. To find the reduced concentrations we need to know the concentrations x_1, x_2, x_3 and the elements of matrix Q. To find the numerical values of the elements of matrix Q, we establish the relation between the transfer coefficients D_{ij}, λ, D_i^T and the phenomenological coefficients a_{ij}.

To do this we write (1) and (2), using (3), in the form

$$J_i = \sum_{k=1}^{f} (A_k x_i - a_{ik}) \operatorname{grad} \psi_k \quad (i = 1, 2, \ldots, f), \tag{12}$$

$$J_q = h \sum_{k=1}^{f} A_k \operatorname{grad} \psi_k, \tag{13}$$

Here $A_k = \sum_{i=1}^{f} a_{ki}$.

In the ordinary form the mass and energy equations are

$$J_i = -T \times \sum_{k=1}^{f} L_{ik} \operatorname{grad} \psi_k - L_{iu} \frac{1}{T} \operatorname{grad} T \quad (i = 1, 2, \ldots, f), \tag{14}$$

$$J_q = -T \sum_{k=1}^{f} L_{uk} \operatorname{grad} \psi_k - L_{uu} \frac{1}{T} \operatorname{grad} T. \tag{15}$$

Let us examine the case of mechanical equilibrium grad p = 0. In this case the Gibbs-Duhem equation takes the form

$$h\,\mathrm{grad}\,\frac{1}{T}-\sum_{i=1}^{f}x_i\,\mathrm{grad}\,\psi_i=0. \qquad (16)$$

Determining the value of grad T from (16), and substituting it into (14) and (15), we obtain

$$J_i=T\sum_{k=1}^{f}\left(L_{iu}\frac{x_k}{h}-L_{ik}\right)\mathrm{grad}\,\psi_k \quad (i=1,\,2,\,\ldots,f), \qquad (17)$$

$$J_q=T\sum_{k=1}^{f}\left(\frac{L_{uu}}{h}x_k-L_{uk}\right)\mathrm{grad}\,\psi_k. \qquad (18)$$

By equating values of coefficients of the independent variables Ψ_k in (12) and (17), and (13) and (18), we obtain the system of equations

$$A_kx_i-a_{ik}=\left(L_{iu}\frac{x_k}{h}-L_{ik}\right)T, \qquad (19)$$

$$hA_k=T\left(L_{uu}\frac{x_k}{h}-L_{uk}\right). \qquad (20)$$

Solving this system, we find the connection between coefficients a_{ik} and L_{ik}, L_{ui}, L_{uu}:

$$a_{ik}=\left[L_{ik}-\frac{1}{h}(x_iL_{uk}+x_kh_{iu})+\frac{x_ix_k}{h^2}L_{uu}\right]T. \qquad (21)$$

It may be shown [2] that

$$\frac{L_{uu}}{T}=\lambda_m+\frac{2}{T}\sum_{k=1}^{3}L_{uk}h_k-\frac{1}{T}\sum_{i=1}^{3}h_i\sum_{k=1}^{3}L_{ik}h_k, \qquad (22)$$

$$L_{iu}=D_i^T-\sum_{k=1}^{3}L_{ik}h_k. \qquad (23)$$

The diffusion coefficients of a multicomponent mixture are [4]

$$L_{ij}=\frac{n^2n_jm_im_j}{\rho^2\cdot p}\left[-\rho\,m_iD_{ij}+\sum_{\substack{k=1\\k\neq i}}^{f}n_km_k^2D_{ik}\right]. \qquad (24)$$

Thus, the following method is suggested for calculation of the effective thermal conductivity λ_{eff}.

Knowing the concentration, pressure, temperature, and coefficients of thermal conductivity, diffusion, and thermodiffusion of the components of the mixture, the values of coefficients L_{ij} are determined from (24). Having determined the enthalpy of the component h_i from thermodynamic tables (or by calculation), we find the values of L_{uu} and L_{ui} from (22) and (23), and then from (21) we determine the coefficients a_{ik}.

The elements of matrix Q are determined from (7)–(11). Then, from (5) and (6), we find the reduced molar concentrations x_2^* and x_3^*. The effective thermal conductivity is determined from (4).

The method proposed for calculating the effective thermal conductivity differs from that proposed by Schott [5], in that in the given case the expression for calculating the effective thermal conductivity takes into account not only diffusion, but also thermodiffusion components. The method proposed, and the relation established between the phenomenological coefficients of type a_{ij} and the ordinary coefficients L_{uj}, L_{uu}, L_{ij}, allows calculation of the effective thermal conductivity of any multicomponent mixture with a single chemical reaction.

NOTATION

x_i—molar fraction of i-th component; J_q—energy flux; J_q'—heat flux; J_i—mass flux of i-th component; T—absolute temperature; μ_i—molar chemical potential of i-th component; L_{ik}, L_{qq}, L_{iu}, L_{iq}, L_{uu}, a_{ij}—phenomenological coefficients related, respectively, to mass transfer, energy transfer, and superimposed phenomena; h_i—enthalpy of i-th component; D_{ij}—diffusion coefficient of multicomponent mixture; D_i^T—thermodiffusion coefficient of i-th component in the multicomponent system; ρ—density; n—mixture particle number density; n_i—particle number density of i-th component; m_i—molecular mass of i-th component; p—pressure of mixture; f—number of components of mixture; $\psi_i = -\mu_i/T$—Planck potential; h—mixture enthalpy; K_i—fluxes (see (1) and (2)); D_{ij}—cofactor of matrix a; ν—a quantity proportional to the stoichiometric coefficient; b—matrix characterizing flow of chemical reactions in the given system.

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Moscow Institute of Power Engineering