

THERMAL CONDUCTIVITY OF A CHEMICALLY REACTING TERNARY GAS MIXTURE

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Inzhenerno-Fizicheskii Zhurnal, Vol. 9, No. 6, pp. 729-734, 1965

UDC 536.23

On the basis of the thermodynamics of irreversible processes, an expression is derived for the thermal conductivity of a chemically reacting gas mixture.

The thermal conductivity of a chemically reacting gas mixture is considerably greater than that of a nonreacting gas. The reason for the increase was first pointed out by Nernst [1], who examined the dissociation of nitrogen tetroxide.

In contrast to a nonreacting gas, in which heat is transmitted mainly by collisions of molecules and the heat flux vector is proportional to the temperature field gradient, there arises in a reacting gas mixture an additional heat flux transferred as chemical enthalpy of the molecules diffusing due to the concentration gradient produced in the reaction.

In a number of papers [2-5] the expression proposed by Nernst for the thermal conductivity has since been refined, and simple cases of chemical reactions of the type $A \rightleftharpoons 2B$ have been examined.

In the steady state, and in the presence of chemical equilibrium, the effective thermal conductivity is

$$\lambda_u = \lambda_m + \lambda_D - \lambda_{TD}. \quad (1)$$

This expression contains three terms: the ordinary thermal conductivity λ_m , the "diffusion" conductivity λ_D due to the chemical reaction, and, finally, the term λ_{TD} connected with thermodiffusion and the Dufour effect. Substituting values of the respective components of the conductivity [2] into (1), we obtain

$$\lambda_u = \lambda_m + D\rho \frac{H_R^2 C_1 C_2}{R^2 T^3} - 2D_r \rho \frac{H_R}{RT^2}. \quad (2)$$

The topic of this paper is an examination of the most general case—the thermal conductivity of a gas reacting according to the scheme $A \rightleftharpoons B + C$.

Let the gas mixture be located between two plates at temperatures T and $T + \Delta T$. Since there is a temperature gradient between the plates, in the presence of a reaction a concentration gradient of dissociated and undissociated molecules arises at every point in space. Then the heavy undissociated molecules diffuse into the region at the higher temperature and there dissociate, absorbing heat. Conversely, the light dissociation products diffuse into the lower-temperature region and there recombine, emitting heat. As a result of mutual diffusion in this cyclic process, heat transfer increases in the direction opposite to the temperature gradient. In examining the thermal conductivity of reacting gases we

must also take into account thermodiffusion and the Dufour effect.

We shall examine the steady state of the above cyclic process in a system reacting according to the scheme $A \rightleftharpoons B + C$. We shall introduce, for simplicity, indices 1, 2, and 3, denoting respectively components A, B, and C. We write the phenomenological equations of transfer of mass and energy in the form

$$J_i = \sum_{k=1}^3 L_{ik} X_k + L_{iu} X_u, \quad i = 1, 2, 3, \quad (3)$$

$$J_u = \sum_{k=1}^3 L_{uk} X_k + L_{uu} X_u. \quad (4)$$

We write the values of the affinity quantities X_k and X_u , in the absence of external forces, in the form

$$X_k = -T \text{grad}(\mu_k/T), \quad (5)$$

$$X_u = -\frac{1}{T} \text{grad} T. \quad (6)$$

Taking (5) and (6) into account, we may write (3) and (4) in the form

$$J_i = -\sum_{k=1}^3 L_{ik} \text{grad} \mu_k + \left(\sum_{k=1}^3 L_{ik} \mu_k - L_{ui} \right) \frac{1}{T} \text{grad} T, \quad (7)$$

$$J_q = -\sum_{k=1}^3 L_{uk} \text{grad} \mu_k + \left(\sum_{k=1}^3 L_{uk} \mu_k - L_{uu} \right) \frac{1}{T} \text{grad} T. \quad (8)$$

The chemical potential is a function of temperature, pressure, and the $r - 1$ concentrations x_j

$$\text{grad} \mu_k = -S_k \text{grad} T + v_k \text{grad} p + \sum_{j=1}^{r-1} \left(\frac{\partial \mu_k}{\partial x_j} \right)_{TP} \text{grad} x_j. \quad (9)$$

Since the chemical potential is a function of the $r - 1$ concentrations, by substituting values of the chemical potential gradient (9) into (7) and (8), the partial derivative $(\partial \mu_k / \partial x_j)_{TP}$ in the last term of (9) may be eliminated in some way. We shall eliminate it in such a way that (7) and (8) may be written in the form

$$J_i = \left(\sum_{k=1}^3 L_{ik} T S_k + \sum_{k=1}^3 L_{ik} \mu_k - L_{iu} \right) \frac{1}{T} \text{grad} T - \quad (10)$$

$$-\sum_{j=1}^3 \sum_{k=1}^3 L_{ik} \left(\frac{\partial \mu_k}{\partial x_j} \right)_{pT} \text{grad } x_j, \quad (10)$$

(Cont'd)

$$J_q = \left(\sum L_{uk} S_k T + \sum L_{uk} \mu_k - L_{uu} \right) \frac{1}{T} \text{grad } T -$$

$$-\sum_{j=1}^3 \sum_{\substack{k=1 \\ k \neq j}}^3 L_{uk} \left(\frac{\partial \mu_k}{\partial x_j} \right)_{pT} \text{grad } x_j. \quad (11)$$

Since the specific enthalpy $h_k = \mu_k + TS_k$, we finally obtain

$$J_i = \left(\sum_{k=1}^3 L_{ik} h_k - L_{iu} \right) \frac{1}{T} \text{grad } T -$$

$$-\sum_{j=1}^3 \sum_{\substack{k=1 \\ k \neq j}}^3 L_{ik} \left(\frac{\partial \mu_k}{\partial x_j} \right)_{pT} \text{grad } x_j, \quad (12)$$

$$J_u = \left(\sum_{k=1}^3 L_{uk} h_k - L_{uu} \right) \frac{1}{T} \text{grad } T -$$

$$-\sum_{j=1}^3 \sum_{\substack{k=1 \\ k \neq j}}^3 L_{uk} \left(\frac{\partial \mu_k}{\partial x_j} \right)_{pT} \text{grad } x_j. \quad (13)$$

It is assumed here that the system examined is in mechanical equilibrium, i. e., $\text{grad } p = 0$, and that the velocity of motion of the center of gravity of the system $V = 0$.

We introduce the transfer energy u_k^* , determined by the expression

$$L_{uk} = \sum_{k=1}^3 L_{ik} u_k^*, \quad i = 1, 2, 3, \quad (14)$$

then, taking (3) and (4) into account, and applying the Onsager reciprocity principle, we can write the energy flux equation (4) as

$$J_u = \sum_{i=1}^n u_i^* J_i - \sum_{i=1}^n L_{iu} u_i^* X_u + L_{uu} X_u. \quad (15)$$

The first term on the right side of (15) is the energy transferred by the mass flux, i. e., the transfer of energy by diffusion and thermodiffusion. The second term also describes energy transfer due to diffusion and thermodiffusion. In the case of fast chemical reactions the rate of diffusion is considerably less than the rate of establishment of chemical equilibrium, and the energy transfer process is limited by diffusion, and not by the chemical reaction rate. Therefore, for a steady state of the cyclic type, the first and second terms of (15) are equal and cancel one another. Then (15) takes the form

$$J_u = L_{uu} X_u. \quad (15a)$$

We shall examine the expression for the heat flux, which is the difference between the energy flux J_u and the heat flux carried by diffusion,

$$J_q = J_u - \sum_{i=1}^3 h_i J_i. \quad (16)$$

In the case of no external forces the heat flux J_q may be written in the form

$$J_q = -\frac{L_{qq}}{T} \text{grad } T - \sum_{k=1}^{n-1} \frac{\text{grad}(\mu_k - \mu_n)_T}{T}. \quad (17)$$

Substituting into (16) the values of J_n and J_i from (12) and (13), we obtain

$$J_q = \left(\sum_{k=1}^3 L_{uk} h_k - L_{uu} - \sum_{i=1}^3 h_i \sum_{k=1}^3 L_{ik} h_k + \sum_{i=1}^3 L_{iu} h_i \right) \times$$

$$\times \frac{1}{T} \text{grad } T - \sum_{j=1}^3 \sum_{\substack{k=1 \\ k \neq j}}^3 L_{uk} \left(\frac{\partial \mu_k}{\partial x_j} \right)_{pT} \text{grad } x_j +$$

$$+ \sum_{i=1}^3 h_i \sum_{j=1}^3 \sum_{\substack{k=1 \\ k \neq j}}^3 L_{ik} \left(\frac{\partial \mu_k}{\partial x_j} \right)_{pT} \text{grad } x_j. \quad (18)$$

Applying the Onsager reciprocity principle, we finally obtain

$$J_q = - \left(L_{uu} - 2 \sum_{k=1}^3 L_{uk} h_k + \sum_{i=1}^3 h_i \sum_{k=1}^3 L_{ik} h_k \right) \times$$

$$\times \frac{1}{T} \text{grad } T - \sum_{j=1}^3 \sum_{\substack{i=1 \\ i \neq j}}^3 L_{ui} \left(\frac{\partial \mu_i}{\partial x_j} \right)_{pT} \text{grad } x_j -$$

$$- \sum_{i=1}^3 h_i \sum_{j=1}^3 \sum_{\substack{k=1 \\ k \neq j}}^3 L_{ik} \left(\frac{\partial \mu_k}{\partial x_j} \right)_{pT} \text{grad } x_j. \quad (19)$$

Comparing (17) and (18), and bearing in mind that in the case of mechanical equilibrium the second term in (17) does not depend on the temperature gradient, we obtain

$$\frac{L_{uu}}{T} = \frac{L_{qq}}{T} + \frac{2}{T} \sum_{k=1}^3 L_{uk} h_k - \sum_{i=1}^3 h_i \sum_{k=1}^3 L_{ik} h_k. \quad (20)$$

For any multicomponent mixture, the expression for the mass flux may be written in the following form [6, 7]:

$$J_i = \frac{n^2}{\rho} \sum_{i=1}^n m_i m_j D_{ij} d_j - D_i^* \frac{1}{T} \text{grad } T, \quad i = 1, 2, 3. \quad (21)$$

In the absence of external forces and with the condition $\text{grad } p = 0$, the quantity d_j is equal to the molar concentration gradient of the j -th component. Comparing

coefficients with the gradients in (10) and (21), we obtain the following relations for the diffusion and the thermodiffusion coefficients of a three-component system, expressed in terms of the phenomenological coefficients:

$$D_{ij} = -\frac{\rho}{n^2 m_i m_j} \sum_{k=1}^3 L_{ik} \left(\frac{\partial \mu_k}{\partial x_j} \right)_{pT}, \quad (22)$$

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

where the molar chemical potential μ_k for ideal gases may be written as

$$\mu_k = \mu_0(T, p) + \ln x_i.$$

Here we must satisfy the symmetry conditions

$$D_{ij} = D_{ji}, \quad L_{ik} = L_{ki}, \quad L_{ui} = L_{iu}.$$

The phenomenological coefficients may be expressed in terms of the diffusion coefficients of a multicomponent mixture

$$L_{ij} = \frac{n^2 n_j m_j m_i}{\rho^2 p} \left[-\rho m_j D_{ij} + \sum_{k=1, k \neq j}^3 n_k m_k^2 D_{ik} \right]. \quad (24)$$

Substituting (24) into (20), and taking (23) and the condition $\sum_{i=1}^3 L_{ui} = 0$, into account, we obtain

$$\frac{L_{uu}}{T} = \frac{L_{qq}}{T} - 2 \frac{D_1^T (h_1 - h_3) + D_2^T (h_2 - h_3)}{T} -$$

$$- \frac{n^2}{2\rho p T} \sum_{\substack{i,j=1 \\ k=i,j}}^n D_{ij} m_i m_j [n_k n_j m_k m_i (h_k - h_i)^2 + n_k h_i m_k m_i \cdot$$

$$\cdot (h_k - h_j)^2 - (n_k n_j m_k m_i + n_k n_i m_k m_i + 2n_j m_j m_i) (h_j - h_i)^2]. \quad (25)$$

We write (25) in the general form

$$\lambda_u = \lambda_m - \lambda_{\tau D} + \lambda_D, \quad (26)$$

$$\lambda_u = L_{uu}/T, \quad (27)$$

where

$$\lambda_{\tau D} = 2 [D_1^T (h_1 - h_3) + D_2^T (h_2 - h_3)]/T, \quad (28)$$

$$\lambda_D = -\frac{n^2}{2\rho p T} \sum D_{ij} m_i m_j [n_k n_j m_k m_i (h_k - h_i)^2 +$$

$$+ n_k n_i m_i (h_k - h_j)^2 - (n_k n_j m_k m_i + n_k n_i m_k m_i + 2n_j m_j m_i) (h_j - h_i)^2]. \quad (29)$$

In (26) the first term represents the transfer of heat by ordinary heat conduction, the second term—the transfer of reaction enthalpy due to thermodiffusion and the Dufour effect, and the third term—that due to diffusion.

Expression (25), obtained for the first time, is the general equation for calculating the effective thermal conductivity of a three-component chemically reacting gas mixture. The values of the diffusion and the thermodiffusion components of the thermal conductivity [equations (29) and (28)] appearing in (25), contain the diffusion and thermodiffusion coefficients for a multicomponent mixture.

NOTATION

x_i —molar fraction of i -th component; J_u —energy flux; c_i —mass fraction of i -th component; 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_{uu} , L_{ui} —phenomenological coefficients, associated respectively with the transfer of mass and energy and with the superimposed effects; X_u and X_k —thermodynamic forces associated with the mass and energy fluxes; h_i —enthalpy of i -th component; S —entropy of i -th component; D_{ij} —diffusion coefficient of a multicomponent mixture; D_i^T —thermodiffusion coefficient of i -th component in a multicomponent system; $\mu_0(T, p)$ —chemical potential in standard state; ρ —density; h —number density of mixture particles; h_j —number density of particles of i -th component; m_i —molecular weight of i -th component; p —pressure of mixture; v_i —specific volume of i -th component; H —heat of reaction; r —number of component of mixture; R —gas constant; D_T —thermodiffusion coefficient of a binary mixture.

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10 February 1965

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