

# Heat Transfer from a Nonequilibrium Turbulent Boundary Layer to Catalytic Surfaces

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An analysis has been made of the heat transfer from a supersonic turbulent boundary layer under conditions of recombination or dissociation among gaseous species and catalytic reactions at the wall. The process of thermal diffusion of lower molecular weight species towards high-temperature regions is included. As expected, high transfer increased as the wall catalytic efficiency for the recombination of atoms increased. However, it was found that the surface temperature was quite important in determining the magnitude of this effect. In particular, a hundredfold increase in catalytic parameter when the wall temperature was 1000°K increased the heat transfer 25%, whereas a 3000°K wall temperature resulted in a change of 150%. Thus, materials such as tungsten coated with glass on the surface are required if heat transfer is to be reduced by using noncatalytic surfaces. Thermal diffusion was always found to decrease heat transfer; the maximum reduction found in the present work was 18%. Two different values of Lewis numbers were used, 1.0 and 1.3. It was found that some numerical values of the parameters of the problem produced the apparently anomalous effect of reduced heat transfer with the larger value of Lewis number.

## Nomenclature

$C_{f/2}$	= local value of skin-friction coefficient
$C_p$	= specific heat at constant pressure
$D$	= molecular diffusion coefficient
$\bar{D}$	= energy of dissociation of oxygen molecules
$h$	= enthalpy, sensible + chemical
$H$	= total enthalpy of mixture,
$\sum_i h_i Y_i + \frac{u^2}{2}$	
$k$	= molecular thermal conductivity
$k_r$	= recombination rate coefficient
$K_X$	= equilibrium constant based on mole fraction
$K_C$	= equilibrium constant based on concentration
$Le$	= Lewis number, $Pr/Sc$
$L_T$	= Lewis number based on turbulent properties $Pr_T/Sc_T$
$m$	= mass of atoms or molecules
$M$	= molecular weight of atoms or molecules; molecular weight of mixture.
$M_e$	= Mach number of freestream
$p$	= pressure
$Pr$	= Prandtl number, $C_p \mu / k$
$Pr_T$	= Prandtl number based on turbulent properties
$q_w$	= wall heat-transfer rate per unit area
$\bar{R}$	= gas constant per unit mass
$Re_x$	= Reynolds number
$Sc$	= Schmidt number, $\mu / \rho D$
$Sc_T$	= Schmidt number based on turbulent properties
$t$	= time
$T$	= temperature
$u$	= velocity
$\bar{u}$	= velocity divided by freestream value, $u/u_e$
$u_e$	= freestream value of the velocity
$v$	= velocity normal to surface
$W_1$	= recombination rate of oxygen atoms
$x$	= distance along surface
$\Delta y_r$	= boundary-layer thickness based on efficacy of gas phase reaction
$\Delta y_c$	= boundary-layer thickness based on composition defect
$\Delta y_v$	= boundary-layer thickness based on velocity defect
$y$	= distance normal to surface
$Y$	= mass fraction

## Subscripts

$e$	= freestream
$L$	= conditions at interface of viscous and turbulent layers
$w$	= wall
1	= atoms
2	= molecules
$i$	= a specific component

## Introduction

THE present work is an examination of the heat-transfer characteristics of a high-speed turbulent boundary layer under conditions where there exists recombination or dissociation among gaseous species and catalytic reactions at the wall. Aside from quantitatively studying the interaction of these two reactions, the effect of thermal diffusion of lower molecular weight species toward high-temperature regions is assessed.

For simplicity, the gas chosen for the boundary-layer material was pure oxygen, assumed to flow over a flat plate, with zero pressure gradient at Mach numbers from 1 to 4 and wall catalytic parameter  $\Gamma$  (the fraction of atoms striking the wall which become molecules) between  $10^{-4}$  and  $10^{-2}$ . There is currently considerable interest in coating temperature resistant metals with materials that melt at high temperatures to form a glass-like coating that protects the metal from oxidation. These materials have a very low catalytic efficiency and, hence, "block" heat transfer to the surface by increasing the enthalpy there. The focus on elevated wall temperatures, i.e., above 1000°K, reflects the fact that recombination rates in the gas phase are tremendously accelerated at low temperatures so that the gas immediately adjacent to the wall is in equilibrium, thus making the wall characteristics irrelevant.

## Analysis

The basic two-dimensional boundary equations, including the effects of thermal diffusion and chemical reaction, but without pressure gradient, can be written for a binary mixture of atoms and molecules as follows<sup>1</sup>:

Equation of Continuity

$$(\partial/\partial x)(\rho u) + (\partial/\partial y)(\rho v) = 0 \quad (1)$$

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Equation of Species Continuity

$$\rho u \frac{\partial Y_1}{\partial x} + \rho v \frac{\partial Y_1}{\partial y} = \frac{\partial}{\partial y} \left( \rho D \frac{\partial Y_1}{\partial y} + \alpha Y_1 Y_2 \frac{\partial \ln T}{\partial y} \right) + W_1 \quad (2)$$

Equation of Momentum

$$\rho u \frac{\partial u}{\partial x} + \rho v \frac{\partial u}{\partial y} = \frac{\partial}{\partial y} \left( \mu \frac{\partial u}{\partial y} \right) \quad (3)$$

Equation of Energy

$$\rho u \frac{\partial H}{\partial x} + \rho v \frac{\partial H}{\partial y} = \frac{\partial}{\partial y} \left[ -k \frac{\partial T}{\partial y} - \rho D \left( \frac{\partial Y_1}{\partial y} + \alpha Y_1 Y_2 \frac{\partial \ln T}{\partial y} \right) \times \left( h_1 - h_2 + \frac{\bar{R} T \alpha M^2}{M_1 M_2} \right) + \mu \frac{\partial}{\partial y} \left( \frac{u^2}{2} \right) \right] \quad (4)$$

These equations are very difficult to solve, even for the case of purely laminar flow, because the presence of the term  $W_1$ , involving chemical reactions in the gas phase and the thermal diffusion terms involving the coefficient of thermal diffusivity  $\alpha$ , renders the boundary layer not "self-similar" with these effects included. To simplify matters we make the usual assumption that the boundary layer is composed of a region near the wall, dominated by viscous effects, and a fully turbulent portion everywhere else. Furthermore, we make the conventional assumption that streamlines are parallel to the wall in the viscous region. The equations appropriate to this portion of the flow are obtained by setting the left-hand side of Eqs. (1-4) equal to zero, thereby obtaining the following set of ordinary differential equations:

Species Continuity

$$\frac{d}{dy} \left\{ -\rho D \left( \frac{dY_1}{dy} + \alpha Y_1 Y_2 \frac{d \ln T}{dy} \right) \right\} = W_1 \quad (5)$$

Equation of Momentum

$$(d/dy) [\mu(du/dy)] = 0 \quad (6)$$

Conservation of Energy

$$\frac{d}{dy} \left\{ -k \frac{dT}{dy} - \rho D \left( \frac{dY_1}{dy} + \alpha Y_1 Y_2 \frac{d \ln T}{dy} \right) \times \left( h_1 - h_2 + \frac{\bar{R} T \alpha M^2}{M_1 M_2} \right) - \mu \frac{d}{dy} \left( \frac{u^2}{2} \right) \right\} = 0 \quad (7)$$

Integration of the continuity equation, Eq. (1), in this viscous region yields  $\rho v = \text{const} = (\rho v)_w$ . In the present work we take the wall to be simply a catalytic surface for recombination and dissociation reactions so that  $(\rho v)_w = 0$ .

Because we are interested in the heat transfer to a solid surface rather than details of the actual spatial distribution of  $T$ ,  $Y$ , and  $u$ , it is convenient to integrate Eq. (6) once to get

$$\tau = \tau_w = \mu(du/dy) \quad (8)$$

and change the independent variable in Eqs. (1) and (2) from  $y$  to  $u$ . Introducing the skin-friction coefficient by  $\tau_w = C_{f/2} \rho_e u_e^2$  and  $\bar{u} = u/u_e$ , Eq. (5) becomes

$$\frac{d}{d\bar{u}} \left[ \frac{dY_1}{d\bar{u}} + \frac{\alpha Y_1 (1 - Y_1)}{T} \frac{dT}{d\bar{u}} \right] = \frac{W_1 \mu S c}{(C_{f/2} \rho_e u_e)^2} \quad (9)$$

and the energy equation is transformed, after integrating once, into the form

$$C_p \frac{dT}{d\bar{u}} + L_e \left[ h_1 - h_2 + \frac{\bar{R} T \alpha M^2}{M_1 M_2} \right] \times \left[ \frac{dY_1}{d\bar{u}} + \frac{\alpha Y_1 (1 - Y_1)}{T} \frac{dT}{d\bar{u}} \right] + P_r u_e^2 \bar{u} = \frac{P_r q_w}{C_{f/2} \rho_e u_e} \quad (10)$$

In order to obtain the equations pertinent to the turbulent core, we must take the time averaged value of Eqs. (1-4), the result of which can be written, after some manipulation, as follows:

Equation of Continuity

$$\frac{\partial}{\partial x} (\bar{\rho} \bar{u}) + \frac{\partial}{\partial y} (\bar{\rho} \bar{v} + \bar{\rho}' v') = 0 \quad (11)$$

Equation of Species Continuity

$$\bar{\rho} \bar{u} \frac{\partial \bar{Y}_1}{\partial x} + (\bar{\rho} \bar{v} + \bar{\rho}' v') \frac{\partial \bar{Y}_1}{\partial y} = \frac{\partial}{\partial y} \left( \rho \epsilon_{d,1} \frac{\partial \bar{Y}_1}{\partial y} \right) + \bar{W}_1 \quad (12)$$

Equation of Momentum

$$\bar{\rho} \bar{u} \frac{\partial \bar{u}}{\partial x} + (\bar{\rho} \bar{v} + \bar{\rho}' v') \frac{\partial \bar{u}}{\partial y} = \frac{\partial}{\partial y} \left( \epsilon_v \frac{\partial \bar{u}}{\partial y} \right) \quad (13)$$

Equation of Energy

$$\bar{\rho} \bar{u} \frac{\partial \bar{H}}{\partial x} + (\bar{\rho} \bar{v} + \bar{\rho}' v') \frac{\partial \bar{H}}{\partial y} = \frac{\partial}{\partial y} \left[ \epsilon_\lambda \frac{\partial}{\partial y} \times \left( \bar{h} - \sum_1^2 \bar{h}_i' Y_i' + \frac{u^2}{2} \right) + \rho \epsilon_{d,1} \left( 1 - \frac{1}{L_T} \right) \times (\bar{h}_1 - \bar{h}_2) \frac{\partial \bar{Y}_1}{\partial y} + \epsilon_v \left( 1 - \frac{1}{P_r} \right) \frac{\partial}{\partial y} \left( \frac{u^2}{2} \right) \right] \quad (14)$$

The terms involving the turbulent transport coefficients of heat, mass, and momentum have their usual definitions, viz.,

$$\epsilon_\lambda = -\frac{\overline{\rho v' h'}}{\partial \bar{T} / \partial y} \quad \epsilon_d = \frac{-\overline{v' Y'}}{\partial \bar{Y}_1 / \partial y} \quad \epsilon_v = \frac{-\overline{\rho v' u'}}{\partial \bar{u} / \partial y} \quad (15)$$

All terms involving molecular transport phenomena such as heat conduction and thermal diffusion have been assumed negligible as compared with the turbulent transport terms. Because

$$\bar{h} = \sum_1^2 \bar{h}_i \bar{Y}_i + \sum_1^2 \overline{h_i' Y_i'}$$

$$h' = \sum_1^2 h_i' Y_i + \sum_1^2 Y_i' \bar{h}_i$$

it is clear that

$$\bar{h} \neq \sum_1^2 \bar{h}_i \bar{Y}_i$$

but rather

$$\sum_1^2 \bar{h}_i \bar{Y}_i = \bar{h} - \sum_1^2 \overline{h_i' Y_i'}$$

which accounts for this term in Eq. (14). In order to obtain solution of Eqs. (11-14), which will then be used to join the solutions obtained in the viscous sublayer to freestream conditions, we make the following two simplifications.

1) The rate of recombination is effectively zero in this outer region, i.e.,  $W_1 = 0$ . Eqs. (25a) and (25b) show that  $W_1 \propto T^{-1}$ , so typical conditions of a rapidly rising temperature in the viscous inner layer to higher temperatures in the turbulent region will cause  $W_1$  to decrease very sharply. This approximation was verified a posteriori by use of computed temperature profiles and found to be quite accurate.

2) The total enthalpy and composition are functions of velocity alone in the outer region. Transformation of the equations of species continuity and energy with  $W_1 = 0$  leads to the following forms:

$$\left( \frac{\partial \bar{u}}{\partial y} \right)^{-1} \frac{\partial}{\partial y} \ln \tau \left[ 1 - \frac{1}{S c_T} \right] = \frac{d}{d\bar{u}} \frac{1}{S c_T} \frac{dY}{d\bar{u}} \quad (16)$$

$$\left(\frac{\partial \bar{u}}{\partial y}\right)^{-1} \frac{\partial}{\partial y} \ln \tau \left[ \frac{dH}{d\bar{u}} - \frac{1}{P_T} \frac{dH}{d\bar{u}} - \frac{L_T - 1(h_1 - h_2)}{P_T} \frac{dY}{d\bar{u}} - \frac{P_T - 1}{P_T} \bar{u} u_\infty^2 \right] = \frac{d}{d\bar{u}} \left[ \frac{1}{P_T} \frac{dH}{d\bar{u}} - \frac{L_T - 1(h_1 - h_2)}{P_T} \frac{dY}{d\bar{u}} - \frac{P_T - 1}{P_T} \bar{u} u_\infty^2 \right] \quad (17)$$

where  $\tau = \epsilon_v(du/dy)$ .† We have omitted the symbols indicating averaged quantities since the region of application of Eqs. (16) and (17) will always be evident. Thus,  $\bar{u}$  is now the average velocity divided by the freestream value. It is seen that this assumption requires elimination of  $y$  derivatives from the left-hand side of Eqs. (16) and (17) by taking  $L_T = P_T = Sc_T = 1$ , which stratagem causes the bracketed terms to vanish. A first integration of the remaining equations yields

$$dY/Sc_T d\bar{u} = \text{const} \quad (18)$$

$$(1/P_T) [(dH/d\bar{u}) - (L_T - 1)(h_1 - h_2)dY/d\bar{u} - (P_T - 1)\bar{u}u_\infty^2] = \text{const} \quad (19)$$

The constants in each equation can be found by matching fluxes of mass and energy with Eqs. (9) and (10) at the interface between the viscous and fully turbulent regions. Integrating Eqs. (18) and (19) and performing this matching procedure one obtains, using the definition of  $H$  and making the very accurate approximation that  $h_1 - h_2 = \bar{D}$ , an average dissociation energy:

$$\left(\frac{dY}{d\bar{u}}\right)_L + \frac{\alpha Y_L(1 - Y_L)}{T_L} \left(\frac{dT}{d\bar{u}}\right)_L = \frac{Sc_L}{Sc_T} \frac{Y_\infty - Y_L}{1 - \bar{u}_L} \quad (20)$$

$$C_P T_L = C_P T_\infty + P_T \frac{u_\infty^2}{2} (1 - \bar{u}_L^2) + \bar{D} L_T (Y_\infty - Y_L) - \frac{q_w P_T (1 - \bar{u}_L)}{\rho_\infty u_\infty C_{f/2}} \quad (21)$$

We have not set the turbulent Prandtl and Schmidt numbers equal to unity in these equations for reason of avoiding discontinuous property or flux values at  $\bar{u} = \bar{u}_L$ . Instead we choose  $Sc_L = Sc_T$  and  $Pr = P_T$ . In the special case when these groups are unity, Eqs. (20) and (21) reduce to correct forms; otherwise they are approximate.

Next we must evaluate the velocity ratio at the edge of the viscous sublayer. Study of literature<sup>2</sup> on high-speed turbulent heat transfer suggests that the quantity  $u_L^+$ , defined by  $u_L^+ = \bar{u}_L / (c_f \rho_\infty / 2 \rho^*)^{1/2}$  where  $\rho^*$  is the density at some reference conditions, should be taken as constant, say 11.5. Dorrance<sup>3</sup> studied the effect of a distribution of atoms and molecules on the skin friction and found very little change over its normal high-speed value. Therefore, in the present work, the reference density was taken to be at the well known reference temperature proposed by Eckert<sup>4</sup>; the skin friction was taken to be a function of Reynolds number, freestream Mach number, and ratio of wall to freestream temperature, but not degree of dissociation of the gases.

The reference temperature is defined by

$$T^* = \left( \frac{T_\infty + T_w}{2} \right) + 0.22 P_T^{1/3} \frac{(\gamma - 1)}{2} M_\infty^2 T_\infty$$

with  $\gamma \sim 1.3$  for the degree of freestream dissociation used

† We have dropped the second-order term

$$\sum_{i=1}^2 \bar{h}_i' \bar{Y}_i'$$

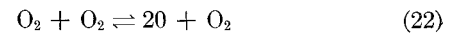
for reasons of simplicity. The true importance of this type of second-order correlation in reacting flows remains to be experimentally determined.

here. Written with the cgs metric system units used in the present work,  $\bar{u}_L$  takes the form

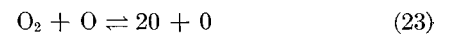
$$\bar{u}_L = \left( \frac{C_f}{2} \right)^{1/2} \left( \frac{T_\infty + T_w + 1.5 \times 10^{-8} u_\infty^2}{2 T_\infty} \right)^{1/2}$$

The skin friction was taken from Dorrance<sup>3</sup> at particular values of  $Re_x$ ,  $T_\infty/T_w$ ,  $M_\infty$ ; fitting the temperature dependence according to the values of the other two parameters, e.g., at  $M_\infty \sim 2$ ,  $Re_x = 4 \times 10^6$ , the skin-friction coefficient is given by  $C_{f/2} = 1.25 \times 10^{-3} (T_\infty/T_w)^{0.12}$ . Again, the results were very insensitive to the precise value of  $\bar{u}_L$  used. This fortunate circumstance will be discussed later. It is enough to note that this result means that the reference temperature plays a very minor role. We now turn to the specific form of the recombination rate  $W_1$ .

Using the experimental results of Matthews,<sup>5</sup> the main reaction taking place in the gas phase can be written as



This formulation states that the secondary reaction



does not contribute significantly to the over-all changes in concentration of atoms or molecules, i.e., the third body is taken to be molecules alone. Clearly, these conclusions cannot be valid when the mixture is initially composed of atomic species. It was found in the present work that the gas phase reaction was most significant at lower temperatures, where the concentration of molecules exceeded that of atoms. Therefore, the first equation was used in this work to give

$$d[\text{O}]/dt = K_c k_r [\text{O}_2]^2 - k_r [\text{O}]^2 [\text{O}_2] \quad (24)$$

Noting that the density of the mixture is given by

$$\rho = \frac{p M_2}{RT(1 + Y_1)} \quad [\text{O}_2] = \frac{\rho(1 - Y_1)}{M_2}$$

$$[\text{O}] = \frac{2\rho Y_1}{M_2} \quad K_c = \frac{\rho(1 + Y_1) K_x}{M_2}$$

where  $K_c$ , the equilibrium constant in terms of concentration, is defined by  $K_c = [\text{O}]^2/[\text{O}_2]$  and  $K_x$  is the equilibrium constant defined in terms of mole fractions, one can write the expression (24) in the form

$$W_1 = \frac{\rho dY_1}{dt} = \frac{k_r}{2} \left( \frac{p}{RT} \right)^3 M_2 \left( \frac{1 - Y_1}{1 + Y_1} \right) \times \left[ K_x \frac{(1 - Y_1)}{(1 + Y_1)} - \frac{4Y_1^2}{(1 + Y_1)^2} \right] \quad (25a)$$

The value of  $k_r$  over the temperature range of interest was estimated from Matthews' data to be proportional to  $T^{-2}$ :

$$k_r = 9 \times 10^{14} (3250/T)^2 \text{ cm}^2/\text{mole}^2 \text{ sec} \quad (25b)$$

The equilibrium constant, obtained from a close approximation to Hansen's tabulated results,<sup>6</sup> was

$$K_x = 1.82 \times 10^3 (T/p) \exp -59,000/T \quad (25c)$$

Transport properties for the  $\text{O}_2 - \text{O}$  system were taken from Yun, Weissman, and Mason.<sup>7</sup> The thermal diffusion factor was well approximated by the following function of temperature and composition:

$$-\alpha = 0.152 + [0.056(2Y_1)/(1 + Y_1)] - [0.023T/4000] \quad (26)$$

The viscosity is a weak function of composition and was taken to be a function of temperature only in the form

$$\mu = 3.34 \times 10^{-6} T^{0.71} \text{ g/cm-sec}$$

Over the range of interest in the present work it was found sufficiently accurate to take the Schmidt number constant and

the Prandtl number constant so that the Lewis number was constant. The value 0.72 was used for  $Pr$ , whereas two different values of  $Sc$  were used, 0.72 and 0.55. It appeared from Ref. 7 that  $Pr = Sc$ . To investigate nonunity Lewis number, the second value of  $Sc$  was chosen so that the Lewis number in this case was 1.31. For use in the first member of Eq. (10), the specific heat of the mixture was taken to be variable according to the relationship

$$C_p = 0.053(T/1000)^{-3/4}Y_1 + 0.26(T/1000)^{1/8} \quad (27)$$

The difference in specific heats between atoms and molecules is  $0.053(T/1000)^{-3/4}$ . The pressure was taken to be 1 atm ( $10^6$  dynes/cm<sup>2</sup>) uniformly across the boundary layer.

### Boundary Conditions

1) The efficiency of the wall as a catalyst for recombination is represented by the quantity  $\Gamma$ , which is the fraction of atoms striking the wall that are converted to molecules and  $\Gamma'$ , which is the corresponding quantity for the dissociation of molecules. Combining this definition with kinetic theory results shows the following:

Rate of Conversion of Atoms

$$\frac{\text{mass}}{\text{time} - \text{area}} = \frac{\Gamma m_1 p_1}{(2\pi m_1 k T)^{1/2}}$$

Rate of Dissociation of Molecules

$$\frac{\text{mass}}{\text{time} - \text{area}} = \frac{\Gamma' m_2 p_2}{(2\pi m_2 k T)^{1/2}} \quad (k = \text{Boltzmann's const})$$

At equilibrium these rates are equal. For oxygen  $m_2 = 2m_1$ , and so

$$\Gamma' = p_{1,eq} \Gamma / 2^{1/2} p_{2,eq} \quad (28)$$

Noting that

$$p_1 = p 2Y_1 / (1 + Y_1) \quad p_2 = p - p_1$$

the net rate of atoms converted to molecules, in dimensional form, is

$$\dot{a}_{\text{net}} = \frac{3.5 \times 10^{-4} p \Gamma Y_{1,w}}{(T_w)^{1/2} (1 + Y_1)_w} \left[ 1 - \frac{Y_{1,eq}(1 - Y_1)}{Y_1(1 - Y_{1,eq})} \right]_w \quad (29)$$

where  $p$  is in dynes per centimeter,  $T$  is in degrees Kelvin. Typical values of  $\Gamma$  are given by Greaves.<sup>9</sup> Equating this form to the flux of atoms received by the wall due to thermal diffusion and concentration gradient we find

$$\left( \frac{dY_1}{d\bar{u}} \right) = \frac{Sc}{C_{f/2} \rho_e u_e (T_w)^{1/2}} \left( \frac{Y_1}{1 + Y_1} \right)_w \times \left[ 1 - \frac{Y_{1,eq}(1 - Y_1)}{Y_1(1 - Y_{1,eq})} \right]_w - \left[ \frac{\alpha Y_1(1 - Y_1)t}{T} \right]_w \quad (30)$$

where  $t \equiv (d\bar{u}/d\bar{u})$ . This expression shows that the wall temperature gradient is coupled to the wall concentration gradient by means of the recombination rate at the wall.

2) The temperature gradient is given by using Eq. (10) and the wall recombination rate to give

$$\left( \frac{dT}{d\bar{u}} \right)_w = \frac{q_w P_e C_{f/2}}{\rho_e u_e C_p} - \frac{L_e}{C_p} \left[ \bar{D} + \frac{\bar{R} T 2\alpha}{(1 + Y_1)^2} \right]_w \times \left[ \frac{Sc}{C_{f/2} \rho_e u_e (T_w)^{1/2}} \frac{Y_1}{1 + Y_1} \right] \left[ 1 - \frac{Y_{1,eq}(1 - Y_1)}{Y_1(1 - Y_{1,eq})} \right]_w \quad (31)$$

3) Except for the case of an insulated surface, the value of  $T_w$  is prescribed. We also require that  $T \rightarrow T_e$  and  $\bar{u} \rightarrow Y_e$ , as  $\bar{u} \rightarrow 1$ , i.e., in the freestream.

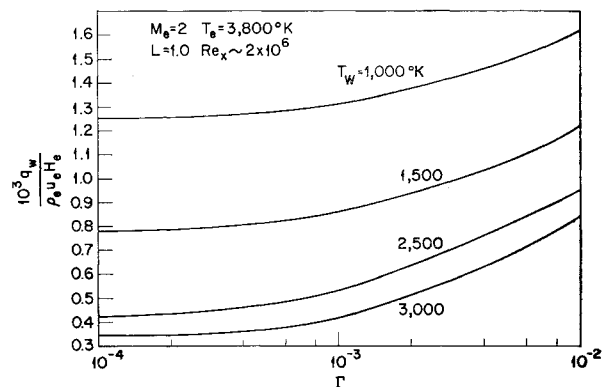


Fig. 1 Dependence of heat transfer on wall temperature and catalytic efficiency.

### Method of Solution

The equations were solved numerically on a high-speed digital computer in the following manner. Freestream temperature and Mach number were selected, which quantities, making an assumption of chemical equilibrium in the freestream, permit the calculation of degree of dissociation, velocity, and total density. The pressure in all calculations was taken to be 1 atm in order to limit the large number of independent variables. The Reynolds number was chosen arbitrarily. Taken together with other quantities, the skin-friction coefficient was calculated from the work of Dorrance, as described earlier. The boundary conditions on the differential equations are given in different locations in the boundary layer so that solutions had to be obtained by tedious iterative procedures. After choosing a value of wall catalytic parameter, values of the two remaining outstanding unknowns (the wall heat-transfer rate and mass fraction of atoms at the wall) were guessed. Integration of Eqs. (9) and (10) was performed to the point  $\bar{u} = \bar{u}_L$ . The various derivatives found at  $\bar{u}_L$  were used in Eqs. (20) and (21) to calculate values of  $Y_L$  and  $T_L$ . If these values of  $T_L$  and  $Y_L$  did not match the ones obtained from the viscous layer integration, new values of  $q_w$  and  $Y_L$  were picked and the process repeated until a close match was obtained. Thus  $q_w$  and  $Y_L$  were obtained for each set of freestream and wall conditions. In addition, results were obtained for identical freestream and wall temperature conditions without the influence of thermal diffusion, i.e.,  $\alpha = 0$  and for two values of Lewis number,  $L = 1.3$  and  $L = 1.0$ . For convenience, the Reynolds number was taken to change with the freestream Mach number by virtue of changing freestream velocity so that all results can be interpreted as applying to a fixed point on the surface.

### Discussion of Results

Heat transfer results may be expressed in the functional form

$$q_w / \rho_e u_e H_e = f[\Gamma, T_e/T_w, M_e, Re_x, \bar{R}T_e/\bar{D}]$$

with  $\alpha$  and the laminar and turbulent Lewis and Prandtl numbers regarded as parameters of the solutions. The pressure is held constant throughout the solutions and all other properties including reaction rate constants apply to the system of molecular and atomic oxygen. The last term in the expression is the freestream static temperature divided by the characteristic temperature for oxygen dissociation. Through its appearance in the expression for the equilibrium constant, the freestream composition is determined.

This function  $f$  is given in Fig. 1 for a range of catalytic parameters  $\Gamma$  and wall temperatures and fixed freestream conditions. All results show that as  $\Gamma$  increases the wall heat transfer increases because of the recombination of atoms at the surface. The more significant fact is that for high wall

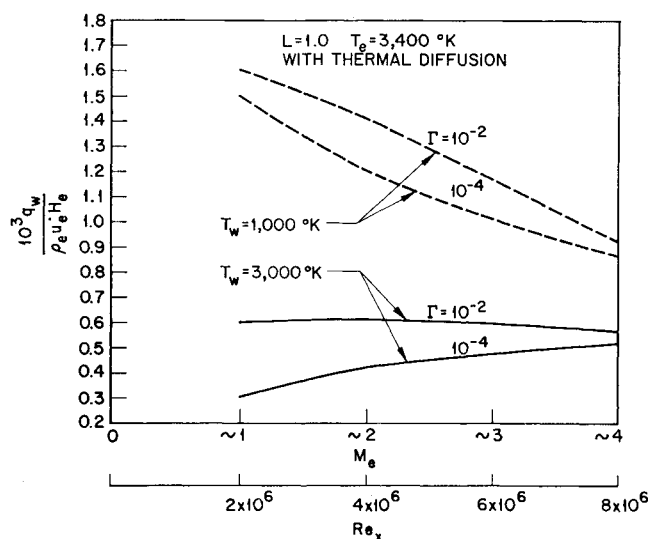


Fig. 2 Dependence of heat transfer on freestream Mach and Reynolds number for a freestream temperature of 3400°K.

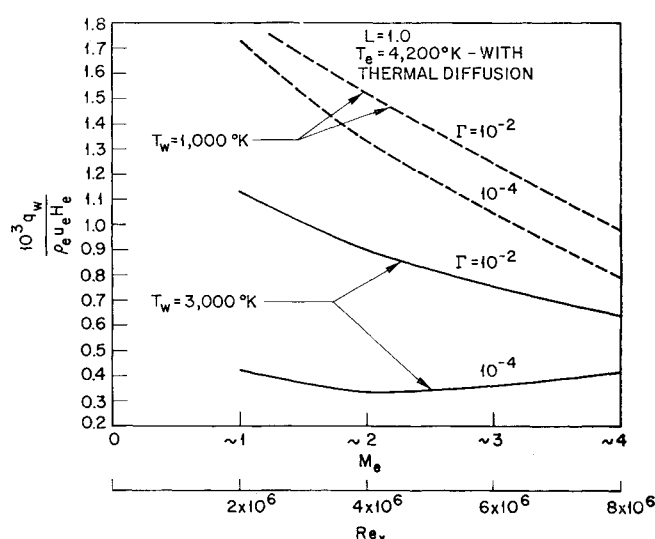


Fig. 4 Dependence of heat transfer on freestream Mach and Reynolds number for a freestream temperature of 4200°K.

temperature, say 3000°K, the influence of the wall catalytic parameter is decisive, heat transfer increasing 2.5 times for a hundred-fold increase in  $\Gamma$ . On the other hand, wall temperatures of 1000°K only increased heat transfer 25% for the same changes in  $\Gamma$ . These observations are indicative of the almost frozen ( $W_1 = 0$ ) state of the boundary layer when temperatures are high so that details of the wall reaction are significant. At cooler temperatures, gas phase reactions are vigorous enough ( $W_1 \gg 0$ ) to bring mixtures near the wall close to equilibrium so wall catalytic reactions become relatively impotent in fixing wall heat transfer.

More details on the influence of the other parameters, in particular the freestream Mach number and static temperature, are shown in Figs. 2-4. The trend of the high wall temperature, low  $\Gamma$  results for  $f$  can be explained from the relationship between  $f$  and the Stanton number [defined by  $q_w = St \rho_e u_e (H_r - H_w)$ ;  $f = St(H_r - H_w)/H_e$ ]. When the surface is hot and noncatalytic, the wall enthalpy is an appreciable fraction of the recovery enthalpy and rises proportionately slower than does  $H_r$ , as the Mach number increases, so that the term  $(H_r - H_w)/H_e$  increases. But it is well

known<sup>3</sup> that  $St$  decreases with increasing Mach number and Reynolds number, so  $f$  undergoes only modest changes. This state of affairs cannot persist indefinitely as  $M_e$  grows because the rapid increase in kinetic energy results in  $H_e \gg H_w$  thereby masking details of the surface chemistry. This effect can be seen in Figs. 2-4 where, even for  $M_e \sim 4$ , values of  $f$  begin to approach each other for all wall conditions. Because the inequality  $H_e \gg H_w$  also holds for relatively cool catalytic walls,  $f$  again follows the Stanton number variation. Having computed  $H_w$  in the course of solution, it is of interest to calculate some values of the Stanton number. Because of the high concentration of atoms which prevail in the boundary layer when the wall is insulated, thus rendering the kinetic energy terms less important than normally is the case, it was found that  $H_r \approx H_e$ . Thus  $St = f/1 - H_w/H_e$  to a very good approximation.

Variation of freestream temperature did not alter the Stanton number (to within a few percent), holding all the other parameters constant. Looking at Fig. 5, it can be seen that the degree of wall catalyticity also has a small effect. These results are important and are consistent with the previous assumptions regarding skin friction. The most influential parameters are the wall temperature and freestream Reynolds and Mach numbers which, of course, are in qualita-

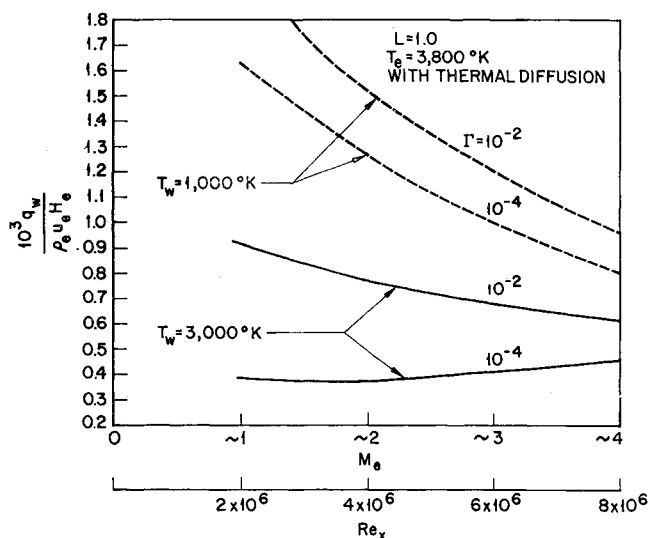


Fig. 3 Dependence of heat transfer on freestream Mach and Reynolds number for a freestream temperature of 3800°K.

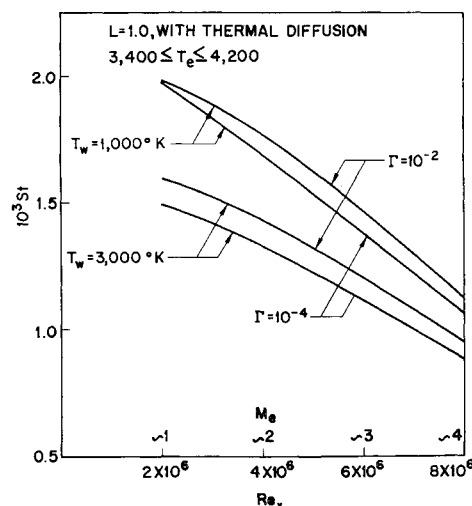


Fig. 5 Dependence of Stanton number on freestream Reynolds and Mach number.

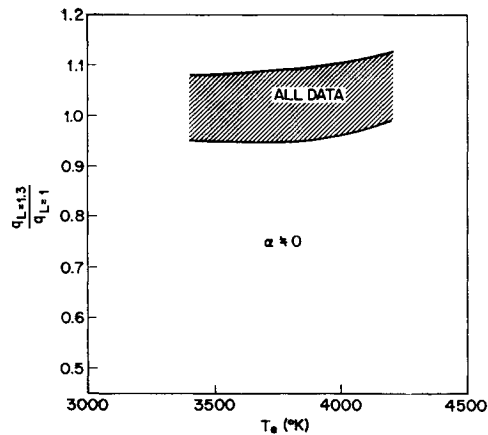


Fig. 6 Ratio of heat transfer at two different Lewis numbers including thermal diffusion.

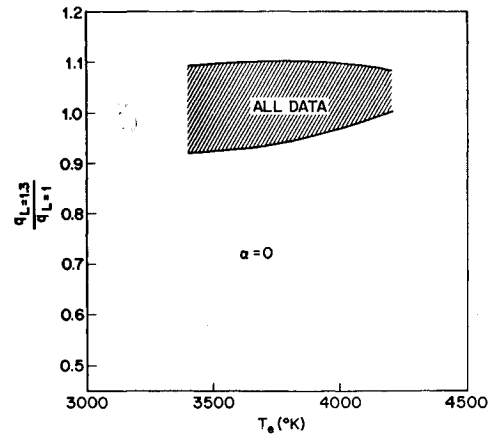


Fig. 7 Ratio of heat transfer at two different Lewis numbers without thermal diffusion.

tive agreement with conventional, nondissociative, heat-transfer results. Of interest also is the validity of the well-known expression for the modified Reynolds analogy  $(St)(Pr)^{2/3} = C_{f/2}$  as shown in Table 1. Also given there is  $St/C_{f/2}$ . It is clear that the  $Pr^{2/3}$  correlation becomes less successful as the wall temperature and freestream Mach and Reynolds numbers increase. Also, changing the exponent on  $Pr$  will not account for all the data, although less extreme deviations can be produced by other choices.

Shown in Figs. 6-8 are the specific effects of nonunity Lewis number and thermal diffusion on heat transfer  $q_w$ . All results obtained by using  $L = 1.3$  were divided by corresponding values for  $L = 1.0$  and lie on the cross-hatched region shown in Fig. 6. As expected, most of the values of  $q_L = 1.3/q = 1$  are above 1.0; surprisingly, some are below this figure. The explanation for this phenomenon is quite revealing.

The boundary condition for  $(dy/d\bar{u})_w$ , Eq. (30), shows its explicit dependence on the value of the Schmidt number, whereas eq. (31) shows that  $(dT/du)_w$  depends on the value of the Prandtl number. The Lewis number was varied by dropping the value of the Schmidt number, keeping the Prandtl number constant at 0.72. Therefore, the effect of a lower Schmidt number is that of a lower  $\Gamma$ , i.e., a reduction in heat transfer. Many previous works on dissociative gas flows consider the extreme limits of a noncatalytic wall,  $\Gamma = 0$ , or a perfectly catalytic wall  $\Gamma \rightarrow \infty$  (equilibrium at the wall), so this effect was eliminated. Furthermore, if the limits of frozen ( $k_r = 0$ ) or equilibrium flow ( $k_r \rightarrow \infty$ ) are imposed on the gas phase reaction the same suppression of Prandtl and Schmidt number effects occurs.

In order to determine whether thermal diffusion was playing any role, every result was recalculated setting  $\alpha$ , the coefficient of thermal diffusion, equal to zero in the differential equations and boundary conditions. The results for  $q_L = 1.3/q_L = 1$ , ( $\alpha = 0$ ) are shown in Fig. 7. The same phenomenon is repeated. Therefore, heat-transfer correlations cannot be made in terms of the Lewis number alone. Physically this occurs because both the wall reaction and gas phase reaction introduce characteristic lengths into the problem<sup>8</sup> so that the boundary-layer thickness is specifically significant.

Table 1 Reynolds analogy factors

$Re_x$	$Me$	$St Pr^{2/3}/C_{f/2}$		$St/C_{f/2}$	
		$T_w = 1,000$	$T_w = 3,000$	$T_w = 1,000$	$T_w = 3,000$
$2 \times 10^6$	1	1.03	0.92	1.28	1.15
$4 \times 10^6$	2	0.95	0.86	1.18	1.07
$8 \times 10^6$	4	0.83	0.80	1.03	1.0

Because  $\tau \sim T_w \sim \mu \Delta u / \Delta y$  or  $(\Delta y)_v \sim \mu / (C_{f/2} \rho_e u_e / 2)$ , it is apparent that the viscosity helps determine the boundary-layer thickness and should not be eliminated from the problem by dividing the Prandtl number with the Schmidt number to obtain the Lewis number.

A characteristic time for the recombination of gases in the boundary layer above unit surface area is given by  $t_R \sim \rho / W_1$ , whereas a characteristic time for the catalytic wall reactions to occur is given by  $t_w$

$$t_w \sim (kT_w)^{1/2} \rho (\Delta y)_c / p \Gamma$$

where  $y_c \sim (\Delta y)_v (Sc)^{-1}$ . These times are converted to lengths by multiplication with  $u_e$  so the ratio of composition boundary-layer thickness to equivalent homogeneous reaction length is

$$\Delta y_c / \Delta y_R \sim \mu W_1 / Sc C_{f/2} (\rho_e u_e)^2 \quad (32)$$

The ratio of the boundary-layer composition thickness to the equivalent length introduced by the wall reaction is

$$\Delta y_c / \Delta y_w = p \Gamma / (kT_w)^{1/2} \rho_e u_e \quad (33)$$

The dimensional part of (32) is precisely the right-hand side of Eq. (9) with the exception of the dimensionless groups  $Sc$  and  $C_{f/2}$  introduced into (9) as a result of the particular transformation used. Similarly, the group in (33) appears in Eq. (30), again in conjunction with the factors  $Sc$  and  $C_{f/2}$ .

Specific effects of thermal diffusion are shown in Fig. 8 which shows that heat transfer is reduced. The additional mass-transfer mechanism of diffusion of atoms away from the wall towards higher temperature regions reduces the concentration gradient and, hence, heat transfer. The maximum effect occurred for a freestream temperature of 3800°K,  $T_w$

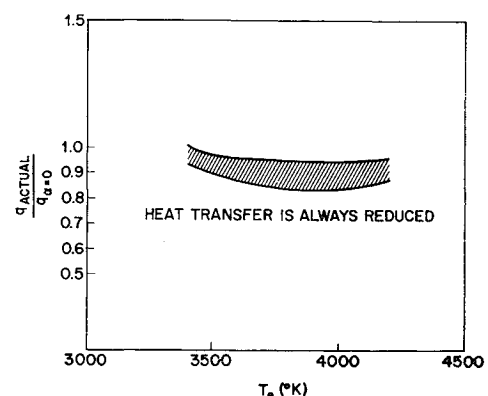


Fig. 8 Ratio of heat transfer to its value without thermal diffusion, Lewis number equals 1.

= 3,000°K,  $Me = 1$ , and  $\Gamma = 10^{-4}$ , for which the heat transfer was reduced by 18%, a not insignificant effect. For the class of problems represented by the present work, it appears that the effects of thermal diffusion are important enough to warrant inclusion in the initial theoretical formulation of the problem.

The effects of thermal diffusion are more pronounced when concentration gradients are small: a condition that occurs when the wall is hot and fairly noncatalytic. Thermal diffusion has a greater effect on heat transfer in the present work than in laminar stagnation point flow treated by Scala<sup>10</sup> and others, because the viscous sublayer is extremely thin.

Using an average value of stagnation point pressure gradient for the Mach number range  $1 < M_e < 4$  and other well known<sup>11, 12</sup> results, one can arrive at a formula for the ratio of viscous layer to stagnation boundary-layer thickness (the length along the surface has been taken equal to the body diameter):

$$\frac{\Delta \text{ viscous layer}}{\Delta \text{ stagnation point}} \sim \frac{(Re_x)^{0.3}(0.037)}{2.5 \exp \{ [(2/C_f)^{1/2} - 11.5]/5.65 \}}$$

For  $Re = 4 \times 10^6$ ,  $C_f/2 \sim 1.3 \times 10^{-3}$  this ratio has the value 0.07. If the independent variables are half their free-stream values at the edge of the viscous layer, average gradients can be seven times those encountered at a stagnation point.

An explanation for the insensitivity of heat-transfer results to the precise value of  $\bar{u}_L$  is to be found in the temperature dependence of the recombination rate  $W_1$ , viz.,  $W_1 \propto T^{-5}$  from Eqs. (25a) and (25b). When the surface is relatively cool ( $T = 1000^\circ\text{K}$ ), the reaction rate is quite vigorous, resulting in a rapid change of concentration with distance normal to the wall, so that any error in an initially guessed value of  $Y_w$  is greatly magnified when the point  $\bar{u} = \bar{u}_L$  is reached. Therefore, moderate changes in  $\bar{u}$  can be accommodated by extremely small changes in the wall composition so that heat transfer is quite constant because of the stable enthalpy difference between surface and freestream.

On the other hand, when  $T_w$  is hot, say  $T_w = 3000^\circ\text{K}$ ,  $W_1$  is small, giving a flux of atoms almost constant across the boundary layer. The resulting composition profiles are of relatively small curvature so that the precise point of matching the viscous layer to the turbulent core is not decisive.

## Conclusions

As a result of the present study of a nonequilibrium turbu-

lent boundary layer, the following may be concluded: 1) surface materials of low catalytic efficiency for the recombination of atoms are effective in reducing heat transfer when the surface is hot (3000°K) but not when it is cool (1000°K); 2) thermal diffusion effects reduce heat transfer (the maximum effect found in the present work was 18%); and 3) Lewis numbers larger than unity do not always result in a heat-transfer increase relative to the  $L = 1.0$  situation because the various homogeneous and heterogeneous reactions introduce characteristic parameters that make the Prandtl and Schmidt numbers separately significant.

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