THE RAYLEIGH PROBLEM FOR A DISSOCIATED GAS

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ABSTRACT

Rayleigh problems are analyzed in which dissociation kinetics are of significant effect, with possible analogies to hypersonic boundary layers with chemical nonequilibrium. The gas is imagined to be partly dissociated, initially in equilibrium, and bounded by a surface of some given degree of catalytic efficiency at the same temperature, and at rest. Then, a small change is specified to occur impulsively at the surface. The consequences are reviewed of one such change, a surface temperature jump. Then, the problem of impulsive plate motion is treated, wherein viscous dissipation drives the gas out of chemical equilibrium, the wall temperature being held at its original level.

It is found that the linearized analysis can proceed by rather familiar methods of heat conduction theory if the physical assumption is made that the gas absorbs much more heat in dissociation than in internal modes, for an equilibrium temperature change. Surface heat transfer rates and atom concentrations are obtained under the combined influences of surface catalycity and (because changes are assumed small) a first-order rate law. For the temperature-jump case, heat transfer behaves in a manner closely related to that found by Fay and Riddell for the hypersonic stagnation point. For the moving wall case, which is presumably analogous to the real-gas, flat plate problem, the heat transfer coefficient suffers a dip at intermediate time. For both cases, final equilibration occurs by the same law.

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Thus, in the case of a combined temperature-velocity disturbance at the surface, the late-time solution is independent of the particular combination of disturbances.

Finally, certain implications of the present study are discussed in reference to the theoretical and experimental study of hypersonic nonequilibrium boundary layers.

INTRODUCTION

In recent years, flows of a real gas subject to dissociation have acquired engineering importance in relation to hypersonic flight. Owing to practical anxieties about such matters as surface heat transfer rate, attention has been focussed on practical flow problems, and insufficient attention has been paid to the real-gas theory of idealized disturbances which often provide powerful analogies to more complicated nonlinear phenomena. In particular, the study of Couette and Rayleigh problems may elucidate nonequilibrium or relaxation effects connected with chemical or electronic activity in boundary layers. This is most difficult to study in realistic hypersonic flow situations; the computations of Fay and Riddell (Ref. 1) and others, for the hypersonic stagnation point represent the only realistic boundary layer solution which has been obtained with dissociative nonequilibrium.

The viscous Couette flow with chemical reaction between two parallel planes in relative motion has been analyzed (Ref. 2), including nonequilibrium effects (Ref. 3). In the case of stationary heat conduction between two parallel planes (a kind of Couette flow), nonequilibrium effects were found to include a "sublayer" in the later stages of relaxation (Ref. 4).

In the present paper, the study is continued of Rayleigh problems with simple chemistry which was begun in Ref. 5. The authors consider a semi-infinite domain that is filled with a partly dissociated diatomic gas, initially at rest and in equilibrium. The bounding plane (Fig. 1) is a solid surface with some given level of catalytic efficiency for recombination, at rest, and at the same temperature as the gas. At some instant, a new constant condition is abruptly established at the surface; in the work reported in Ref. 5 the temperature is suddenly changed, but the plate remains stationary; in the present case the plate temperature remains unchanged, but the surface is set in motion at constant velocity. Either of these

Another treatment of the Rayleigh problem with nonequilibrium chemistry has been provided by Chung (Ref. 3), who emphasized the early stages of relaxation.
actions produce chemical nonequilibrium in a boundary layer which grows, with time, outward from the plate. In the former case the gas next to the surface is thrown out of dissociative equilibrium by the change of surface temperature; in the latter case the driving temperature change results from aerodynamic heating in the boundary layer.

These problems are linearized by assuming small disturbances throughout. A consequence of linearization is that the chemical production is simplified to one of first order, and the description of the catalytic process is simplified. From linearization one may expect to obtain reasonably simple formulas for heat transfer, for example, a formula embracing a complete range of nonequilibrium and catalytic efficiency. For the problem treated in Ref. 5, this was accomplished; the results corresponded closely, in a qualitative way, to the stagnation point solution of Fay and Riddell. Similarly, the present case of a moving surface may indicate qualitative features of nonlinear hypersonic flows over a flat plate, just as, classically, Rayleigh flow corresponds to the Blasius problem. However, if such analogous solutions are to be useful, it is essential that they be extremely simple. Arduous numerical calculations are inappropriate; here, the authors are concerned with power of illustration, not with engineering facts. Therefore, just as in a previous study of nonequilibrium sound waves (Ref. 7), analytic solutions are insisted upon, and a physical assumption beyond linearization is employed, in order to achieve the desired type of result. Specifically, it is found helpful and surprisingly accurate to assume that for a given temperature increase at constant pressure the equilibrium increase of energy in dissociation is much greater than that in the internal degrees of freedom.

After formalizing the general problem that has been described, a review in outline shall be given of the wall-temperature-jump solution (Ref. 5), and then the moving wall case is to be treated in more detail. Finally, it shall be indicated how the results for the two problems, being linear, may be combined for cases in which the surface undergoes simultaneous jumps in temperature and velocity.

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4 Broadwell (Ref. 6) and Chung (Ref. 3) used a linear rate law in conjunction with otherwise nonlinear boundary layer problems; here all physical quantities are consistently linearized.
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FORMULATION OF THE GENERAL PROBLEM

The investigators imagine that the diatomic gas situated in the semi-infinite domain above the plane \( y = 0 \) is at first in an equilibrium state of partial dissociation at some suitably elevated temperature, and it is contemplated that this equilibrium is disturbed by time dependent changes imposed at the bounding surface. It is assumed that all thermodynamic and chemical changes so produced are small in comparison with the corresponding quantities at rest. For example

\[ a = a_\infty + a', \quad T = T_\infty + T', \text{ etc.} \]

Thus, transport coefficients may be assumed constant, and the usual Rayleigh problem for velocity results from the equation for momentum parallel to the surface, together with boundary conditions specifying that the surface is suddenly set in parallel motion at time

\[ u_t - \nu u_{yy} = 0; \quad u(0,t) = u_w(t); \quad u(\infty, t) = u(y, 0) = 0 \tag{1} \]

Subsequently, an appropriate limit shall be placed on the magnitude of imposed wall velocity \( u_w \) for this problem.

Similarly, if Prandtl and Lewis numbers are taken to be unity, if thermal diffusion is neglected, and if the boundary layer assumption of constant pressure is made, the perturbation of total enthalpy

\[ H' = C_p \frac{T'}{p_\infty} + h(0) a' + \frac{1}{2} u^2 \tag{2} \]

is found to obey, as does \( u \), the classical heat equation. Under the same assumptions, the equation of continuity of atoms is

\[ a_t - \nu a_{yy} + \frac{1}{\lambda} [a' - a_\infty(T_\infty)] = 0 \tag{3} \]

where the third term expresses the fact that, for small changes, the production of atoms is simply proportional to the difference existing between the actual level of atom concentration and the level which would exist in equilibrium at that temperature. The constant of proportionality is denoted by the reciprocal of a "relaxation time" \( \lambda \).

In addition to the foregoing differential equations, a set of boundary conditions on disturbance quantities are required. The conditions on velocity in Eqs. 1 have already been noted.
Now, one may impose a temperature disturbance at the surface, expressed by the boundary conditions

\[ T(0,t) = T_w'(t); \ T(\infty,t) = 0 \]  

(4)

The functions \( u_w(t) \) and \( T_w'(t) \) may be chosen to furnish particular examples. Boundary conditions are also needed for the remaining dependent variable \( a' \). The arrival by diffusion of atoms at the surface is to be balanced by the rate of catalytic recombination at the surface. Linearized, this catalytic wall condition may be written in the form

\[ \nu_\infty (a_\gamma)'_w = \partial \left( \frac{RT_\infty}{\pi m} (1-a_\infty^{-1})(a'_w-a'_e)_w \right) ; \ a'(\infty,t) = 0 \]  

(5)

The quantity \( \partial \) is a "catalytic efficiency" ranging numerically between 0 and 1. The requirement that all disturbances vanish far from the plate is embodied in Eqs. 1, 4 and 5.

Next, the authors proceed to arrange these differential equations and boundary conditions in a simple form suitable for further analysis. First, it may be observed that the quantity \( a'_e \), which represents perturbation of equilibrium concentration, may, for a constant pressure boundary layer process, be regarded as a measure of temperature. A new symbol \( \theta \) is introduced to express this equivalence

\[ a'_e = (\partial a_e / \partial T)_p T' = \partial' \]  

(6)

and two dimensionless parameters are introduced

\[ \epsilon = \frac{c_p}{h(0)(\partial a_e / \partial T)_p} \]  

(7)

\[ \Gamma = \frac{\gamma}{1-a_\infty} \sqrt{\frac{\epsilon(1+\epsilon)(\lambda RT_\infty)}{\pi m V_\infty}} \]  

(8)

The first of these has been mentioned in the Introduction. Carrying the differential \( \partial T \) into the numerator Eq. 7, it may be seen that \( \epsilon \) is a quantity which compares the energy absorbed in internal degrees of freedom and the energy absorbed chemically, during an equilibrium change at constant pressure. Figure 2 illustrates the variation of equilibrium concentration with temperature computed under the Lighthill approximation (Ref. 8), and the values of the energy ratio \( \epsilon \) for cor-
responding pressures. Especially at low pressures, the quantity \( \epsilon \) may apparently be quite small over a certain range of temperature. The quantity \( \Gamma \) in Eq. 8 will prove to be a suitable coefficient of catalytic effectiveness. It is important to note that even though \( \gamma \) cannot exceed one, it is multiplied by the square root of a Reynolds number which may be sufficiently large such that the quantity \( \Gamma \) may often be regarded as effectively infinite, even for small values of \( \gamma \). Hereafter, a fully catalytic surface shall be considered as one for which the quantity \( \Gamma = \infty \).

Time and distance normal to the surface may be made dimensionless in relation to the homogeneous chemical reaction time and the kinematic viscosity of the atom-molecule mixture

\[
t = \frac{1 + \epsilon}{\epsilon} \frac{t}{\lambda}; \quad \eta = \frac{1 + \epsilon}{\epsilon \lambda \nu_\infty} y
\]

(9)

Enthalpy perturbation will be expressed in the dimensionless form

\[
\psi = \frac{H'}{h'(\alpha)} = a' + \epsilon \theta' + \sigma \omega^2
\]

(10)

where Eqs. 6 and 7, together with a definition of dimensionless velocity

\[
\omega = u/u_w; \quad \sigma = \frac{u_w^2}{2h'(\alpha)}
\]

(11)

have been inserted into Eq. 2. Also, a new quantity is defined to represent the excess of atom concentration over that appropriate to equilibrium

\[
\phi = a' - a_e' = a' - \theta'
\]

(12)

Under the foregoing redefinitions, the new variables \( \omega, \psi, \phi \) satisfy the following differential equations, which replaces Eqs. 1 and 3

\[
\omega_r - \omega \eta \eta = 0
\]

(13)

\[
\psi_r - \psi \eta \eta = 0
\]

(14)
\[ \phi + \phi_r - \phi_{\eta \eta} + \kappa \omega_{\eta}^2 = 0; \quad \kappa = 2\alpha/\epsilon \]  

(15)

Physically, Eq. 15 states that one may imagine the gas to be driven out of equilibrium by viscous dissipation, represented by the last term on the left of Eq. 15.\(^5\) The magnitude of \(\phi\) is clearly controlled by the quantity \(\kappa\) defined in the foregoing. Now, the present small perturbation assumption requires that \(\phi\) be small. Therefore, since \(\omega\) is of unit order, \(\kappa\) must be small. Using Eqs. 7 and 11, it is found that \(\kappa\) is of the order of the square of the Mach number of plate motion. This quantity must be small, and, further, if \(\epsilon\) is small, Eq. 15 indicates that \(\sigma\) must be still smaller.

The boundary conditions to which the foregoing differential equations are subject are, by transformation of Eqs. 1, 4 and 5

\[ \omega(0,r) = \omega_w \quad \text{III} \omega(\infty,r) = 0 \]  

(16)

\[ (\psi - \phi)_w = (1 + \epsilon)\theta_w + \sigma \omega_{w}^2 \text{III} \psi(\infty,r) = 0 \]  

(17)

\[ (\psi_{\eta} + \epsilon \phi_{\eta} - 2\sigma \omega_{\eta})_w = \Gamma \phi_{w} \text{III} \phi(\infty,r) = 0 \]  

(18)

In the foregoing set of boundary conditions, the quantities to be specified are the wall velocity \(\omega_w\) and the wall temperature perturbation \(\theta_{\omega}\).

Equations 13 to 18 define the boundary value problem with which the authors are concerned. The ideal-gas version of this problem is, of course, rather easily solved by ordinary methods of heat conduction theory. More general solutions are now sought which display effects of gas kinetics and surface catalysis; these solutions may be obtained by the same basic methods of classical analysis. The essential difficulty to be surmounted is that the variables \(\psi\) and \(\phi\) are coupled through the wall temperature and wall catalysis boundary conditions Eqs. 17 and 18. Velocity, however, is uncoupled from the remaining variables and may be found directly from Eqs. 13 and 16. In

\(^5\)In the case of an ideal gas for which \(a'\) is zero, \(\phi\) may be replaced by temperature, according to Eq. 12, and the first term of Eq. 15, representing chemical production, is dropped. The resulting inhomogeneous heat equation has been studied by Emmons (Ref. 9).
order to effect reasonably simple solutions for the thermodynamic variables $\Psi$ and $\Phi$, all possible use shall be made of the idea that $\epsilon$ and also $\sigma$ may be considered small quantities.

Throughout the present study, the investigators shall be interested in surface heat transfer rate which are here defined in dimensionless form

$$Q = (\Psi - 2\sigma \omega \omega)_{w}$$

(19)

The shear-work term is excluded, in order to focus attention on the thermal and chemical components of heat transfer.

STATIONARY WALL WITH AN ABRUPT CHANGE OF TEMPERATURE

The boundary value problem stated in Eqs. 13 through 18 is quite easily solved in the case of unsteady one-dimensional heat conduction resulting when the wall, at rest, suffers a small step-function change of temperature. A review is now given of the method of solution (Ref. 5) applicable for this problem, adding a comparison with the hypersonic stagnation point solution of Fay and Riddell (Ref. 1). In the equations and boundary conditions, all terms involving $\omega$ are discarded, and it is specified that the wall is suddenly cooled so that Eq. 17 gives

$$\psi - \phi)_{w} = -1(r)$$

(20)

Extremes of Early and Late Time

At the earliest time, just after the abrupt change of wall temperature takes place, the gas must be out of equilibrium so long as the surface is not fully catalytic ($\Gamma \neq \infty$). Since the boundary layer would be expected to be thin at early time, the gradient of $\phi$, which represents nonequilibrium, would be expected to be much larger than $\phi$ itself. Therefore, for earliest times, Eq. 15 may be replaced by the heat equation. Then, an easy analysis using Eqs. 18 and 20 yields the surface heat transfer rate defined in Eq. 19

$$Q = \frac{\epsilon}{1 + \epsilon}$$

(21)

The foregoing result is independent of surface catalycity so long as $\Gamma$ is finite. If $\Gamma = \infty$, then, by Eq. 18, $\phi_{w}$ must vanish, and the appropriate solution of Eq. 15 is identically zero. With $\phi = 0$, a straightforward solution of Eqs. 14 and 20 yields the classical heat transfer rate

$$Q = 1$$

(22)
This result is applicable for all time if $\Gamma = \infty$. Of course, even if $\Gamma$ is not infinite, the equilibration must be completed for some sufficiently large time, and then for subsequent times, Eq. 22 would apply.

In summary, if the wall is not infinitely catalytic, the heat transfer rate must rise from an initial level of $\epsilon/(1 + \epsilon)$ at early times to 1 at very late times, and if $\Gamma = \infty$, the value 1 applies for all time. The quantity $\epsilon/(1 + \epsilon)$ defines the "frozen heat blockage" for this problem; that is, before atom concentration has a chance to adjust chemically to the lowered surface temperature, there is no gradient of concentration and hence no transport of the chemical component of enthalpy. In other words, only the enthalpy difference based on internal degrees of freedom is, at first, responsible for heat transfer. Much later, when atom concentration has been reduced to its equilibrium level at the cooled surface, additional heat transfer occurs, in proportion to the chemical component of enthalpy difference across the boundary layer. Thus, it is not surprising that inspection of Eq. 7 shows that the blockage ratio may be expressed as a ratio of internal to total enthalpy difference

$$\frac{\epsilon}{1 + \epsilon} = \left[ \frac{C_p \partial T}{C_p \partial T + h'(0) \partial \rho} \right]_p$$

The foregoing result is directly analogous to the frozen heat blockage calculated by Fay and Riddell for hypersonic stagnation point flow. In their case, heat is blocked in the ratio of internal enthalpy to total enthalpy, evaluated in the hot gas just outside the boundary layer. That result is the nonlinear equivalent of Eq. 23, remembering that their surface is assumed to be cold.

Nonequilibrium Solution for Catalytic Wall

Of course, the solutions for early and late time do not tell the length of time required for equilibration, and how this time depends on the properties of the surface $\Gamma$ and the gas $\epsilon$. For this purpose more complete solutions are needed in terms of time $\tau$. In passing, one should note that in the case of the hypersonic stagnation point, nonequilibrium effects depend on a "recombination-rate parameter" (Ref. 1), defined as a ratio of time necessary for diffusion to operate across the boundary layer to the normal lifetime of an atom. The present variable $\tau$ has a similar interpretation: By ordinary diffusion theory, the time for diffusion across a boundary layer is of the order of the square of the boundary layer thickness divided by kinematic viscosity. In the problem being reviewed here, the
boundary layer is roughly parabolic, and the foregoing "diffusion time" is proportional directly to \( t \), while the relaxation time \( \lambda \) characterizes the lifetime of an atom. Hence, the present quantity corresponding to the recombination-rate parameter is \( \tau / \lambda \), which, by Eq. 9, is proportional to \( r \).

The nonequilibrium solution of Eqs. 14, 15, 16 and 20 (with \( \omega = 0 \)) has been obtained exactly (Ref. 10). The analysis is difficult, and will not be reviewed here. Rather, it shall be outlined how these equations may be solved simply, under an additional assumption that \( \epsilon \) is small. For a wall with non-zero catalycity, the following method is appropriate: One may use as dependent variables \( a' \) and \( \phi \) instead of \( \psi \) and \( \phi \), and obtain the following system of equations in which, so far, \( \epsilon \) has been neglected only in comparison to 1

\[
\begin{align*}
a' \psi' + a' \eta' &= -\epsilon \phi' \; \; \; \; \; \; \; (a' - \frac{1}{\Gamma} a'_w) = -1(r) \tag{24}
\end{align*}
\]

\[
\phi + a' \phi' - \phi \eta' = 0 \; \; ; \; \; \phi_w = a'_w + 1(r) \tag{25}
\]

This system of equations shows that, if \( \epsilon \phi \) is neglected in Eqs. 24, one may proceed to determine the atom concentration directly. Then, using that solution for \( a' \), one may proceed to solve Eqs. 25. When this process is carried out (Ref. 5), the following surface heat transfer formula results

\[
Q = \frac{\epsilon}{1 + \epsilon} + \frac{1}{1 + \epsilon} \sqrt{\pi r} \epsilon e^{\Gamma 2 r} \text{erfc}(\Gamma \sqrt{r}) \tag{26}
\]

In this formula, the factor \( 1 + \epsilon \) is a matter of indifference under the approximation employed; however, it has the effect of making Eq. 26 agree with the exact solutions Eqs. 21 and 22 in the limits of early and late time. This heat transfer formula, shown in Fig. 3, was found to be in excellent agreement with the exact calculations (Ref. 10), even for \( \epsilon \) as large as one half.

The question of neglecting \( \epsilon \phi \) in Eq. 24 is briefly reconsidered. It is noted that this neglect is equivalent to an assertion that atom concentration is governed in the gas only by diffusion while chemistry operates only at the surface, according to the catalytic boundary condition contained in Eq. 24. In effect, a small value of \( \epsilon \) implies that large energy changes are connected with the production of atoms, and this high energy requirement constitutes a sort of thermodynamic inertia, so far as dissociation in the gas is concerned. In
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Fig. 3 the solution for a noncatalytic wall illustrates the increased time required when atom production occurs only in the gas and it is concluded that a small value of $\epsilon$ contributes to heat blockage not only in terms of the initial limit $\epsilon/(1+\epsilon)$, but by causing a delay of equilibration.

Nonequilibrium Solutions for Noncatalytic Wall

For a noncatalytic wall, the analysis just outlined cannot be used, because of the infinite factor which would appear in Eq. 24. In this case, it is found necessary to separate the equilibration process into an early and a late period. In the early period, atom concentration tends to be small, and definitions 10 and 12 suggest that $\psi$ may be neglected in comparison with $\phi$. Making this approximation in Eq. 20, Eq. 15 may be solved immediately under the simple boundary condition $\phi_w = 1(r)$, and, in view of the boundary condition of Eq. 18, determine heat transfer directly from the normal gradient of $\phi$ evaluated at the surface. From this calculation, the heat transfer formula

$$Q = \frac{\epsilon}{1 + \epsilon} \left( r^2 + \frac{\pi r}{\sqrt{\pi r}} \text{erfc} \sqrt{\tau} \right)$$

results, in which, again, the quantity $1 + \epsilon$ is inserted to insure agreement with the exact solution at early time.

For late time, one must consider a Hirschfelder "sublayer" (Ref. 4), which is a thin layer of adjustment necessary because the concentration gradient which would exist under conditions of complete equilibrium near the surface is not generally consistent with the noncatalytic requirement that no atoms diffuse to the surface. In the present problem, the sublayer may be shown (Ref. 5) to have the form

$$\phi = f(r)e^{-\eta}$$

Thus, at late times, the concentration imbalance $\phi$, has a profile of constant thickness, which, of course, becomes a progressively smaller proportion of the overall boundary layer, which grows parabolically. The function $f(r)$ must be determined from the differential equations. This done, the late solution for surface heat transfer rate is

$$Q = \epsilon \sqrt{\pi r} e^{\epsilon^2 r} \text{erfc} \sqrt{\epsilon^2 r}$$

The formulas given in Eqs. 27 and 29 are displayed in Fig. 3 for two values of $\epsilon$. 

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It is interesting that final equilibration for a noncatalytic wall goes by the same formula as does a catalytic wall, except that \( \varepsilon \) replaces \( \Gamma \).

**Surface Abruptly Set into Motion with No Change in Temperature**

The authors now turn to the Rayleigh problem which is, in effect, the reverse of the problem considered in the previous section. One may now imagine that the surface is suddenly set into motion at constant velocity in its own plane, but that its temperature remains unchanged, being held at the equilibrium temperature of the gas far from the surface. The motion of the surface results in a growing boundary layer, or shear wave, and, even though the surface temperature is unchanged, a temperature rise will occur in the boundary layer owing to viscous dissipation of mechanical energy. In the present instance, it is this temperature rise due to dissipation which causes chemical imbalance and subsequent nonequilibrium processes of adjustment.

The solution of Eqs. 13 and 16 may be written immediately, choosing \( \omega_w = l(r) \) as the specific boundary condition

\[
\omega = \text{erfc} \left( \frac{\eta}{2\sqrt{r}} \right) \tag{30}
\]

The remaining thermodynamic differential equations and boundary conditions, Eqs. 14, 15, 17 and 18 become

\[
\psi_r - \psi_{\eta \eta} = 0 \tag{31}
\]

\[
\phi + \phi_r - \phi_{\eta \eta} = -\frac{\kappa}{n} e^{-\eta^2/2r} (=-\kappa \omega^2 \eta) \tag{32}
\]

\[
(\psi - \phi)_{\eta \eta} = \sigma \tag{33}
\]

\[
(\psi_{\eta} + \epsilon \phi_{\eta})_{\eta} + 2\sigma / \sqrt{r} = \Gamma \phi_w \tag{34}
\]

**Early and Late Times**

The foregoing set of equations are then to be solved in the limits of small and large \( r \). As in the previous case, it may be argued that, at first, the gradients of \( \phi \) greatly exceed \( \phi \) itself. Then, dropping the first term of Eq. 32, one may immediately write a solution for \( \psi - \phi \) satisfying Eq. 33.
Next, the derivative of Eq. 35 at the wall is evaluated and the resulting term in $\phi_\eta$ is eliminated by substitution of Eq. 34 in which the term $\Gamma \phi_\eta$ is neglected relative to gradients appearing on the left. This neglect is correct so long as $\Gamma$ is finite. The foregoing process, together with Eq. 19, yields a heat transfer formula for small time

$$\pi \tau \frac{Q}{\sigma} = 1$$

(36)

This is the classical result for heat transfer in the Rayleigh problem. In the event that $\Gamma = \infty$, it is inferred from Eq. 34 that $\phi_w = 0$, and hence, that $\psi = \phi w$, and, again, the classical result given in Eq. 36 applies. At late times, one may anticipate that equilibration is complete, so that $\phi = 0$ throughout the boundary layer, and Eq. 36 applies again.

Thus, it is seen that the problem of the moving wall differs from the previous case of wall temperature change in that there is no heat blockage associated with early frozen conditions. The reason for this qualitative difference is, of course, connected with the different ways in which the driving enthalpy difference appears. In the case of the wall with temperature change, a lowered constant temperature at the surface was imposed, and thus, across the boundary layer, the difference of total enthalpy $\psi$ increased from a level of order $e$ to a level of unit order as the atom concentration came into equilibrium with the temperature change. Thus, the enthalpy potential for that boundary layer increased with time, and an increased heat transfer rate at later time was expected. In the present case of a moving wall, however, the enthalpy difference is the same for both early and late times, because a surface which suffers no temperature change is not out of equilibrium at either early or late time. Thus, no heat transfer difference between these two extremes is to be expected, apart from that due to the normal parabolic growth of the boundary layer. However, at intermediate times, nonequilibrium effects will produce deviations from the classical result, as will be seen.

Nonequilibrium for a Fully Catalytic Wall

In the present Rayleigh problem for a constant temperature surface, it is not true, as it was in the temperature-jump case, that a fully catalytic surface ($\Gamma = \infty$) assures complete equilibrium for all time in the boundary layer. The reason is, of course, that the surface reaction cannot take place until atoms are produced in the gas, and then arrive at the surface.
by diffusion. Until that happens, there is no chemical im-
balance upon which catalycity can operate, even though the in-
terior of the boundary layer may be out of equilibrium. Thus,
although \( \phi_w = 0 \) when \( \Gamma = \infty \), the differential Eq. 32 for \( \phi \) is
inhomogeneous and therefore has a nontrivial solution under that
condition.

To find the desired solution of Eq. 32, it is first noted that
the function \( e^r \phi \) satisfies the classical equation of heat con-
duction with distributed heat sources. This equation may be
solved by classical methods, subject to homogeneous boundary
conditions. The result is quite complicated. However, the in-
vestigators are especially interested in the normal gradient of
\( \phi \) at the surface, and this latter quantity may be expressed in
reasonably simple form

\[
(\phi \tau)_{w} = -\frac{\kappa}{2} \frac{e^r}{\sqrt{\pi r}} \left( 1 - e^{rt^2} \right) = -\frac{\kappa}{2\sqrt{\pi}} F(r)
\]  

(37)

where the function \( F(r) \) is defined for future reference. De-
tails of the solution for \( \phi \) and the derivation of \( (\phi \tau)_w \) are
given in Ref. 11.

Nonequilibrium Solution for a Wall with Finite Catalycity

Now, Eq. 37 has application in a wider class of problems than
that for which it was derived. It has been said that \( \phi_w = 0 \)
when \( \Gamma = \infty \) in order that the left-hand side of Eq. 34 may have
finite value. No assumptions that \( \epsilon \), \( \sigma \) and \( \kappa \) are small were
used. If these assumptions are now introduced, it is found that
the homogeneous boundary condition \( \phi_w = 0 \) applies for any level
of catalycity. This conclusion may be obtained by inspection
of the differential equation and boundary condition, Eqs. 32 and
33: If it is assumed that \( \psi \) and \( \phi \) are roughly of the same order
at the surface (this may be verified by examination of solutions
which result), then \( \phi \) at the surface must be of order \( \sigma \), by
Eq. 33. However, Eq. 32 implies that \( \phi \) generally through the
boundary layer must be of order \( \kappa \), which is larger than \( \sigma \) by a
factor \( 1/\epsilon \) according to Eq. 15. The presence of the factor
\( 1/\tau \) on the right-hand side of Eq. 32 suggests that this order-
ing of magnitudes is not valid for very large times, and, in
fact, it shall be found that at very large times, for a non-
catalytic wall, a sublayer type of analysis is necessary. Now,
if \( \phi \) in the boundary layer is very much larger than \( \phi \) at the \( \phi 
\) surface, then the homogeneous boundary condition \( \phi_w = 0 \) is ap-
propriate for any degree of catalycity.
Thus, for the case of finite catalycity and small $\epsilon$, $\phi$ is taken to be known from the previous analysis and proceed to use Eqs. 31, 33 and 34 to determine the appropriate solution for $\psi$, the enthalpy perturbation. Combining Eqs. 33 and 34, and using Eq. 37, the new boundary condition for $\psi$ is found

$$ (\psi_\eta - \Gamma \psi)_w = -\sigma \left[ \Gamma + \frac{2}{\pi r} \cdot \frac{1}{\pi} \cdot F(r) \right] \tag{38} $$

Of course, $\psi_\eta - \Gamma \psi$ satisfies the heat equation, which may be solved subject to Eq. 38. Then, knowing $\psi_\eta - \Gamma \psi$, one has a first-order ordinary differential equation to solve for $\psi$ itself. One may immediately write the first step in this process using classical heat conduction theory

$$ \psi_\eta - \Gamma \psi = \sigma \left[ 2\omega_\eta - \Gamma \omega + \frac{2}{\pi} \int_{\eta/2}^{\infty} \frac{F(r - \eta^2/4 \xi^2)}{r} e^{-\xi^2 d\xi} \right] \tag{39} $$

The next step, to find $\psi$ by solving Eq. 39, is formally quite simple, although matters quickly become complicated. Rather than do this, an evaluation is made instead of surface heat transfer rate; that is, the wall value of $\psi_\eta$. This may be accomplished by noting the identity, based on Eq. 31

$$ (\frac{\partial}{\partial r} \cdot \Gamma^2) \psi_\eta = (\frac{\partial}{\partial r} + \Gamma \frac{\partial}{\partial \eta})(\psi_\eta - \Gamma \psi) $$

into which Eq. 39 may be inserted, and evaluating the result at the wall. Then a suitable integration with respect to $r$ yields

$$ \frac{\sqrt{\pi \tau} \cdot Q}{\sigma} = \sqrt{\pi \tau} \cdot e^{\Gamma^2 r} \left[ \Gamma \cdot \text{erfc} (\Gamma \sqrt{\tau}) \right] \frac{1}{\sqrt{\pi \tau}} \int_r^\infty e^{-\xi^2} F(1(t)) \, dt + \frac{\Gamma}{\pi} \int_r^\infty e^{-\xi^2} \frac{d}{dt} \int_0^t \frac{F(\xi) d\xi}{t - \xi} \, dt \right] \tag{40} $$

By manipulation of Eq. 40, it may be shown that for early times the heat transfer is given by

$$ \frac{Q}{\sqrt{\pi \tau} / \sigma} = 1 - (0.273) r \left[ 1 - \frac{1}{2} \Gamma \cdot \pi r + G(r) \right] \tag{41} $$

which indicates a falling-off from the early-time limit of unity. At late time, as has been seen, the quantity $Q \pi r / \sigma$ again approaches unity, and asymptotic development of Eq. 40 shows that the final approach is given by the expression
This approach is from below and in conjunction with Eq. 41 suggests that a dip in heat transfer coefficient occurs at intermediate times, when the wall is not fully catalytic.

In the particular case $\Gamma = 1$, Eq. 40 has been calculated to yield the result displayed in Fig. 4. Even though Eq. 40 embodies the approximation that $\epsilon$ is small, the formula for $Q$ is clearly not very simple to evaluate. Therefore, one should note the somewhat simpler formula appropriate for large $\Gamma$. For large $\Gamma$, the three terms of Eq. 40 are of order 1, $1/\Gamma^2$ and $1/\Gamma$, respectively, and yield

$$\frac{Q \pi r}{\sigma} = 1 + \frac{1}{\Gamma} \cdot \frac{\ln r}{\pi r} + 0 \left( \frac{1}{r^{3/2}} \right)$$

For $\Gamma = 1$ and 2, Eq. 42 yields the result indicated in Fig. 4. Comparison with the more exact calculation suggests that Eq. 42 is fairly accurate for $\Gamma > 2$.

From the foregoing analysis, it is a simple matter to find the change of atom concentration at the surface, $a'$, which is identical with $\phi_w$, for the present case. Equation 34, into which the approximate (small $\epsilon$) value of $(\phi_{\eta})_w$ is incorporated, yields

$$a'_w = \frac{\sigma}{\Gamma \sqrt{\pi r}} \left\{ \frac{Q \pi r}{\sigma} \cdot e^r \left[ 1 - erf \left( \frac{r}{\sqrt{2}} \right) \right] \right\}$$

The second term in the brace is shown in Fig. 4, and $a'_w$ is proportional to the excess of the heat transfer coefficient over this universal function. Figure 5 displays $(\Gamma/\sigma)a'_w$ for $\Gamma = 1$, and a universal function obtained by setting $\sqrt{\pi r} Q/\sigma = 1$. This last must be quite accurate for large values of $\Gamma$, by inspection of Fig. 4.

The foregoing results for surface heat transfer rate and atom excess at the surface may be explained in the following way. At first, as atoms are produced in the heated portion of the boundary layer, no change in enthalpy gradient at the surface.

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6 Properties of the convolution of $F$, appearing in Eqs. 40 and 42, are discussed in Ref. 11.
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appears; only a redistribution of enthalpy occurs among the modes of the gas in parts of the boundary layer away from the wall. However, as time proceeds, these atoms begin to diffuse to the surface, and unless the wall is fully catalytic, they do not all recombine there. Thus, the gas at the surface will begin to show the atom excess displayed on Fig. 5. In effect, chemical enthalpy is partly frozen at the surface, and the heat transfer must fall. The third term of Eq. 41 shows that catalycity tends to suppress this effect. Subsequently, the atom excess near the surface must disappear by the combined action of recombination in the gas and surface catalysis, with the result, finally, the heat transfer rate must approach its final equilibrium level.

The depth of the heat transfer dip (and the peak of atom excess at the surface) are determined by the interplay of diffusion and recombination processes. Clearly, for moderate catalycity, this competition results in a rather shallow dip of the order of 20%. The heat transfer dip and the concentration peak occur at roughly the same time, the time being comparable to the chemical relaxation time. Presumably, the effects described in Figs. 4 and 5 are accentuated if the surface is noncatalytic, so that only the homogeneous reaction remains to compete with diffusion. This case is now considered setting $\Gamma = 0$.

Solution for a Noncatalytic Wall

The solution just described for a catalytic surface is not valid in the limit $\Gamma \rightarrow 0$. Especially for late time, a different kind of solution must be found. The solution for $\phi$ previously described may be carried over, so long as $\epsilon$ is considered small and time is not too late. In the case of the noncatalytic wall, comparing Eqs. 19 and $34^*$, it is seen that heat transfer may be written down immediately as the surface gradient of $\phi$ is given in Eq. 37
\[
\sqrt{\frac{\pi r}{\sigma}} \frac{Q}{\phi} = e' (1 - erf^2 \sqrt{r})
\]
(44)

This heat transfer result (coincidentally displayed in Fig. 4 and again in Fig. 6) has the proper value of unity in the limit of small time. However, Eq. 44 yields zero in the limit of large time, which is, of course, an incorrect result.

Before dealing with the late-time problem, the surface concentration $\phi_w$ for early time should be found, corresponding to Eq. 44. Previously, $(\phi_x)_w$ was found (and hence $\phi_w$) on the basis that $\phi_w$ is negligible in comparison with $(\phi_y)_w$ when $\epsilon$ is small. Now the small quantity $\phi_w$ must be found. For this pur-
pose, an iteration process, mathematically related to that leading to Eq. 40, is appropriate. Substituting Eq. 37 into Eq. 34 for \( \Gamma = 0 \), a boundary condition on \( \psi_\eta \) is

\[
(\psi_\eta)_w = \sigma \left[ \frac{1}{\sqrt{\pi}} F(r) - \frac{2}{\sqrt{\pi} r} \right]
\]

By classical heat conduction theory, the surface value of \( \psi \) is simply the convolution of \( (\psi_\eta)_w \). Then, knowing \( \psi_w, \phi_w \) is found directly from Eq. 33. Carrying out these operations obtains

\[
\frac{1}{\sigma} \phi_w = 1 - \frac{1}{\pi} \int_0^r \frac{F(\xi) d\xi}{\sqrt{r - \xi}}
\]

which is displayed in Fig. 7. It is seen that surface atom concentration \( \phi_w \) rises from zero to a level of order \( \sigma \) at intermediate times. However, Eq. 45 yields a constant for late time, whereas it is known that \( \phi_w \) must fall off to zero as \( r \to \infty \). Thus, for surface atom concentration as well as for heat transfer, an additional solution is required which is valid at late time.

In seeking a late-time solution which governs the final approach to equilibrium, a "sublayer" must be dealt with of the type described by Hirschfelder in Ref. 4. Crudely, it may be said that, when \( \Gamma = 0 \), then \( (\phi_\eta)_w \) must vanish like \( 1/r \) for large time, in order to balance the remaining terms of Eq. 34. This decay is much slower than that appropriate for \( \Gamma \neq 0 \), which, from the asymptotic form of Eq. 37, is as \( 1/r \). Thus, the authors are led to imagine a sublayer across which the variation of \( \phi \) is quite rapid. For times so large that \( 1/r \) is small, the right side of Eq. 32 is neglected, and, in accordance with the sublayer idea, \( \phi_r \) is neglected in comparison with \( \phi \) and \( \phi_\eta \). The remaining terms of Eq. 42 are satisfied by Eq. 28, wherein the function \( f(r) \) is to be determined. This equation defines a constant-thickness sublayer of gas out of equilibrium. When Eq. 28 is substituted into Eqs. 43 and 44, the boundary conditions

\[
\psi_w - \phi = \sigma \left( \psi_\eta \right)_w - \epsilon f + \frac{2\sigma}{\sqrt{\pi} r} = 0
\]

result. Now, \( f \) may be eliminated between these, yielding a single boundary condition on \( \psi_\eta - \epsilon \psi_w \). The heat Eq. 31 may easily be solved under this condition, and then \( f(r) \) may be found by returning to Eq. 46. For surface heat transfer and atom concentration, one finds
In the foregoing, no explicit assumption of small $\varepsilon$ has been made; rather, $\mu r$ was assumed large. The solution is evidently in terms of $\varepsilon r$ and in writing Eqs. 47 and 48 rather than their asymptotic forms, it is assumed that $\varepsilon r$ belongs to a smaller order than $r$ itself. In this sense, $\varepsilon$ is assumed small.

Equation 47 is the same as Eq. 29, and it is concluded that the same final sublayer adjustment process occurs for the moving surface at constant temperature and the stationary surface with a temperature change. Equations 47 and 48 are plotted for two values of $\varepsilon$ on Figs. 6 and 7. Both curves have the correct large-time limits. Thus, the sublayer, being thin, cannot affect the ultimate heat transfer rate, although it dominates the process of equilibration when $\Gamma = 0$. Both sets of curves cross the corresponding curves for early time, giving what are, no doubt, the correct indications:

a) The minimum of heat transfer is lower, and the peak of atom concentration is higher for smaller $\varepsilon$.

b) Also, the occurrence of this minimum and peak is delayed, in keeping with a slower equilibration process, when $\varepsilon$ is smaller.

c) These changes and associated delays are greater for $\Gamma = 0$ than for finite $\Gamma$ (Figs. 4 and 5).

Nevertheless, it would be desirable to have a correction to these results which would provide a smooth transition between early and late time. It shall be indicated how this may be done, in a plausible but not rigorous way; strictly speaking, Figs. 6 and 7 show that a smooth transition is already in evidence in the limit of our assumption of small $\varepsilon$. For example, if $\varepsilon = 0.001$, the late-time curves would be shifted to the right by 4 decades from their position when $\varepsilon = 0.1$, and the early and late solutions would connect quite smoothly. Unfortunately, a value of $\varepsilon = 0.001$ is absurdly small (the authors were more fortunate in the case of the stationary surface; Fig. 3 shows a satisfactorily smooth transition even for $\varepsilon = 0.4$).
It is postulated that $\phi$ is a combination of the correct early solution and a sublayer

$$\phi = \phi^{(1)} + g(r) e^{-\eta}$$

(49)

where $\phi^{(1)}$ is the solution of Eq. 32 for which $\phi^{(1)} = 0$ and $(\phi^{(1)} \eta \eta)_w$ is given by Eq. 37, and where $g(r)$ is to be found. The fact may be ignored that $g(r) e^{-\eta}$ is a complementary solution only if $g^{(1)}(r) < g(r)$, and one may proceed without further approximation. Substitution of Eq. 49 into Eqs. 33 and 34, and elimination of $\Phi$, yields a boundary condition

$$\left( \psi_w \cdot e \cdot \psi \right)_w = - \sigma \left[ e + \frac{2}{\sqrt{\pi r}} e^{-\eta} \left( 1 - \text{erf} \frac{2}{\sqrt{\pi r}} \right) \right]$$

which is identical to Eq. 38 with $\epsilon$ substituted for $\Gamma$. Hence, making the same substitution, Eq. 40 may be immediately identified as the desired result for heat transfer rate. The foregoing parallel also applies to the determination of $\Phi$ ($= a_w$). One finds that Eq. 43 applies, again replacing $\Gamma$ by $\epsilon$. Figures 6 and 7 show how solutions based on Eqs. 40 and 43 go smoothly between early and late times.

As noted earlier, the smoothing corrections obtained in the foregoing are not necessarily correct. However, the smooth solutions reduce to the correct formulas (Eqs. 44 and 45 for early time and Eqs. 47 and 48 for late time). It is remarkable that Eqs. 40 and 43 may be used for either the catalytic or noncatalytic cases. In fact, one may show, using Eq. 49 for the general case (any $\Gamma$), that Eqs. 40 and 43 are still recovered, $\Gamma$ being replaced by $\Gamma + \epsilon$.

Discussion of Nonequilibrium Profiles of Temperature and Concentration

Before leaving the problem of the moving constant-temperature surface, it may be helpful to review the nonequilibrium process in terms of changes in the boundary layer profiles of pertinent quantities. With difficulty these could be calculated from the foregoing analysis. However, for purposes of qualitative discussion, it is much simpler and equally useful to consider profiles derived from an exponential solution of the type discussed in Ref. 5; if $\omega_w = e^{2\eta}$ instead of $1(r)$, Eqs. 13 to 18 have simple solutions of the forms, as explained in Ref. 11

$$e^{-2\eta} = \sigma A(\Gamma, \epsilon, \beta) e^{\sqrt{2\beta}} \eta$$
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\[ e^{-2\beta r} \phi = \left[ B(\epsilon, \beta) e^{-2\sqrt{\beta}} \eta + C(\Gamma, \epsilon, \beta) e^{\sqrt{1+2\beta}} \eta \right] \]

Now, it develops that a close analogy exists between the quantity \( \beta \) appearing on the right of these equations and the reciprocal of \( \tau \) appearing in the Rayleigh type of problem. In fact, suitably normalized curves of surface heat transfer and atom concentration vs. \( 1/\beta \) for the exponential solution reproduce all the qualitative features of Figs. 4 through 7. Accordingly, in Fig. 8, the profiles are shown of atom concentration and temperature vs. \( \eta/\sqrt{\beta} \) for various values of \( 1/\beta \) during the nonequilibrium process associated with an exponential increase in velocity of an isothermal noncatalytic surface. These profiles are thought to represent quite well the corresponding profiles of \( \theta' \) and \( a' \) vs. \( \eta/2\sqrt{\Gamma} \) for the Rayleigh problem, and the discussion to follow will, for convenience, be couched in terms of the Rayleigh problem.

It has been noted previously that at the beginning of the motion and again at large times thereafter the atom concentration on the surface must be zero, because the authors have imagined that the plate temperature has been kept at its original undisturbed level. Figure 8a describes the boundary layer in the beginning of the nonequilibrium process at rather early times. Precisely at the start of the motion, the perfect gas result (Ref. 9) for temperature would apply and the atom concentration would be everywhere zero in the boundary layer. Soon after, as shown on the same curve, the temperature level has fallen rather uniformly through the boundary layer and a slight disturbance of concentration has appeared. The particular "time" at which these profiles apply is indicated by \( 1/\beta = 1 \), which corresponds roughly to a fraction \( \epsilon \) of the chemical relaxation time. Thus, it is found that, even at quite early time, a chemical imbalance occurs at the surface owing to diffusion of atoms from regions of the boundary layer in which atoms are produced. The difference between the profiles of temperature and concentration is, according to the definitions of this paper and in particular in Eq. 12, the chemical potential then existing, that is, the degree of nonequilibrium. From this point of view, it can be seen that at early time, through most of the boundary layer, there is a large deficiency of atoms which must subsequently be made up by chemical reaction in the gas. Near the wall, however, the chemical potential is opposite in sign, that is, there is an atom excess which must subsequently disappear by recombination.

Figure 8b illustrates the changes in profiles which have resulted when \( 1/\beta \) is approximately 100. Even if \( \epsilon \) is as small as 0.1 (the value for which these profiles were calculated), this time is of the order of ten times longer than the typical
chemical relaxation time. It is at this rather late time that the maximum atom concentration at the surface occurs and the dip in heat transfer coefficient is most pronounced. Now, it is seen that dissociation has proceeded in the gas, diminishing the temperature profile, making the concentration profile much fuller and tending toward an equilibrium balance of energy in the gas. Even though in most of the boundary layer there is a strong approach to equilibrium (congruence of the two profile functions) atom concentration at the surface continues to rise, because the recombination process near the surface is overwhelmed by the diffusion of the now more numerous atoms toward the surface. Since the surface is noncatalytic, these atoms do not recombine directly on reaching the surface, and since they carry energy abstracted from the gas during dissociation the heat transfer to the surface may be expected to be diminished. If one goes to a "time" corresponding to \( l/\beta = 1000 \), final equilibration is found to be in progress. Most of the boundary layer is in equilibrium; that is, the curves of \( a' \) and \( \theta' \) are essentially identical, and homogeneous recombination in the region closest to the surface is beginning to overcome the effect of diffusion, driving the surface concentration of atoms down toward its ultimate equilibrium value of zero. The consequent release of chemical energy stored in the gas near the surface results in an increasing trend of heat transfer coefficient toward its ultimate value of 1.

It is clear from the sketched profiles of \( a' \) that, beyond the time when recombination in the gas near the surface begins to operate strongly \( (l/\beta = 100) \), the important chemical activity takes place in a region very close to the surface. It is for this reason that analysis from that time forward must deal with a "sublayer" of nonequilibrium.

**Simultaneous Change of Temperature and Impulsive Start**

So far, two distinct situations have been considered. In the first case, it has been assumed that the plate would remain stationary while a sudden change of wall temperature occurs. Then the case was treated where the wall temperature remain unchanged while the plate is abruptly set into motion. Inasmuch as the problems which have been so far considered are linear, one may use simple addition to construct the solution for any situation which might be represented by a linear combination of the pertinent boundary conditions. In particular, cases may be considered in which the wall temperature is suddenly changed and, at the same instant, the surface is abruptly set into motion. Comparing the surface heat transfer rates displayed in Figs. 3, 4 and 6 for the two constituent problems, it is seen that the qualitative features of the combined result will depend very
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much on the relation between the imposed temperature change and the speed of motion imparted to the plate surface. Over the greater part of the range of possible combinations, it would seem most typical that the effects of temperature change would dominate. This is inferred from the fact that heat blockage at intermediate times due to plate motion is a considerably weaker effect (even for small $\epsilon$) than heat blockage occurring at early times in the case of surface temperature change. Apart from this difference, the balance between the two constituent problems depends on a comparison of $\theta_w$ and $u_w$ (or $\sigma$). By using the appropriate definitions, one may say that heat transfer history will look qualitatively like Fig. 3 if

$$\frac{T_w}{T} > \epsilon \frac{\gamma - 1}{2} M_w^2$$

The appropriate normalized linear combination for total heat transfer rate is

$$\frac{Q_{\text{total}} \pi r}{\sigma + \theta_w'} = \theta_w' \left( \frac{Q_{\theta} \pi r}{\theta_w'} \right) + \sigma \left( \frac{Q_u \pi r}{\sigma} \right)$$

where the quantities in parentheses on the right are those appearing in Figs. 3, and 4 or 6, respectively. The frozen limit of this expression is

$$\lim_{r \to 0} \left( \frac{Q_{\text{total}} \pi r}{\sigma + \theta_w'} \right) = \frac{\epsilon}{1 + \epsilon} + \frac{\epsilon}{1 + \epsilon} \frac{1}{1 + \theta_w' \sigma} \quad (51)$$

For an arbitrarily chosen case $\theta_w' = 0.4$, assuming a non-catalytic wall and $\epsilon = 0.1$, Eq. 50 yields the total heat transfer result shown in Fig. 9. Here, the wall temperature change is taken to be negative, that is, a condition where the wall is cold, and heat flows toward the surface on that account. If this were the only effect, the heat transfer rate given by Eqs. 27 and 29 would apply, as shown by the dashed line. An effect of the superposition is to diminish the heat blockage occurring at early times, in accordance with Eq. 51. In addition, the dip of heat transfer coefficient associated with wall motion in effect produces a delay of equilibration.

The delay introduced by surface movement tends to bring the solid and dashed lines of Fig. 9 into congruence at late time. Thus, it may be said that when surface temperature change predominates, only the early stages of nonequilibrium are affected by surface motion. Of course, this result follows from the fact that final equilibration is governed by the same formula (Eqs. 29 and 47) in the two separate problems from which the

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combined result is constructed. Of course, if the wall were heated instead of cooled, and positive heat transfer were counted as that into the gas rather than to the surface, surface motion would have the opposite effect; that is, equilibration would be advanced and heat blockage would be increased. This is because the effect of surface motion is always to transfer heat to the surface.

CONCLUDING REMARKS

In the present paper, the authors have studied the nonequilibrium boundary layer produced in a partly dissociated diatomic gas when certain small changes are imposed at a bounding surface, namely, a change of the surface temperature or motion of the surface in its own plane. These problems are analogous to certain problems of hypersonic flow. Therefore the purpose, at least in part, is to find simple methods of solution, with the thought that, if simplifying assumptions are found effective in this linearized class of problems, analogous physical assumptions might hereafter be found fruitful for analyzing the more difficult nonlinear real-gas boundary layer. Of course, certain assumptions used here, such as that Lewis number is unity, are well known to simplify real-gas boundary layer theory. In addition, the assumption of small $\varepsilon$ (a comparison of heat absorbed in internal degrees with heat absorbed in chemical reaction) was found to have a powerful effect in simplifying the present linear analysis, providing results which are actually more accurate than the physical validity of that assumption would suggest. It should be emphasized that $\varepsilon$ tends to be smaller at low pressure (Fig. 2), and, therefore, something like the present assumption may be particularly useful in connection with low density flows.

In the case of surface temperature change without wall movement, it is found that the assumption of small $\varepsilon$ provides that heat transfer equilibration at a surface with some degree of catalycity may be analyzed as though the homogeneous chemical reaction involves atoms which have been conveyed to the surface by diffusion. Apparently, it is not proper to describe this result by the simple statement that the surface reaction is faster than the gas reaction. Of course, the surface reaction must be "fast" ($\Gamma \neq 0$ ) if it is to dominate the chemistry; however, $\varepsilon$ is an equilibrium constant of the gas, and its smallness implies "slow" gas reaction only in relation to the energy-exchange processes in the gas. That is, $\varepsilon$ refers to the

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7For the stationary plate with temperature change, effects of Lewis number that are different from 1 are found in Ref. 10.
energy of reaction that must be supplied by ordinary heat conduction or viscous dissipation, and a small $\epsilon$ implies a high chemical inertia of the dynamic system.

The general features of the heat transfer result obtained for temperature change at a stationary wall are qualitatively the same as that found by Fay and Riddell (Ref. 1) in their calculations of the nonequilibrium stagnation point boundary layer, and it is interesting that the heat-blockage ratio of $\epsilon/(1+\epsilon)$ that is obtained in the present linear problem is the differential equivalent of that found by Fay and Riddell. Thus, it appears that one of two simple problems is closely related to cases of nonequilibrium hypersonic flow about blunt bodies. Of course, the present authors, dimensionless time and Fay and Riddell's "recombination-rate parameter" are connected only in a qualitative way, so that numerical comparisons are not feasible.

When the plate temperature is not changed, but the plate is set into motion instead, thermal changes occur in the boundary layer by viscous dissipation, and these thermal changes induce chemical nonequilibrium in the boundary layer and on the surface. For this problem, unlike the surface temperature change problem, the atom concentration at the surface is the same for early and late times and, therefore, it is not surprising that the heat transfer coefficient is the same at early and late times. When Lewis number is 1, this is also true for the nonlinear flat plate boundary layer in the frozen (early) and equilibrium (late) limits (Ref. 12). However, at intermediate times, for the Rayleigh problem, chemical composition does change at the surface owing to diffusion, and, unless the wall is fully catalytic, a certain amount of chemical potential energy is frozen at the surface. Consequently, a transient dip in heat transfer coefficient results; whether this freezing process occurs at intermediate distances from the leading edge in the hypersonic flat plate boundary layer is not known; however, by analogy, the possibility that it does may be suggested.

Further, on the basis of a presumed analogy between the Rayleigh problem and the flat plate problem, the possibility that nonequilibrium effects on heat transfer rate may not be very powerful in the latter case may tentatively be suggested; it is observed that the dip in heat transfer coefficient shown in Fig. 6 is quite shallow, even for small $\epsilon$, and furthermore occurs at a time when the heat transfer itself is quite low anyway, owing to its proportionality to reciprocal square root of time. The surface concentration of atoms is not negligible, however. The peak concentration, according to Figs. 5 and 7, reaches a substantial fraction of the fully frozen level. It is therefore suggested that experimental studies of nonequilib-
rium effects in flat plate boundary layers are likely to be quite disappointing if emphasis is placed on measurement of surface heat transfer rates. Measurement of surface atom concentration, although more difficult, would be more fruitful. Of course, measurement of surface heat transfer is more appropriate for stagnation point flow because of the earlier and stronger heat blockage. Even so, the fall-off with $l/r$ would tend to mask the equilibration process, and, again, measurement of surface concentration would presumably yield more complete information about catalycity, diffusion coefficients, reaction rates, and the like.

Two generalizations should be emphasized concerning the array of formulas collected in this investigation: First, it is noted that formulas obtained for a catalytic surface ($\Gamma \neq 0$) generally apply for the case $\Gamma = 0$ with $\Gamma$ replaced by $\epsilon$. For a noncatalytic surface, $\epsilon$ plays the role of $\Gamma$. This suggests that, in experiments designed for sensitive measurement of the chemical activity of a surface, it would be desirable to arrange that $\epsilon$ be small. Second, for a noncatalytic surface, the equilibration process at late time is the same for the two problems treated. In effect, the sublayer behaves in the same way for the two cases.

The latter point assumes importance when the various possible superpositions of these two basic problems are considered, involving both temperature change and motion at the surface. For all such problems the final equilibration of heat transfer and surface concentration follows the same law, and only the early stages of nonequilibrium depend on the particular combination of boundary conditions. This result raises the question whether, by a sort of local similarity, the Fay-Riddell type of nonequilibrium calculation might apply in the case of the hypersonic flat plate, or even hypersonic boundary layers in general, subject to proper interpretation of the recombination-rate parameter and a suitable adjustment of frozen heat blockage.

Finally, the observation is made that even though the present study might potentially offer suggestions for the analysis of more complicated nonequilibrium boundary layer problems, the present study is incomplete. It is clear, for example, that in the present problem, surface effects are very strongly influenced by the competition between diffusion, which tends to produce chemical imbalance at a surface, and reaction rate in the gas, which tends to drive the gas toward equilibrium. This competition is one in which Lewis number would be an important parameter, being a measure of multicomponent diffusion rates in comparison with the viscous effects which determine boundary layer thickness. Here, Lewis number has been taken to be 1.
Also, it should be recalled that rather stringent limitation was placed on wall velocity to preserve the linearization necessary for simple analysis. It may be that the effort to remove this restriction, so that the Rayleigh problem may properly be solved under conditions of large dissipation rates, would modify the results of the present study to a significant degree. For this purpose, the chief requirement would be the adoption of a rate law more realistic than the linear (first-order) rate law employed in this study.

NOMENCLATURE

\( \alpha \) = mass concentration of atoms

\( C_p \) = specific heat at constant pressure

\( \text{erf} \ x \) = error function, \( \frac{2}{\sqrt{\pi}} \int_0^x e^{-\xi^2} \ d\xi \)

\( \text{erfc} \ x \) = complementary error function, \( \frac{2}{\sqrt{\pi}} \int_x^\infty e^{-\xi^2} \ d\xi \)

\( F(r) \) = defined in Eq. 37

\( f(r) \) = defined in Eq. 28

\( g(r) \) = defined in Eq. 49

\( H \) = total enthalpy

\( h^{(0)} \) = heat of dissociation

\( \kappa \) = defined in Eq. 15

\( M \) = Mach number of surface, based on undisturbed sound speed

\( m \) = molecular weight of diatomic gas

\( Q \) = heat transfer rate, Eq. 19

\( R \) = universal gas constant

\( T \) = temperature

\( t \) = time

\( u \) = velocity parallel to the surface

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\( y \) = distance normal to the surface

\( \mathbb{1}(r) \) = unit step function ( = 0, \( r < 0 \); = 1, \( r > 0 \))

\( \beta \) = rate of exponential increase of surface disturbances in exponential solution

\( \Gamma \) = effective surface catalycity, Eq. 8

\( \gamma \) = catalytic efficiency

\( \epsilon \) = ratio of internal to chemical energy change, Eq. 7

\( \eta \) = dimensionless coordinate normal to surface, Eq. 9

\( \theta \) = dimensionless temperature, Eq. 6

\( \lambda \) = relaxation time for homogeneous reaction

\( \nu \) = kinematic viscosity

\( \sigma \) = dimensionless measure of wall velocity, Eq. 11

\( r \) = dimensionless time, Eq. 9

\( \phi \) = measure of nonequilibrium, Eq. 12

\( \psi \) = dimensionless enthalpy perturbation, Eq. 10

\( \omega \) = dimensionless velocity, Eq. 11

primes = disturbance quantities

Subscripts

\( \infty \) = undisturbed state (far from surface)

\( w \) = value at surface

\( e \) = equilibrium value

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Fig. 1 Boundary layer growing into dissociated gas over an infinite plane surface, with typical profiles of velocity, temperature and atom concentration.

Fig. 2 Equilibrium concentration and ratio of internal to chemical energy absorption. $p_d$ and $T_\infty$ are characteristics of the gas (Ref. 8). For oxygen $p = 2$ atm when $p_d/p = 10^7$. 

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Fig. 3 Surface heat transfer for sudden temperature change at stationary wall, from Eqs. 26 (catalytic wall) and Eqs. 27 and 29 (noncatalytic wall).
Fig. 4 Surface heat transfer for impulsive motion of catalytic surface but no change in surface temperature, from Eqs. 40 (moderate $\Gamma$) and Eq. 42 (large $\Gamma$).

Fig. 5 Surface concentration of atoms for impulsive motion of catalytic surface but no change in surface temperature, from Eq. 43.
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**Fig. 6** Surface heat transfer for impulsive motion of non-catalytic surface, no change in surface temperature.

**Fig. 7** Surface concentration of atoms, for impulsive motion of noncatalytic surface, no change in surface temperature.
Fig. 8 Profiles of concentration and temperature disturbance for noncatalytic surface moved with exponentially increasing velocity, $\omega w = e^{\beta t}$, but held at constant temperature; $\epsilon = \sigma = 0.1$.

Fig. 9 Total surface heat transfer when noncatalytic surface suffers simultaneous impulsive velocity increment and drop of temperature, in the ratio $\alpha/\theta_w = 0.4$, compared with heat transfer due only to temperature change; $\epsilon = 0.1$. 

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