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Heat Diffusion in Gases, Including Effects of Chemical Reaction

C. FREDERICK HANSEN¹Ames Research Center,
NASA
Moffett Field, Calif.

The diffusion of heat through gases is treated where the coefficients of thermal conductivity and diffusivity are functions of temperature. The diffusivity is taken proportional to the integral of thermal conductivity, where the gas is ideal, and is considered constant over the temperature interval in which a chemical reaction occurs. The heat diffusion equation is then solved numerically for a semi-infinite gas medium with constant initial and boundary conditions. These solutions are in a dimensionless form applicable to gases in general, and they are used, along with measured shock velocity and heat flux through a shock reflecting surface, to evaluate the integral of thermal conductivity for air up to 5000 K. This integral has the properties of a heat flux potential and replaces temperature as the dependent variable for problems of heat diffusion in media with variable coefficients. Examples are given in which the heat flux at the stagnation region of blunt hypersonic bodies is expressed in terms of this potential.

THIS paper will consider some aspects of heat conduction through gases. Specifically, it will be confined to the case of pure diffusion; that is, heat transfer by mass convection and by radiation will not be treated. Finally, it will consider briefly the role of the diffusion process in heat transfer to the stagnation region of high speed vehicles.

Heat Diffusion in Ideal Gases

The classical solutions to the heat diffusion equation have generally made use of the assumption that the coefficient of thermal conductivity is a constant [see (1 and 2) for example].² However, for the problem of interest here, the conduction of heat through gases, thermal conductivity must be treated as a strong function of temperature (3). In such a case, it is useful to replace the usual dependent variable, temperature, with a quantity φ

$$\varphi = \int_0^T k dT \quad [1]$$

which is the coefficient of thermal conductivity integrated over temperature. Then the differential equation of heat conduction takes the usual form of the diffusion equation

$$\partial \varphi / \partial t - a \nabla^2 \varphi = 0 \quad [2]$$

where a is the thermal diffusivity. The dependent variable φ will be called the heat flux potential, since the heat flux at any point in the medium is just the gradient of φ

$$q = \text{grad } \varphi \quad [3]$$

Note that just as the reference level used for temperature is arbitrary, so the lower limit of the integral (Eq. [1]) is arbitrary. However, it will prove convenient to choose this lower limit somewhere near absolute zero for the case of conduction in gases.

Consider now the one-dimensional heat flow through a semi-infinite gas medium, where the initial conditions and the boundary conditions are constants. The initial potential throughout the gas will be designated by φ_∞ and the boundary value by φ_0 , the diffusivities by a_∞ and a_0 , respectively (see Fig. 1). Normalized coordinates will be used such that φ_0 and a_0 are both taken to be unity. The results can easily be generalized to account for arbitrary units of these boundary conditions, of course.

The idealization of constant initial and boundary conditions will be approximately realized in a physical situation where the reservoir is a slab of material with a very large heat capacity and a large thermal conductivity, such as a metal. Then the wall can soak up heat fast enough to maintain nearly constant conditions at the interface. The slab might be suddenly immersed in a constant temperature gas, for example, or, alternatively, the gas might be heated suddenly by a plane shock wave reflecting from the solid interface.

Boltzmann (4) has shown that the solution to this problem may be expressed with perfect generality as a function of x/\sqrt{t} . Therefore, the time and distance variables are transformed to the single dimensionless parameter y

$$y = x/\sqrt{4a_0t} \quad [4]$$

where a_0 is the diffusivity of the gas at the boundary. The coefficient a_0 is unity, of course, in the present normalized coordinate system, but this is not an essential feature of the transformation. In terms of this parameter y , the partial differential equation of heat conduction becomes the dimen-

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¹ Chief, Physics Branch. Member ARS.

² Numbers in parentheses indicate References at end of paper.

sionless, total differential equation

$$a \frac{d^2 \varphi}{dy^2} + 2y \frac{d\varphi}{dy} = 0 \quad [5]$$

The factor 4 in the parameter y (Eq. [4]) is an arbitrary stretching factor. It is chosen merely so that the solutions to Equation [5] reduce to the usual error function form when the diffusivity is constant, that is when a equals a_0 . The merit in using the normalized form for the potential φ (that is, φ/φ_0) is that one set of integrations for Equation [5] will suffice for all possible boundary conditions. All that is required before one proceeds with the integration is that the diffusivity a be evaluated. Two cases will be considered, one in which the gas is ideal and inert, and the second in which the gas is in local equilibrium but is chemically active with a large heat of reaction.

According to the kinetic theory of inert gases (5), the coefficient of thermal conductivity is approximately proportional to a power n of the temperature, where n is close to $\frac{1}{2}$. Thus the integral of thermal conductivity is proportional to the $n + 1$ power of temperature

$$\int k dT \propto T^{n+1} \quad [6]$$

Now the thermal diffusivity equals the conductivity divided by the heat capacity per unit volume $C\rho$. Since the density ρ is inversely proportional to temperature, for an ideal gas, the diffusivity is proportional to the $n + 1$ power of temperature also

$$k/C\rho \propto T^{n+1} \quad [7]$$

It follows that diffusivity is proportional to the potential φ , and in the present normalized coordinates this means that

$$a = \varphi \quad [8]$$

Sometimes a linear relation between a and φ with a finite intercept will best fit measured values, but this can always be transformed to the direct proportionality of Equation [8] by appropriate adjustment of the lower limit of the integral, Equation [1]. Generally, this limit will be close to absolute zero.

It may be remarked that even if one accounts for the variations of heat capacity which occur in a real gas, the preceding relations are valid to the order of approximation that Prandtl number is a constant. This can be seen from the fact that diffusivity is just the kinematic viscosity divided by the Prandtl number

$$a = \frac{\mu/\rho}{Pr} \quad [9]$$

and the kinematic viscosity is again approximately proportional to the $n + 1$ power of temperature, at least in gases composed of neutral particles.

When the result of Equation [8] is used, the heat diffusion equation takes the simple but nonlinear form

$$\varphi \frac{d^2 \varphi}{dy^2} + 2y \frac{d\varphi}{dy} = 0 \quad [10]$$

Analytic solutions to Equation [10] are known, but none which satisfy the boundary conditions, namely

$$\varphi(0) = 1 \quad [11a]$$

$$\lim_{y \rightarrow \infty} \varphi \rightarrow \varphi_\infty \quad [11b]$$

However, it is relatively easy to integrate the equation numerically, starting from a given value of the boundary derivative $\varphi'_0 = (d\varphi/dy)_0$, and terminating as the solution asymptotically approaches a limit φ_∞ . The solutions are something like error functions stretched slightly out of shape. Three of these solutions are shown in Fig. 2 as functions of

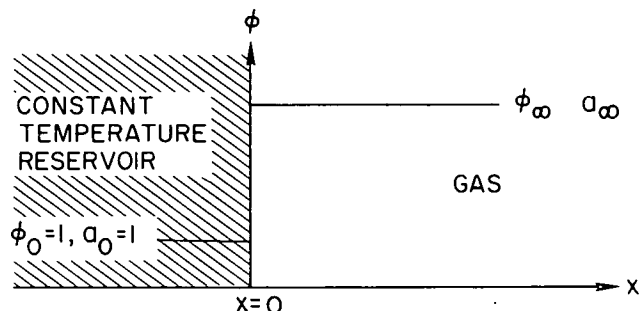


Fig. 1 One-dimensional heat diffusion

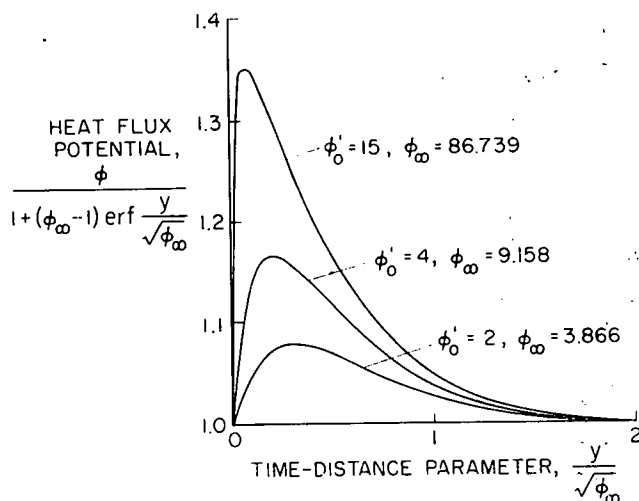


Fig. 2 Heat potentials in inert gases

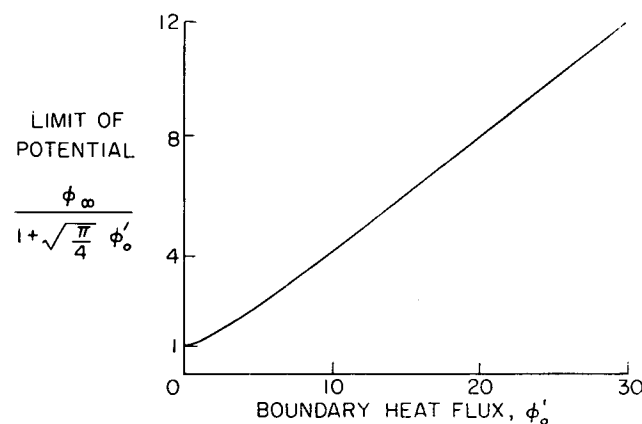


Fig. 3 Heat diffusion in inert gases

$y/\sqrt{\varphi_\infty}$. The solutions φ are shown divided by the error functions, $1 + (\varphi_\infty - 1) \operatorname{erf}(y/\sqrt{\varphi_\infty})$. The φ functions rise more steeply than the error functions near the origin, go through a maximum deviation, then approach the error function as a limit.

The value of φ_∞ is uniquely related to the derivative at the origin, φ'_0 . This relation is shown in Fig. 3. The derivative φ'_0 is equivalent to a dimensionless heat flux at the boundary, whereas the normalizing function $1 + \sqrt{\pi/4} \varphi'_0$ is the value which φ_∞ would have if diffusivity were a constant. We shall return to this relation between φ_∞ and φ'_0 after considering the case of the chemically reacting gas.

Heat Diffusion in a Chemically Reacting Gas

A chemical reaction in the gas behaves as a reservoir which soaks up heat as temperature is increased, and liberates heat when temperature drops. Consequently, the specific heat is very large if the heat of reaction is large compared to RT . Hirschfelder (6) has shown that the coefficient of thermal conductivity, for gases in local equilibrium, is also very large; in fact it is approximately proportional to the specific heat. Thus, the Prandtl number is relatively constant and the diffusivity is a function of temperature which is not greatly affected by the chemical reaction. The integral of thermal conductivity, on the other hand, is greatly increased as a result of the reaction. This situation is illustrated in Fig. 4.

The diffusivity increases linearly with φ up to the point where the chemical reaction occurs; there it flattens out until the reaction is about complete, and then it increases again in a more or less linear manner. The solid lines are theoretical estimates, calculated from results in (7) for the case of air in which oxygen dissociation occurs. The pressure dependence of the curve for φ less than $2\varphi_c$ has been removed by normalizing both ordinate and abscissa with the factor

$$\varphi_c = (T_c/T_0)^{n+1} \quad [12]$$

where

T_0 = boundary temperature

T_c = temperature where thermal conductivity is a maximum, i.e., where diffusivity is most nearly independent of the conductivity integral

The temperature T_c may be calculated from equations

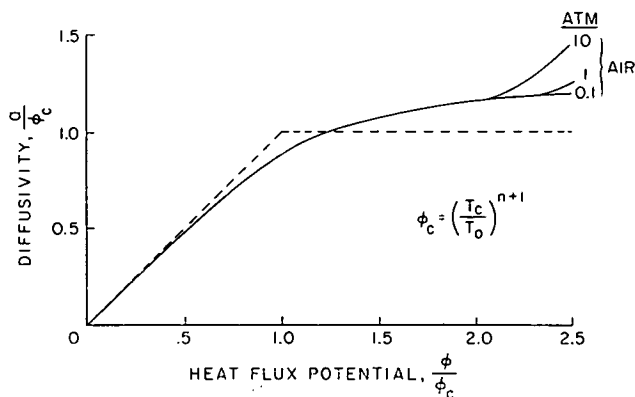


Fig. 4 Diffusivity function

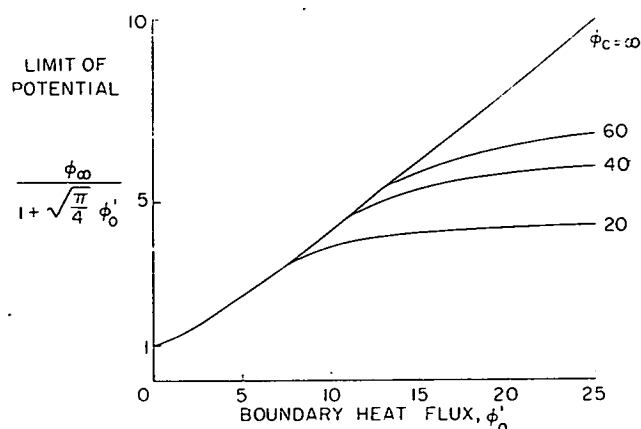


Fig. 5 Chemical equilibrium heat diffusion

derived by Butler and Brokaw (8) for the thermal conductivity of reacting gas mixtures.

It should be noted that the calculation of the relation between diffusivity and the conductivity integral does not depend on precise numerical values of the transport coefficients. For example, the estimate shown for air in Fig. 4 is based on simple kinetic theory and very approximate collision cross sections (7). However, the corrections introduced by more exact calculations affect both the diffusivity and the conductivity simultaneously in such a way that the functional relation between the two is maintained.

The relation for reacting gases in general will be similar to that for air. The dashed curve on Fig. 4 is a limit which is approached as the heat of reaction becomes very large. This limiting relation has been used in the integrations which follow; that is, a is assumed to equal φ up to the point φ_c , and thereafter is taken to be constant. Up to the point φ_c then, the solutions are the stretched out error functions which were discussed earlier, and which are shown in Fig. 2. At φ_c these solutions are joined by the solution for constant diffusivity which has a matching slope at the junction $(d\varphi/dy)_c$.

$$\varphi = \varphi_c + \sqrt{\frac{\pi\varphi_c}{4}} \left(\frac{d\varphi}{dy} \right)_c \left(\exp \frac{y^2}{\varphi_c} \right) \times \left(\operatorname{erf} \frac{y}{\sqrt{\varphi_c}} - \operatorname{erf} \frac{y_c}{\sqrt{\varphi_c}} \right) \quad [13]$$

In Fig. 5, the limit of the potential φ_∞ is shown for a reacting gas as a function of the boundary heat flux φ'_0 . The solution now depends on the value of φ_c , which in turn depends on the boundary temperature, the pressure and the chemical reaction being considered. For example, in the case of air and a boundary temperature of zero deg C, the values 20, 40 and 60 for φ_c correspond to pressures about 10^{-4} , 10^0 and 10^2 atm, respectively. The solutions for values of φ_c corresponding to other pressures and different boundary temperatures can be obtained fairly accurately by interpolation between the numerically integrated solutions, such as the curves plotted in Fig. 5. The inert gas solution (Fig. 3) corresponds to φ_c equal to infinity (Fig. 5). It should be noted that these solutions can only be used up to the point where the chemical reaction goes to completion. Beyond this, the increase in diffusivity must again be taken into account. The domain of validity is a characteristic of each specific reaction. Within this limitation, the curves of Fig. 5 apply to chemically reacting gases in general.

Heat Flux Potentials for Air

The foregoing solutions (Fig. 5) have been put to use, in conjunction with experiment, to evaluate the heat flux potential for air as a function of temperature (3). In this experiment, a plane shock wave is reflected from the end wall of a shock tube. The heat flux to the wall is measured, and this fixes the abscissa for the graphical solution in Fig. 5. The temperature at the wall and the pressure of the gas after the shock reflection determine the value of φ_c (see Eq. [12]). Hence the value of the ordinate in Fig. 5 is fixed, and the value of φ_∞ is determined. The temperature of the gas associated with this heat flux potential is taken to be the equilibrium temperature after the shock reflection, and this is a known function of the measured shock velocity. This procedure, of course, implies that the experiments are conducted under conditions where the chemical relaxation times are short compared to the test interval.

Results of the experiments and calculations are shown in Fig. 6. The heat flux potential is shown divided by the inert gas value, where the coefficient n is taken to be $\frac{1}{2}$

$$\varphi_{\text{inert}} = \frac{2}{3} k_0 T_0 \left(\frac{T}{T_0} \right)^{1/2} = 3.2 \times 10^{-6} T^{1/2} \frac{\text{cal}}{\text{cm sec}} \quad [14]$$

and T is in deg K. Thus the ratio $\varphi/\varphi_{\text{inert}}$ should be unity if the coefficient of thermal conductivity is proportional to the one half power of temperature. This appears to be approximately true up to the temperature where oxygen dissociation begins. At the pressures involved in the present shock tube experiments, this occurred at about 2500 K. At higher temperatures, the heat flux potential becomes more than twice as large as the inert gas value as a result of the dissociation of oxygen. The solid curve on Fig. 6 shows a theoretical estimate of the heat flux potential, based on the coefficients of thermal conductivity presented in (7). The experimental points were obtained by the method described in (3), except that somewhat better instrumentation has been used to improve the reliability of the data. The small departure from ideal gas values which occurs at low temperatures is a result of the effect on thermal conductivity of vibrational energy excitation and of the formation of nitric oxide. However, the oxygen dissociation process has the large heat of reaction required to produce a sizable increase in the heat flux potential. The theory and experiment clearly show the same behavior owing to this effect.

It will be of interest next to examine an application of the heat flux potential to some problems of heat transfer in hypersonic flow.

Applications to Hypersonic Flow

Normally, heat transfer in fluid flow exhibits a complex interdependence between conduction and convection processes. However, at the stagnation region of hypersonic vehicles, it has been shown (9) that, to a first approximation, the conduction and convection effects are separable, and solutions can be expressed in a form which has a simple physical interpretation in terms of the heat flux potentials. The heat flux at the wall is given by the difference between the potential at stagnation conditions φ_t and its value at the wall φ_w all divided by a characteristic length δ

$$q = (\varphi_t - \varphi_w)/\delta \quad [15]$$

The quantity δ can be interpreted as a thermal boundary layer thickness defined such that the gas temperature at the edge of the layer is a maximum, approximately the stagnation temperature (Fig. 7). According to this model then, the heat transfer at the stagnation region occurs essentially by a diffusion process, although the mass convection processes are responsible for establishing the magnitude of δ . For an axially symmetric stagnation region, for example, the thickness δ is approximately given by [see (9)]

$$\frac{1}{\delta} \approx \frac{\sqrt{Re}}{r} \left(\frac{\rho_2}{\rho_1} - 1 \right)^{1/4} \left(\frac{\mu_1}{\mu_t} \right)^{1/2} \quad [16]$$

where the subscript t refers to stagnation conditions and the subscripts 1 and 2 refer, respectively, to the free stream and to conditions just following the shock wave (see Fig. 7). The Reynolds number Re is based on free stream conditions and on a length equal to the effective radius of curvature of the body.

None of the factors in the expression for the thermal boundary layer thickness (Eq. [16]) is strongly influenced by chemical reaction. In the integral φ_t however, the integrand k is greatly increased, and the upper limit of the integral T_t is greatly decreased by the reaction

$$\varphi_t = \int_0^{T_t} k dT \quad [17]$$

It can be shown that these two effects almost compensate one another, and to a first approximation φ_t is just a function of the vehicle velocity, the Prandtl number and a weighted average coefficient of viscosity

$$\varphi_t \approx u^2 \bar{\mu} / 2Pr \quad [18]$$

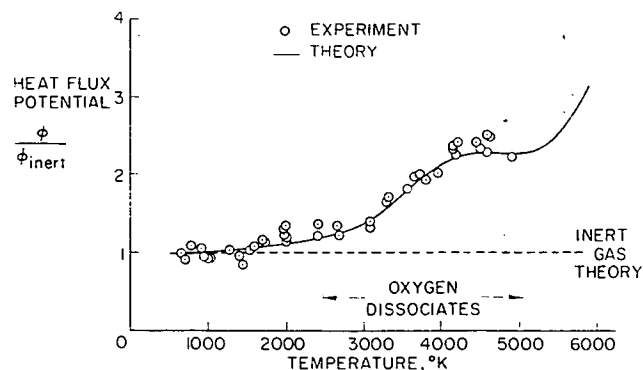


Fig. 6 Heat flux potential for air

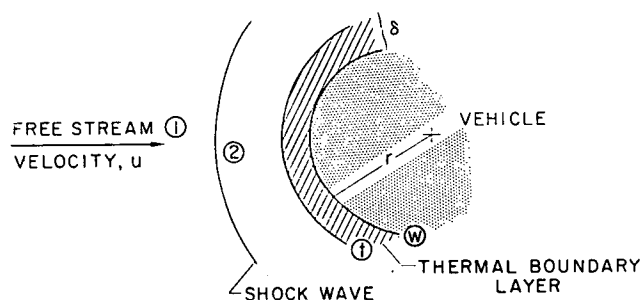


Fig. 7 Stagnation region nomenclature

where

$$\bar{\mu} = \int_0^{T_t} \mu C_p dT / \int_0^{T_t} C_p dT \quad [19]$$

The viscosity coefficient, however, is not strongly influenced by chemical reactions, unless a high percentage ionization is produced [see (7)]. Consequently, stagnation region heating is relatively insensitive to dissociation effects, and is not a good quantity to measure for the purpose of evaluating transport properties or real gas effects in dissociating gases. It also becomes clear why calculations based on ideal gas properties have been observed to have the correct magnitude in spite of the unrealistically high stagnation temperature predicted by this method. Another method, found to give reasonable results where chemical reactions occur, assumes heat flux proportional to the enthalpy gradients. This is, of course, consistent with the fact that thermal conductivity is approximately proportional to the specific heat in the domain of the reaction, so that the integral φ is approximately proportional to enthalpy.

The heat transfer to cylindrical stagnation regions can likewise be expressed in terms of the heat flux potentials. Equation [15] applies to this case without change, except that δ is slightly larger than for the axially symmetric case [see (9)].

$$\frac{1}{\delta} \approx \frac{\sqrt{Re}}{r} \left(\frac{3}{4} \right)^{1/4} \left(\frac{\rho_2}{\rho_1} - 1 \right)^{1/4} \left(\frac{\mu_1}{\mu_t} \right)^{1/2} \quad [20]$$

The analysis can also be extended to yawed cylindrical stagnation regions, such as the leading edge of a swept hypersonic wing. It is found that the chemical reaction effects are canceled in somewhat the same manner as in the stagnation heating of axially symmetric bodies. In the limit as the stagnation temperature becomes large compared to the wall temperature, the ratio of heat flux at angle of yaw $q(\lambda)$ to the value at zero yaw $q(0)$ is approximately given by

$$\frac{q(\lambda)}{q(0)} = \cos \lambda \left(\cos^2 \lambda + \left(\frac{3}{4} \right) Pr \sin^2 \lambda \right) \quad [21]$$

For a Prandtl number of $\frac{3}{4}$ and yaw angles up to 70 deg, this is very close to the $\cos^{3/2} \lambda$ relation proposed by Goodwin, Creager and Winkler (10) for the total heat transfer to yawed cylinders. This effect has been checked experimentally in hypersonic flow (9,11).

Concluding Remarks

Although the preceding solutions are based on some decidedly first-order approximations to the Navier-Stokes equations, it is felt that the essential functional relationships which influence stagnation region heat transfer are probably retained, inasmuch as the results compare favorably with more rigorous calculations which are now available, such as those performed by Fay and Riddell (12). Perhaps the principal value of these approximations, at least in domains where the rigorous solutions have been worked out, lies in providing a somewhat simplified physical insight into the problems. It may be noted, however, that the concept of the heat flux potential is free of restrictions concerning the behavior of the Lewis number, and it can be applied to problems where multiple diffusion coefficients are involved in the heat transfer process. This situation exists, for example, where ionization or two or more simultaneous chemical reactions occur. However, at ionization temperatures the effects of emission and adsorption of radiation in the gas may be difficult to analyze separately from heat diffusion. In this case, temperature again becomes the normal dependent variable to use in the problem, and the functional dependence of thermal conductivity on temperature becomes important. This function could be approximately obtained from values of the integral φ , but the differentiation of the data involves a considerable loss of accuracy. It is advisable to treat a favorable comparison between theoretical and experimental values of φ as satisfying merely a necessary but not sufficient check of the theory.

In summary, some solutions have been presented for the

nonsteady diffusion of heat through a semi-infinite gas having constant initial and boundary conditions. It is found that the heat flux potential function φ is a natural parameter to use as the dependent variable for problems involving heat diffusion through media in which thermal conductivity is a function of temperature. This potential has been evaluated by experiment for air up to 5000 K, including the influence of oxygen dissociation, and the results agree reasonably well with theoretical estimates. Finally, some relations between the heat flux potentials and heat transfer at the stagnation region of high speed vehicles have been discussed.

References

- 1 Carslaw, H. S. and Jaeger, J. C., "Conduction of Heat in Solids," Oxford University Press, England, 1947.
- 2 Jacob, M., "Heat Transfer," vols. I and II, John Wiley and Sons, Inc., N. Y., 1949.
- 3 Hansen, C. F., Early, R. A., Alzofon, F. E. and Witteborn, F. C., "Theoretical and Experimental Investigation of Heat Conduction in Air Including Effects of Oxygen Dissociation," NASA Rep. 27, 1959.
- 4 Boltzmann, L., "Zur Integration der Diffusionsgleichung bei Variablen Diffusionscoefficienten," *Annalen der Physik*, vol. 53, 1894, pp. 959-964.
- 5 Kennard, E. H., "Kinetic Theory of Gases," McGraw-Hill Book Co., Inc., N. Y., 1938, chap. IV.
- 6 Hirschfelder, J. O., "Heat Transfer in Chemically Reacting Mixtures. I," *J. Chem. Phys.*, vol. 26, no. 2, Feb. 1957, pp. 274-281.
- 7 Hansen, C. F., "Approximations for the Thermodynamic and Transport Properties of High Temperature Air," NASA Rep. 50, 1959.
- 8 Butler, J. N. and Brokaw, R. S., "Thermal Conductivity of Gas Mixtures in Chemical Equilibrium," *J. Chem. Phys.*, vol. 26, no. 6, June 1957, pp. 1636-1643.
- 9 Eggers, A. J., Jr., Hansen, C. F. and Cunningham, B. E., "Theoretical and Experimental Investigation of the Effect of Yaw on Heat Transfer to Circular Cylinders in Hypersonic Flow," NACA RM A55E02, 1955.
- 10 Goodwin, G., Creager, M. O. and Winkler, E. L., "Investigation of Local Heat-Transfer and Pressure Drag Characteristics of a Yawed Circular Cylinder at Supersonic Speeds," NACA RM A55H31, 1956.
- 11 Cunningham, B. E. and Kraus, S., "Experimental Investigation of the Effect of Yaw on Rates of Heat Transfer to Transverse Circular Cylinders in a 6500-Foot-per-second Hypersonic Air Stream," NACA RM A58E19, 1958.
- 12 Fay, J. A. and Riddell, F. R., "Theory of Stagnation Point Heat Transfer in Dissociated Air," Avco Res. Rep. no. 1, Everett, Mass., June 1956.