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Thermal Conductivity of Gas Mixtures in Chemical Equilibrium. II

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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 the 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 ν independent chemical reactions involving μ chemical species (both reactants and diluents) may be written in balanced form as

$$\sum_{k=1}^{\mu} n_{ik} X^k = 0 \qquad i=1, 2, \cdots j, \cdots \nu. \tag{1}$$

Here X^k represents the kth chemical species and n_{ik} is the stoichiometric coefficient for species k in reaction i. The heat of this reaction is

$$\Delta H_i = \sum_{k=1}^{\mu} n_{ik} H_k \qquad i=1, 2, \cdots j, \cdots \nu, \tag{2}$$

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

$$\lambda_r = -\frac{1}{RT^2} \frac{\begin{vmatrix} A_{11} & \cdots & A_{1\nu} & \Delta H_1 \\ \vdots & & \vdots & \vdots \\ A_{1\nu} & \cdots & A_{\nu\nu} & \Delta H_\nu \\ \Delta H_1 & \cdots & \Delta H_\nu & 0 \end{vmatrix}}{\begin{vmatrix} A_{11} & \cdots & A_{1\nu} \\ \vdots & & \vdots \\ A_{1\nu} & \cdots & A_{\nu\nu} \end{vmatrix}} \tag{3}$$

where

$$A_{ij} = A_{ji} = \sum_{k=1}^{\mu-1} \sum_{l=k+1}^{\mu} (RT/D_{kl}P) x_k x_l [(n_{ik}/x_k) - (n_{il}/x_l)][(n_{jk}/x_k) - (n_{jl}/x_l)] \quad i, j = 1, 2, \cdots \nu. \tag{4}$$

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

[1] J. N. Butler and R. S. Brokaw, J. Chem. Phys. 26, 1636 (1957).

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

$$X^i = \sum_{k=1,k\neq i}^{\mu} n_{ik}' X^k \quad i=1, 2, \cdots j, \cdots \nu, \tag{5}$$

where $n_{ik}' \equiv -n_{ik}/n_{ii}$. We can transform Eq. (3) by dividing each row and column by the $-n_{ii}$ or $-n_{jj}$ appropriate to that row or column in both numerator and denominator determinants. The form of Eq. (3) is maintained, but the quantities ΔH_i and A_{ij} are transformed, and indicated by primes:

$$\Delta H_i' \equiv -(\Delta H_i/n_{ii}) = \sum_{k=1,k\neq i}^{\mu} n_{ik}' H_k - H_i \tag{6}$$

The A_{ij}' are given by Eq. (4) if the n_{ik}, n_{il}, n_{jk}, and n_{jl} are replaced by n_{ik}', n_{il}', n_{jk}', and n_{jl}'. 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_{ik} 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 ν; summation in this series is indicated by the index p or q. The second series sums over all other species from $\nu+1$ to μ; summation in this instance is over indices r and s. Accordingly,

$$A_{ij}' = \tfrac{1}{2}\sum_{k=1}^{\mu}\sum_{l=1}^{\mu} = \tfrac{1}{2}\sum_{p=1}^{\nu}\sum_{q=1}^{\nu} + \sum_{p=1}^{\nu}\sum_{r=\nu+1}^{\mu} + \tfrac{1}{2}\sum_{r=\nu+1}^{\mu}\sum_{s=\nu+1}^{\mu}. \tag{7}$$

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

$$n_{ip}' = n_{iq}' = -1, \quad p, q = i; \quad n_{jp}' = n_{jq}' = -1, \quad p, q = j$$
$$= 0, \quad p, q \neq i; \qquad = 0, \quad p, q \neq j.$$

If we define $\Delta_{kl} \equiv RT/D_{kl}P$, we find that the terms of Eq. (7) are

$$\tfrac{1}{2}\sum_{p=1}^{\nu}\sum_{q=1}^{\nu} = -\Delta_{ij}, \quad j\neq i$$
$$= \sum_{p=1,p\neq i}^{\nu} \Delta_{pi}(x_p/x_i), \quad j=i$$

$$\sum_{p=1}^{\nu}\sum_{r=\nu+1}^{\mu} = \sum_{r=\nu+1}^{\mu}\sum_{p=1}^{\nu} n_{ir}' n_{jr}' \Delta_{pr}(x_p/x_r)$$
$$+ \sum_{r=\nu+1}^{\mu}(n_{ir}'\Delta_{jr} + n_{jr}'\Delta_{ir}), \quad j\neq i$$
$$= \sum_{r=\nu+1}^{\mu}\sum_{p=1,p\neq i}^{\nu} n_{ir}'^2 \Delta_{pr}(x_p/x_r)$$
$$+ \sum_{r=\nu+1}^{\mu} \Delta_{ir}[(x_r + n_{ir}'x_i)^2/x_i x_r], \quad j=i$$

$$\tfrac{1}{2}\sum_{r=\nu+1}^{\mu}\sum_{s=\nu+1}^{\mu} = \sum_{r=\nu+1}^{\mu-1}\sum_{s=\nu+1}^{\mu} \Delta_{rs}\frac{(n_{ir}'x_s - n_{is}'x_r)(n_{jr}'x_s - n_{js}'x_r)}{x_r x_s}, \quad j\neq i$$
$$= \sum_{r=\nu+1}^{\mu-1}\sum_{s=\nu+1}^{\mu} \Delta_{rs}[(n_{ir}'x_s - n_{is}'x_r)^2/x_r x_s], \quad j=i$$

After summing the appropriate terms of Eq. (7), the elements A_{ij}' and A_{ii}' are found to be identical to the elements A_{ik} 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 heretofore.

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 programing for computing machines.

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