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Thermal Conductivity of Gas Mixtures in Chemical Equilibrium. II

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(Received November 2, 1959)

The expression for the thermal conductivity of gas mixtures in chemical equilibrium is presented in a simpler and less restrictive form. This new form is shown to be equivalent to previous equations.

In a previous paper\(^1\) an explicit expression for the increase in thermal conductivity due to chemical reaction was developed for gas mixtures in which chemical equilibrium exists locally throughout the temperature gradient. This expression is applicable to mixtures involving any number of reactants, inert diluents, and chemical equilibria. It is the purpose of this brief paper to present the expression for thermal conductivity due to reaction in a simpler and less restrictive form, and to show that this form is equivalent to previous equations.

A system of \(v\) independent chemical reactions involving \(u\) chemical species (both reactants and diluents) may be written in balanced form as

\[
\sum_{k=1}^u n_{ik} x^k = 0 \quad i = 1, 2, \ldots, v \tag{1}
\]

Here \(x^k\) represents the \(k\)th chemical species and \(n_{ik}\) is the stoichiometric coefficient for species \(k\) in reaction \(i\). The heat of this reaction is

\[
\Delta H_i = \sum_{k=1}^u n_{ik} \Delta H_k \quad i = 1, 2, \ldots, v \tag{2}
\]

where the \(\Delta H_k\) are the enthalpies of the species referred to a common base. For this system the thermal conductivity due to reaction is

\[
\lambda_v = -\frac{1}{RT^2} \begin{vmatrix} A_{11} & \cdots & A_{1v} & \Delta H_1 \\ \vdots & \ddots & \vdots & \vdots \\ A_{1v} & \cdots & A_{vv} & \Delta H_v \end{vmatrix} \tag{3}
\]

where

\[
A_{ij} = \sum_{k=1}^u \sum_{l=1}^u (RT/D_{kl}P)x_kx_l[(n_{ik}/x_k) - (n_{jl}/x_l)] \quad i, j = 1, 2, \ldots, v 
\]

Here \(R\) is the gas constant in pressure-volume units, \(T\) is the absolute temperature, \(P\) the pressure, and \(D_{kl}\) the binary diffusion coefficient between components \(k\) and \(l\); \(x_k\) and \(x_l\) are the corresponding mole-fractions. Any gas inert to reaction \(i\) or \(j\) must be included, but has a zero stoichiometric coefficient for the reaction in which it does not participate.

Equations (1)–(4) are most easily verified by assuming them correct and deriving the previous result (Eqs. (10)–(12) of reference 1). In the previous paper an independent component was identified in each reaction and given a stoichiometric coefficient of \(-1\). This

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form can be achieved as follows: First Eq. (1) is rewritten

\[ X^r = \sum_{k=1}^{v} n_{ak}^r X^k \quad i = 1, 2, \ldots, j , \ldots, v \]  

(5)

where \( n_{ak}^r = n_{ak}/n_{i0} \). We can transform Eq. (3) by dividing each row and column by the \( -n_{i0} \) or \(-n_{ij}\) appropriate to that row or column in both numerator and denominator determinants. The form of Eq. (3) is maintained, but the quantities \( \Delta H_i \) and \( A_{ij} \) are transformed, and indicated by primes:

\[ \Delta H_i' = (\Delta H / n_{i0}) = \sum_{k=1}^{v} n_{ak}' H_k - H_i \]  

(6)

The \( A_{ij}' \) are given by Eq. (4) if the \( n_{ak}, n_{i0}, n_{ij}, n_{ik} \), and \( n_{ij} \) are replaced by \( n_{ak}', n_{i0}', n_{ij}', n_{ik}' \), and \( n_{ij}' \). Equations (5) and (6) are now of the form used in reference 1. It remains only to show that the \( A_{ij}' \) are equal to the \( A_{ij} \) and \( A_{kk} \) defined by Eqs. (10) and (11) of reference 1. To prove this we split the double sum of Eq. (4) into two series. The first series sums over the independent components from 1 to \( v \); summation in this instance is over indices \( r \) and \( s \). Accordingly,

\[ A_{ij}' = 4 \sum_{p=1}^{u} \sum_{q=1}^{s} - \sum_{p=1}^{u} \sum_{q=1}^{s} + \sum_{p=1}^{u} \sum_{q=1}^{s} - \sum_{p=1}^{u} \sum_{q=1}^{s} \]  

(7)

Since by definition the independent species occur in only one reaction, we find

\[ \Delta h_{ij}' = \Delta h_{ij}' = -1, \quad \rho, q = i \quad \rho, q = i \quad \rho, q = j \quad \rho, q = j \]

\[ = 0, \quad \rho, q = j \quad 0, \quad \rho, q \neq j \].

If we define \( \Delta h_{ij} = RT/D_{k1} P \), we find that the terms of Eq. (7) are

\[ \sum_{p=1}^{u} \sum_{q=1}^{s} = - \Delta h_{ij} \]  

\[ \sum_{p=1}^{u} \sum_{q=1}^{s} = \Delta h_{ij}' (x_p/x_i), \quad j = i \]  

\[ \sum_{p=1}^{u} \sum_{q=1}^{s} = \sum_{p=1}^{u} \sum_{q=1}^{s} n_{i0}' n_{ij}' \Delta h_{ij}' (x_p/x_i) \]  

\[ + \sum_{p=1}^{u} \sum_{q=1}^{s} (n_{i0}' \Delta h_{ij} + n_{ij}' \Delta h_{ij}' ), \quad j \neq i \]  

\[ = \sum_{p=1}^{u} \sum_{q=1}^{s} n_{i0}' \Delta h_{ij}' (x_p/x_i) \]  

\[ + \sum_{p=1}^{u} \sum_{q=1}^{s} \Delta h_{ij}' [(x_p + n_{i0}' x_i)^/d x_p] \], \quad j = i \]  

\[ \sum_{p=1}^{u} \sum_{q=1}^{s} \sum_{p=1}^{u} \sum_{q=1}^{s} \Delta h_{ij}' [(n_{ij}' x_i - n_{ij}' x_i) (n_{ij}' x_i - n_{ij}' x_i)] \]  

\[ x_p x_i \]  

\[ j \neq i \]  

\[ = \sum_{p=1}^{u} \sum_{q=1}^{s} \sum_{p=1}^{u} \sum_{q=1}^{s} \Delta h_{ij}' [(n_{ij}' x_i - n_{ij}' x_i)^/d x_p x_i] \], \quad j = i \]  

After summing the appropriate terms of Eq. (7), the elements \( A_{ij}' \) and \( A_{kk} \) are found to be identical to the elements \( A_{ak} \) and \( A_{kk} \) of reference 1. (There are differences in the symbols, particularly in the letters chosen for the indices.) Hence, Eqs. (1) through (4) are entirely equivalent to the expression for the thermal conductivity of a reacting gas presented here-tofore.

In conclusion, it is perhaps worthwhile to state specifically how the formulas presented here are superior to the previous expressions. First and foremost, it is not necessary to identify a specific independent component with each reaction; that is to say Eq. (1) is less restrictive than Eq. (5). As a consequence the contribution of each component to each reaction is handled entirely through the stoichiometric coefficients, and a single, and relatively simple, expression suffices for all the \( A_{ij} \) [Eq. (4)]. This is not only convenient for hand calculations; it should also simplify programming for computing machines.