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A SOLUTION FOR GAS-PHASE RECOMBINATION AND DISSOCIATION IN THE LAMINAR BOUNDARY LAYER OF A FLAT PLATE

Robert J. Vidal

Cornell Aeronautical Laboratory, Inc.

April 1970

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FOREWORD

The research reported here was sponsored by the Arnold Engineering Development Center, Air Force Systems Command, Arnold Air Force Station, Tennessee, under Program Element 61102F, Project 8951, Task 06. Air Force program No. 61102F is entitled Research and Experimental Study of Surface Catalysis in Nonequilibrium Flows which is devoted to developing a probe with a discontinuous catalytic surface as a diagnostic device for high temperature wind tunnels.

The research was performed in the Aerodynamic Research Department of the Cornell Aeronautical Laboratory, Inc. at Buffalo, New York, under Contract No. F40600-69-C-0005 during the period September 1967 to September 1969 under the technical cognizance of Lt. Vincent Rocco, AELR. This particular theoretical study was initiated to provide a basis for determining the onset of gas-phase reactions in the boundary layer on the probe. Hence, the theory provides a basis for defining the range of applicability for a catalytic probe. This report is also identified as CAL Report No. AF-2753-A-1 and was released for publication on 14 November 1969.

This technical report has been reviewed and is approved.

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ABSTRACT

An existing theory for predicting the onset of dissociation in a laminar boundary layer is generalized and extended to account for dissociation in the boundary layer and gas-phase recombination near a cold wall. The existing theory shows that dissociation first occurs in a thin layer centered on the maximum temperature in the boundary layer. The present extension shows that for cold walls, there will be a dense layer near the wall with relatively long particle residence times to promote recombination. Hence, at least initially, the reacting boundary layer on a cold wall is characterized by a dissociation layer embedded in the boundary layer and a recombination layer near the wall. The theory is derived without specifying the gas model, and numerical results are given which are based upon a realistic gas model. It is shown that the effects of dissociation and recombination tend to compete, and under certain conditions the effects at the wall tend to cancel.

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LIST OF SYMBOLS

C_R, C_D	Eq. (18a) and (18b)
C_p	specific heat at constant pressure
f	$\int_0^1 u/u_e d\eta$
G	Eq. 19
h_s	species heat of formation
H	total enthalpy
k_f, k_r	forward and reverse reaction rates (see Table I)
K_e	the equilibrium constant
m	molecular weight
M	Mach number
q	convective heat transfer rate
S	auxiliary variable
t	time and dummy variable of integration
T	temperature
T_D	characteristic dissociation temperature
u	velocity
U	auxiliary variable
v	$\int_0^1 \frac{f''(t)}{S^2(t)} dt$
w	species mass rate of formation per unit volume per unit time
W	auxiliary variable
x, y	chordwise and normal coordinates
α	species mass fraction
γ	specific heat ratio
ζ	$\xi/\rho_w \mu_w u_e^2 \tau$
η	Eq. 1
θ	$C_p T/u_e^2$
λ	α/α_e
μ	viscosity
ξ	Eq. 1
ρ	density
τ_D, τ_R	characteristic times for dissociation and recombination

Subscripts

e	edge of boundary layer
f	forward
i, j	species i or j
o	frozen conditions
r	reverse
w	wall conditions
η, ξ, ζ	$\frac{\partial}{\partial \eta}, \frac{\partial}{\partial \xi}, \frac{\partial}{\partial \zeta}$
∞	condition at infinity
$*$	Eq. 27

I. INTRODUCTION

The occurrence and implications of thermochemical nonequilibrium in hypersonic flowfields has been widely recognized, and there is a large body of theoretical and experimental literature addressed to certain aspects of the problem. The major emphasis has been on chemical relaxation in the inviscid flowfield, and theoretical methods are available for idealized gas flows¹⁻³, for comprehensive models of reacting air flows⁴⁻⁷, and for scaling the initial relaxation processes^{8,9}. The importance of thermochemical relaxation in viscous flowfields has been acknowledged, but the body of literature dealing with this aspect is relatively sparse. Most of the literature on this topic reports machine solutions for specific isolated problems^{10,11}, and while these offer important information on reacting viscous layers, it is difficult to scale these results to other problems of practical interest.

One problem not treated fully in the literature is chemical relaxation in the boundary layer of a slender body. This problem is of potential importance in hypersonic wind tunnel experiments with a cold model in which the ambient flow is not equilibrated, and consequently contains a significant concentration of atomic species. Chemical relaxation could occur in two ways. As noted by Rae¹², viscous heating will produce temperatures in the boundary layer that exceed those in the inviscid flowfield. Consequently, dissociation would occur initially in a thin layer centered on the maximum temperature in the boundary layer. Rae's analysis can be applied to predict the onset and consequences of this relaxation. For a cold-wall model, there is a second and competing recombination effect which could take place. In the vicinity of the wall, the low gas temperature coupled with the low gas velocities could produce the high densities and long particle residence times required for recombination. Consequently, recombination could occur initially in a thin layer near the wall. These two relaxation processes could begin sequentially or simultaneously, depending on the ambient conditions, thereby altering the energy transport to the surface. These effects could be important in routine experiments to determine heat transfer rates for particular configurations. It would be of crucial importance in applications of the slender catalytic probe being developed in this contract.

The purpose of this report is to present an approximate theoretical method for predicting the onset of chemical relaxation processes in the laminar boundary layer on a two-dimensional flat plate or wedge. The theory is an extension of Rae's theory to include recombination near the wall and a generalization in the sense that Lighthill's idealized gas model is not used.

Rae's analysis is paralleled in the next section to arrive at the most general theoretical result without specifying a gas model. Following that, consideration is given to the most important recombination and dissociation reactions in high temperature air to arrive at numerical results.

II. THEORY

The theoretical development begins by writing down the boundary layer equations for a reacting gas and transforming these using the Levy-Lees coordinates. The boundary layer equations are available in any standard text^{13, 14} and are not repeated here. It is assumed that both the Prandtl number and the Schmidt number are unity and that the viscosity of the gas varies linearly with temperature. Moreover, it is assumed that variations in the specific heat through the boundary layer are negligibly small, and that the difference in the enthalpy of the atomic and molecular species is small in comparison with the heat of formation. These approximations are consistent with the spirit of the analysis; to identify the initial relaxation processes.

Using the transformation

$$\xi = \int_0^x \rho_w \mu_w u_e dx \quad \eta = \frac{u_e}{\sqrt{2\xi}} \int_0^y \rho dy \quad (1)$$

the boundary layer equations become

$$f_{\eta\eta} + f f_{\eta\eta} = 2\xi (f_\eta f_{\xi\xi} - f_\xi f_{\eta\eta}) \quad (2)$$

$$T_{\eta\eta} + f T_{\eta\eta} = \frac{2\xi h_o}{\rho_w \mu_w C_p u_e^2} \frac{\omega_i}{\rho} - \frac{u_e^2}{C_p} f_{\eta\eta}^2 + 2\xi (f_\eta T_\xi - f_\xi T_\eta) \quad (3)$$

$$\alpha_{\eta\eta} + f \alpha_{\eta\eta} + \frac{2\xi}{\rho_w \mu_w u_e^2} \frac{\omega_i}{\rho} = 2\xi (f_\eta \alpha_\xi - f_\xi \alpha_\eta) \quad (4)$$

If it is assumed that boundary layer displacement effects are negligible, then terms involving f_ξ can be neglected. In this case, Eq. (2) reduces to the Blasius equation, and the solution can be taken from any standard text, for example Ref. 15.* The energy and species equations are made nondimensional by dividing by a reference temperature, u_e^2/C_p , and the atom mass fraction at the edge of the boundary layer, α_e . An additional transformation is made,

$$\zeta = \frac{\xi}{\rho_w \mu_w u_e^2 \tau}$$

*It should be noted that Ref. 15 provides a solution for the equation,

$2f_{\eta\eta} + f f_\eta = 0$, and if these results are used, the appropriate numerical transformation must be made.

where τ is a characteristic time to be determined with the chemical rate equations. With these manipulations, the energy and the species equations become

$$\theta_{\eta\eta} + f \theta_{\eta} - 2 \zeta f_{\eta} \theta_{\zeta} + f_{\eta\eta}^2 = -2 \frac{\alpha_e h_p}{u_e^2} \frac{\omega_i \tau}{\rho \alpha_e} \quad (5)$$

$$\lambda_{\eta\eta} + f \lambda_{\eta} - 2 \zeta f_{\eta} \lambda_{\zeta} = 2 \zeta \frac{\omega_i \tau}{\rho \alpha_e} \quad (6)$$

The method used by Rae to obtain solution to Eq. (5) and (6) is to assume that the dimensionless temperature and atom fraction can be expressed in a series form

$$\theta(\eta, \zeta) = \theta_0(\eta) + \zeta \theta_1(\eta) + \dots$$

$$\lambda(\eta, \zeta) = \lambda_0(\eta) + \zeta \lambda_1(\eta) + \dots$$

and to substitute these in Eq. (5) and (6) to obtain a system of ordinary differential equations. Using just the first two terms in each series expansion, the resulting system of equations is

$$\theta_{0\eta\eta} + f \theta_{0\eta} + f_{\eta\eta}^2 = 0 \quad (7)$$

$$\lambda_{0\eta\eta} + f \lambda_{0\eta} = 0 \quad (8)$$

with the boundary conditions,

$$\eta \rightarrow 0 : \theta_0 \rightarrow \theta_w, \lambda_0 \rightarrow 1.0$$

$$\eta \rightarrow \infty : \theta_0 \rightarrow \theta_e, \lambda_0 \rightarrow 1.0$$

$$\theta_{1\eta\eta} + f \theta_{1\eta} - 2 f_{\eta} \theta_1 = 2 \frac{\alpha_e h_p}{u_e^2} \left(\frac{\omega_i \tau}{\rho \alpha_e} \right)_0 \quad (9)$$

$$\lambda_{1\eta\eta} + f \lambda_{1\eta} - 2 f_{\eta} \lambda_1 = -2 \left(\frac{\omega_i \tau}{\rho \alpha_e} \right)_0 \quad (10)$$

with the boundary conditions

$$\begin{aligned}\eta \rightarrow 0: \theta_1 &\rightarrow 0, \lambda_{1\eta} \rightarrow 0 \\ \eta \rightarrow \infty: \theta_1 &\rightarrow 0, \lambda_1 \rightarrow 0\end{aligned}$$

Equations (7) and (8) are the governing relations for frozen flow and their solutions are

$$\theta_o = \theta_w (1 - f_h) + \frac{1}{2} f_h (1 - f_h + 2 \theta_e) \quad (11)$$

$$\lambda_o = 1.0 \quad (12)$$

Equations (9) and (10) govern the initial departures from the frozen flow, and because of the series form assumed for the solution, the production term, $\frac{\omega_i \tau}{\rho \alpha_e}$, is evaluated at the frozen conditions. This single feature makes an analytic solution possible. Continuing to follow Rae's analysis, the method of solution is to make the standard substitution,

$$\theta_1 = S(\eta) U(\eta) \quad \lambda_1 = S(\eta) W(\eta)$$

to arrive at the following system of equations.

$$S_{\eta\eta} + f S_\eta - 2 f_h S = 0 \quad (13)$$

$$U_{\eta\eta} + 2 U_\eta \frac{S_\eta}{S} + f U_\eta = \frac{2}{S} \frac{\alpha_e h_p}{u_e^2} \left(\frac{\omega_i \tau}{\rho \alpha_e} \right)_o \quad (14)$$

$$W_{\eta\eta} + 2 W_\eta \frac{S_\eta}{S} + f W_\eta = -\frac{2}{S} \left(\frac{\omega_i \tau}{\rho \alpha_e} \right)_o \quad (15)$$

with the boundary conditions

$$\begin{aligned}\eta = 0: S(o) &= 1, S_\eta(o) = 0, U(o) = 0, W_\eta(o) = 0 \\ \eta \rightarrow \infty: U &= W = 0\end{aligned}$$

The boundary conditions on $S(\eta)$ are arbitrary and were selected by Rae for convenience. Those on $W(\eta)$ and $U(\eta)$ are chosen to be consistent with the boundary conditions for Eq. (9) and (10). Rae has solved Eq. (13) numerically and tabulates that solution in Ref. 12 along with the associated

function,

$$v(\eta) = \int_0^\eta \frac{f''(t)}{S^2(t)} dt$$

where the prime notation indicates differentiation with respect to the dummy variable, t . They are reproduced here in Table I for convenience. The solutions to Eq. (14) and (15) are obtained in a conventional manner and are

$$U(\eta) = - \frac{\alpha_e h_p}{u_e^2} \left\{ \frac{v(\eta)}{v(\infty)} C - v(\eta) G(\eta) + \int_0^\eta 2 \frac{v(t) S(t)}{f''(t)} \left[\frac{\omega_i \tau}{\rho \alpha_e} \right]_0 dt \right\} \quad (16)$$

$$W(\eta) = C - v(\eta) G(\eta) + \int_0^\eta 2 \frac{v(t) S(t)}{f''(t)} \left[\frac{\omega_i \tau}{\rho \alpha_e} \right]_0 dt \quad (17)$$

$$C = 2 v(\infty) \int_0^\infty \left[1 - \frac{v(t)}{v(\infty)} \right] \frac{S(t)}{f''(t)} \left[\frac{\omega_i \tau}{\rho \alpha_e} \right]_0 dt \quad (18)$$

$$G(\eta) = 2 \int_0^\eta \frac{S(t)}{f''(t)} \left[\frac{\omega_i \tau}{\rho \alpha_e} \right]_0 dt \quad (19)$$

$$\theta = \theta_0 + \zeta S(\eta) U(\eta) \quad (20)$$

$$\lambda = 1 + \zeta S(\eta) W(\eta) \quad (21)$$

The above relations, combined with Eq. (11) and (12) provide a complete solution to the problem.

Two quantities of interest are the atom concentration at a noncatalytic wall and the convective heat transfer to a noncatalytic wall. Noting that for a flat plate or wedge, $\zeta = \frac{\chi}{u_e \tau}$, the relations for the atom fraction and heat transfer are

$$\frac{\alpha_w}{\alpha_e} = 1 + C \frac{\chi}{u_e \tau} \quad (22)$$

$$\frac{q}{q_0} = 1 - \frac{\alpha_e h_p}{u_e^2} \frac{\chi}{u_e \tau} \frac{C/v(\infty)}{1/2 + \theta_e - \theta_w} \quad (23)$$

where q_c denotes the convective heat transfer when there are no chemical reactions present. It can be seen that the solution depends upon evaluating the constant, C , which in turn requires integrating the production term across the boundary layer. A similar integration involving the production term is also required to obtain the species and energy profiles.

A general rate equation for dissociation and recombination is

$$\frac{d\alpha_A}{dt} = \frac{w_i}{\rho} = \left[\frac{\rho \alpha_m}{m_m} - \frac{1}{K_c} \left(\frac{\rho \alpha_A}{m_A} \right)^2 \right] \sum_i \frac{m_A}{m_i} \alpha_i k_{f,i} \quad (24)$$

where the subscripts, m and A , refer to the molecular and atomic state of the reacting species, and the subscript, i , refers to the inert species that enter as collision partners. The general relations for the equilibrium constants and the forward and reverse reaction rates are

$$K_c = C_c T^{-n_c} e^{-T_D/T} \quad k_{f,i} = C_{f,i} T^{-n_{f,i}} e^{-T_D/T} \quad k_{r,i} = \frac{k_{f,i}}{K_c} = C_{r,i} T^{-n_{r,i}}$$

and where T_D is the characteristic temperature for dissociation.

Restricting attention to the case $T_w < T_e$, it can be seen that integration of Eq. (24) will produce two parts. In the vicinity of the wall, the temperature will be low relative to the rest of the boundary layer and the dissociation component of Eq. (24) will be exponentially small in comparison with the recombination component. Since the present analysis is concerned only with the initial relaxation process, it can be argued further that the recombination term will be important only in the coldest part of the boundary layer; a narrow region immediately at the wall. The same arguments apply to the dissociation component, as pointed out by Rae. Initially at least, dissociation will be important only in a narrow region centered on the maximum temperature in the boundary layer, and the recombination term can be neglected in effecting this part of the integration. As a consequence, Eq. (18) takes on the form, $C = C_R + C_D$, where C_R and C_D are the recombination and the dissociation components of the integration and are given by

$$C_R = -4 v(\infty) \tau \int_0^{\eta_1} \left[1 - \frac{v(t)}{v(\infty)} \right] \frac{S(t)}{f'(t)} \left(\frac{\rho \alpha_A}{m_A} \right)^2 \sum_i \frac{m_A}{m_i} \frac{\alpha_i}{\alpha_A} k_{r,i} dt \quad (18a)$$

$$C_D = 4 v(\infty) \tau \int_{\eta_1}^{\infty} \left[1 - \frac{v(t)}{v(\infty)} \right] \frac{S(t)}{f''(t)} \frac{\rho \alpha_m}{m_m} \sum_i \frac{m_A}{m_i} \frac{\alpha_i}{\alpha_A} k_{f,i} dt \quad (18b)$$

The evaluation of Eq. (18) can proceed in two separate steps, first considering the recombination reaction near the wall and then the dissociation reaction in the boundary layer.

WALL RECOMBINATION

The method used to evaluate Eq. (18a) is based on the fact that attention is restricted to a thin region near the wall. In this region, the following approximations are valid.

$$f'(\eta) \approx f''(0) \eta, \quad \theta_e(\eta) \approx \theta_w + [1 + 2\theta_e - 2\theta_w] f''(0) \eta, \quad v(\eta) \approx f''(0) \eta, \quad S = 1.0$$

Using these and the general expression for the reverse reaction rate, Eq. (18) becomes after some algebraic manipulation,

$$C_R = - \frac{4\tau v(\infty)}{[f''(0)]^2} \left[\frac{\rho_e \alpha_{R_e}}{m_R} \right]^2 \left[\frac{T_e/T_w}{\frac{T_e}{T_e} - \frac{T_w}{T_e}} \right] \sum \frac{m_R}{m_i} \frac{\alpha_i}{\alpha_R} \frac{k_{r,i}(T_w)}{(1 + n_{r,i})} \quad (25)$$

where $C_p T_o \equiv H \cdot \sum \alpha_e h_p$ and $k_{r,i}(T_w)$ indicates the reverse reaction is evaluated at the wall temperature. The above expression neglects $(\theta_e)^{-(n_{r,i}+1)}$ in comparison with $(\theta_w)^{-(n_{r,i}+1)}$, which is consistent with the cold wall approximation introduced earlier.

DISSOCIATION REACTION

A comprehensive discussion of the technique for integrating Eq. (18) for the dissociation reaction is given in Ref. 12. Briefly, it is based upon the previous observation that the reaction is confined to a thin region centered on the maximum temperature in the boundary layer. This makes it possible to approximate the integral using the Laplace method^{12, 16}. This method states that if in the integral

$$\int_a^b V(t) e^{-B\omega(t)} dt$$

$V(t)$ is bounded in the interval from a to b , and if there exists a point in this interval where $\omega'(t_s) = 0$, $\omega''(t_s) > 0$, then for $B > 0$, the integral

can be approximated by

$$\sqrt{\frac{2\pi}{B\omega''(t_*)}} V(t_*) e^{-B\omega(t_*)}$$

Applying this to Eq. (18 b), and after some algebraic manipulation, the relation for the dissociation component of the constant becomes

$$C_D = 4A v(\infty) \tau \frac{\rho_e \alpha_m}{m_m} \sqrt{2\pi \theta_e \frac{T_e}{T_D}} \sum_i \frac{m_A}{m_i} \frac{\alpha_i}{\alpha_A} k_{f,i}(T_*) \quad (26)$$

where the notation, $k_{f,i}(T_*)$ indicates the forward reaction rate is evaluated at the temperature, T_* ,

$$\theta_* = \theta_w + \left(\frac{1}{2} + \theta_e - \theta_w \right)^2 \quad (27)$$

As indicated in Ref. 12, the above method applies only for $\theta_e - \theta_w < \frac{1}{2}$

The constant A in Eq. (26) is defined as

$$A = \frac{S(\eta_*)}{[f''(\eta_*)]^2} \left[1 - \frac{v(\eta_*)}{v(\infty)} \right]$$

It can be taken to be unity with errors of less than 15% for $0.18 < (\theta_e - \theta_w) < 0.46$ which covers much of the range of interest.

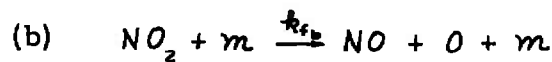
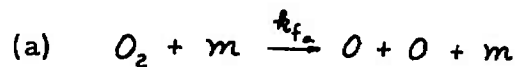
The parameter governing the species concentrations at the wall and the convective heat transfer to the wall is $\frac{\chi}{u_e \tau} \left[\frac{C_D + C_R}{v(\infty)} \right]$. This follows from Eq. (25) and (26).

$$\begin{aligned} \frac{\chi}{u_e \tau} \frac{C}{v(\infty)} = \frac{\chi}{u_e} \left\{ 4A \frac{\rho_e \alpha_m}{m_m} \sqrt{2\pi \theta_e \frac{T_e}{T_D}} \sum_i \frac{m_A}{m_i} \frac{\alpha_i}{\alpha_A} k_{f,i}(T_*) \right. \\ \left. - 18.12 \left[\frac{\rho_e \alpha_A}{m_A} \right]^2 \left[\frac{T_e/T_w}{T_e/T_e - T_w/T_e} \right] \sum_j \frac{m_A}{m_j} \frac{\alpha_j}{\alpha_A} \frac{k_{r,j}(T_w)}{1 + n_{r,j}} \right\} \quad (28) \end{aligned}$$

The two terms in the braces can be identified respectively as $\frac{1}{\tau_D}$ and $\frac{1}{\tau_R}$ where τ is a characteristic relaxation time and the subscripts D and R refer to dissociation and recombination. The competing effects of gas-phase dissociation and recombination are apparent. It is possible, at least in principle, to have significant dissociation and recombination occurring within the boundary layer without any observable effect at the surface. This would correspond to the two terms within the braces being equal and non-zero.

GAS MODEL

A simplified gas model for air will be used to assess the importance of gas-phase dissociation and recombination in the boundary layer of a flat-plate. The primary interest here is on experiments in a hypersonic wind tunnel which is characterized by a nonequilibrium flow in the nozzle expansion. Consequently, the ambient flow would be a mixture of atomic and molecular oxygen, nitric oxide, and molecular nitrogen. Atomic nitrogen will not be considered here because it is energetically important only at very high temperatures. The two reactions considered are



The first is the dominant reaction for producing oxygen atoms, but the second is an important reaction for oxygen atom consumption at low temperatures. Rigorously, a third reaction should be included, $NO + O_2 \xrightarrow{k_f} NO_2 + O$, because the reverse reaction can also be important at low temperatures. However, only the species present in the ambient flow enter into the results, and the only source of NO_2 is the products of the (b) reaction. Hence the above reaction must be neglected in the present analysis. The rate equation for the two reactions listed is

$$\begin{aligned} \frac{d\alpha_o}{dt} = & \frac{\rho \alpha_{o_2}}{m_{o_2}} \sum_i 2 k_{f,a,i} \frac{m_o}{m_{m,i}} \alpha_{m,i} - \left(\frac{\rho \alpha_o}{m_o} \right)^2 \sum_j 2 k_{r,a,j} \frac{m_o}{m_{m,j}} \alpha_{m,j} \\ & - \frac{\rho^2 \alpha_o \alpha_{no}}{m_o m_{no}} \frac{m_o}{m_m} \alpha_m k_{r,b} \end{aligned}$$

where the subscripts, O , O_2 , and NO refer to that species, and the subscript m refers to the inert third body.

The characteristic relaxation time identified in Eq. (28) can be cast into the following form.

$$\frac{1}{\tau_D} = A \frac{P_0 \alpha_{01}}{m_{01}} \sqrt{\frac{\pi T_0/T_D}{\frac{T-1}{2} M_e^2 (1 + \frac{T-1}{2} M_e^2)}} \sum_i \frac{m_0}{m_i} \frac{\alpha_i}{\alpha_0} k_{f,i}(T_*) \quad (29 a)$$

$$\frac{1}{\tau_R} = \frac{18.12 \left(\frac{P_0 \alpha_0}{m_0}\right)^2 \sum_j \frac{m_0}{m_j} \frac{\alpha_j}{\alpha_0} \frac{k_{r,j}(T_w)}{(n_{r,j} + 1)}}{\frac{T_w}{T_0} \left(1 - \frac{T_w}{T_0}\right) \left[1 + \frac{T-1}{2} M_e^2\right]^2} \quad (29 b)$$

The reaction rates were evaluated using the data given in Refs. 17-20 and summarized in Table II. The resulting numerical expressions for use in Eq. (29) above are

$$\sum_i \frac{m_0}{m_i} \frac{\alpha_i}{\alpha_0} k_{f,i}(T_*) = 1.808 \times 10^{14} \left(\frac{T_D}{T_*}\right)^2 e^{-T_0/T_*} \left[1 + .362 \frac{\alpha_{01}}{\alpha_0} \sqrt{\frac{T_*}{T_D}} + .104 \frac{\alpha_{02}}{\alpha_0} \sqrt{\frac{T_*}{T_D}}\right]$$

$$\sum_j \frac{m_0}{m_j} \frac{\alpha_j}{\alpha_0} \frac{k_{r,j}(T_w)}{(1 + n_{r,j})} = 4.10 \times 10^{16} \left(\frac{T_r}{T_w}\right)^{3/2} \left[1 + .135 \frac{\alpha_{01}}{\alpha_0} \left(\frac{T_r}{T_w}\right) + .0322 \frac{\alpha_{01}}{\alpha_0} \sqrt{\frac{T_w}{T_r}}\right. \\ \left. + .0093 \frac{\alpha_{02}}{\alpha_0} \sqrt{\frac{T_w}{T_r}}\right]$$

where $T_R = 300^\circ\text{K}$ is an arbitrary reference temperature. The characteristic relaxation times have been numerically evaluated assuming the bracketed terms in the above reaction rates are unity. These are plotted in Figs. 1 and 2. It should be noted the relaxation time in Figs. 1 and 2 is overestimated because of the above assumption. For typical conditions, the error amounts to 10% to 25% and it can be corrected, if desired, by multiplying the ordinate by the appropriate value of the bracketed quantity.

It will be noted that Fig. 1 was evaluated for $T_w/T_0 = 0$. The wall temperature ratio enters into the determination for the temperature governing the dissociation, T_* , and it is a relatively weak function of the wall temperature. The wall temperature ratio was taken to be zero for this reason and because present interests are primarily on the cold wall case. It will be noted in Fig. 1 that the characteristic time for dissociation goes through a minimum. This behavior arises because of the pre-exponential temperature dependence in the rate equation. It is of academic interest only because it corresponds to a stagnation temperature of $T_0 \approx 10^5^\circ\text{K}$.

The characteristic time for recombination, Fig. 2, is a simple function of the wall temperature ratio and the Mach number at the edge of the boundary layer. It was evaluated for the case of $T_w = 300^\circ\text{K}$, but the results can be corrected to any other wall temperature by dividing the ordinate by $(T_w)^{3/2}$.

It was noted earlier that it would be possible to have significant dissociation and recombination occurring in the boundary layer, but because the effects tend to compete, there might be no net effect at the wall. The following conditions illustrate this effect. For $\rho_e/\rho_{sl} \approx 10^{-2}$, $\alpha_o = \alpha_{o_1} = 0.1$ and $M_e \approx 4$, the characteristic times for dissociation and recombination are equal for $T_p/T_o \approx 4$, and are $\frac{1}{\tau_a} = \frac{1}{\tau_p} \approx 1.5 \times 10^3/\text{sec.}$. Using a typical length of one foot and a typical velocity of 10^4 ft/sec, Eq. (22) shows that each effect could alter the atom fraction at the wall by about 10%. However, because the characteristic times are equal, the two effects just cancel and leave the wall concentration unaltered.

III. CONCLUDING REMARKS

An existing theory for predicting the onset of dissociation in a laminar flat plate boundary layer¹² has been extended to account for gas-phase recombination near the wall. The basis for this extension is the observation that near a cold wall, the combination of the low gas temperature and low velocity could produce the high density and relatively long particle residence time necessary for gas-phase recombination. In affecting this extension, Rae's theory¹² is generalized to allow for a more realistic gas model of air. The extension to account for recombination centers on approximating the boundary layer profiles near the wall in order to integrate the species production term in the region where recombination is important.

Numerical results were obtained to illustrate the effects of the gas-phase reactions. These results show that dissociation can occur in the boundary layer while gas-phase recombination is occurring near the wall. These effects tend to compete, and under certain conditions, significant dissociation and recombination can occur with no net change in atom concentration or heat transfer to the wall.

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TABLE I
FUNCTIONS IN THE BOUNDARY LAYER SOLUTION
(FROM REF. 12)

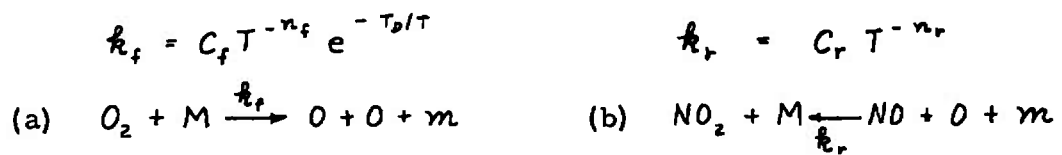
η	$S(\eta)$	$v(\eta)$	$f''(\eta)$
0.	1.000000	0.	0.46960
0.1	1.000157	0.04696	0.46956
0.2	1.001252	0.09385	0.46931
0.3	1.004227	0.14051	0.46861
0.4	1.010021	0.18667	0.46725
0.5	1.019576	0.23198	0.46503
0.6	1.033840	0.27599	0.46173
0.7	1.053762	0.31822	0.45718
0.8	1.080302	0.35817	0.45119
0.9	1.114429	0.39539	0.44303
1.0	1.157121	0.42950	0.43438
1.1	1.209372	0.46021	0.42337
1.2	1.272191	0.48736	0.41057
1.3	1.346600	0.51096	0.39599
1.4	1.433639	0.53110	0.37969
1.5	1.534358	0.54799	0.36181
1.6	1.649818	0.56194	0.34249
1.7	1.781086	0.57327	0.32195
1.8	1.929224	0.58236	0.30045
1.9	2.095288	0.58953	0.27825
2.0	2.280312	0.59514	0.25567
2.1	2.485301	0.59946	0.23301
2.2	2.711216	0.60276	0.21058
2.3	2.958970	0.60526	0.18867
2.4	3.229407	0.60712	0.16756
2.5	3.523301	0.60851	0.14748
2.6	3.841343	0.60953	0.12861
2.7	4.184138	0.61028	0.11112
2.8	4.552198	0.61082	0.09511
2.9	4.945944	0.61121	0.08064
3.0	5.365708	0.61149	0.06771
3.1	5.811736	0.61169	0.05631
3.2	6.284194	0.61183	0.04637
3.3	6.783178	0.61193	0.03782
3.4	7.308724	0.61200	0.03054
3.5	7.860816	0.61205	0.02442
3.6	8.439400	0.61208	0.01933
3.7	9.044389	0.61211	0.01515
3.8	9.675679	0.61212	0.01176
3.9	10.333152	0.61213	0.00904
4.0	11.016685	0.61214	0.00687
4.1	11.726157	0.61214	0.00518
4.2	12.461451	0.61215	0.00386
4.3	13.222460	0.61215	0.00285
4.4	14.009087	0.61215	0.00208
4.5	14.821246	0.61215	0.00151
4.6	15.658863	0.61215	0.00108
4.7	16.521875	0.61215	0.00077
4.8	17.410231	0.61215	0.00054
4.9	18.323887	0.61215	0.00037
5.0	19.262809	0.61215	0.00026
5.1	20.226971	0.61215	0.00018
5.2	21.216352	0.61215	0.00012
5.3	22.230935	0.61215	0.00008
5.4	23.270708	0.61215	0.00005
5.5	24.335662	0.61215	0.00003
5.6	25.425791	0.61215	0.00002
5.7	26.541089	0.61215	...

TABLE II

RATE CONSTANTS FOR THE GAS MODEL OF AIR

$$k_f = C_f T^{-n_f} e^{-T_0/T}$$

$$k_r = C_r T^{-n_r}$$



Reaction	M	C_f	n_f	C_r	n_r	Ref.
a	O	6.4×10^{23}	2.0	5.3×10^{20}	3/2	17
	O ₂	1.9×10^{21}	3/2	1.6×10^{18}	1.0	18
	N ₂	4.8×10^{20}	3/2	4×10^{17}	1.0	19
b	All			5.6×10^{22}	5/2	20

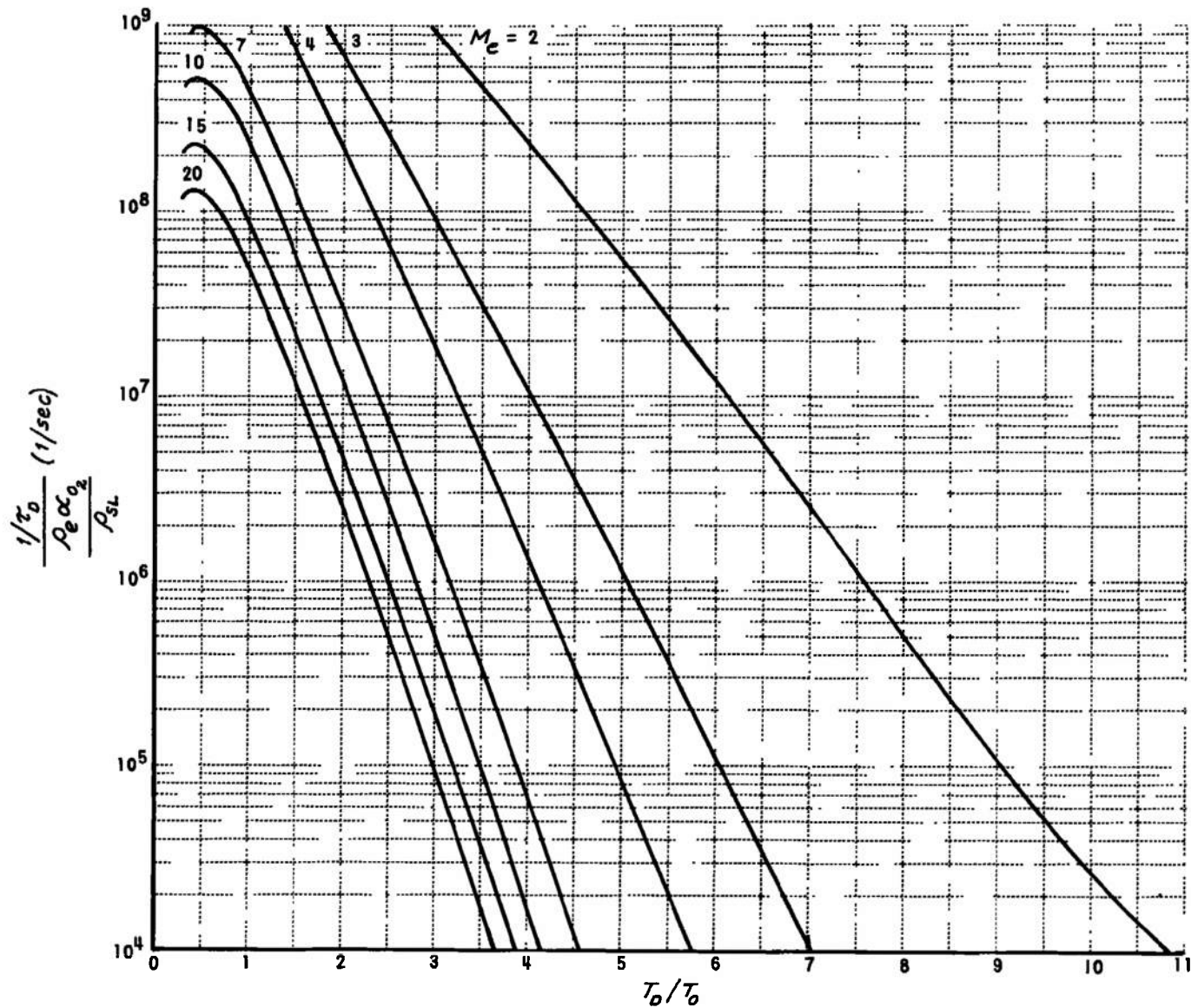


Figure 1 THE CHARACTERISTIC RELAXATION TIME FOR OXYGEN DISSOCIATION IN A LAMINAR BOUNDARY LAYER

$$\gamma = 1.4 \quad T_w/T_o = 0$$

$$C_p T_o = H_e - \sum \alpha_i h_{o,i}$$

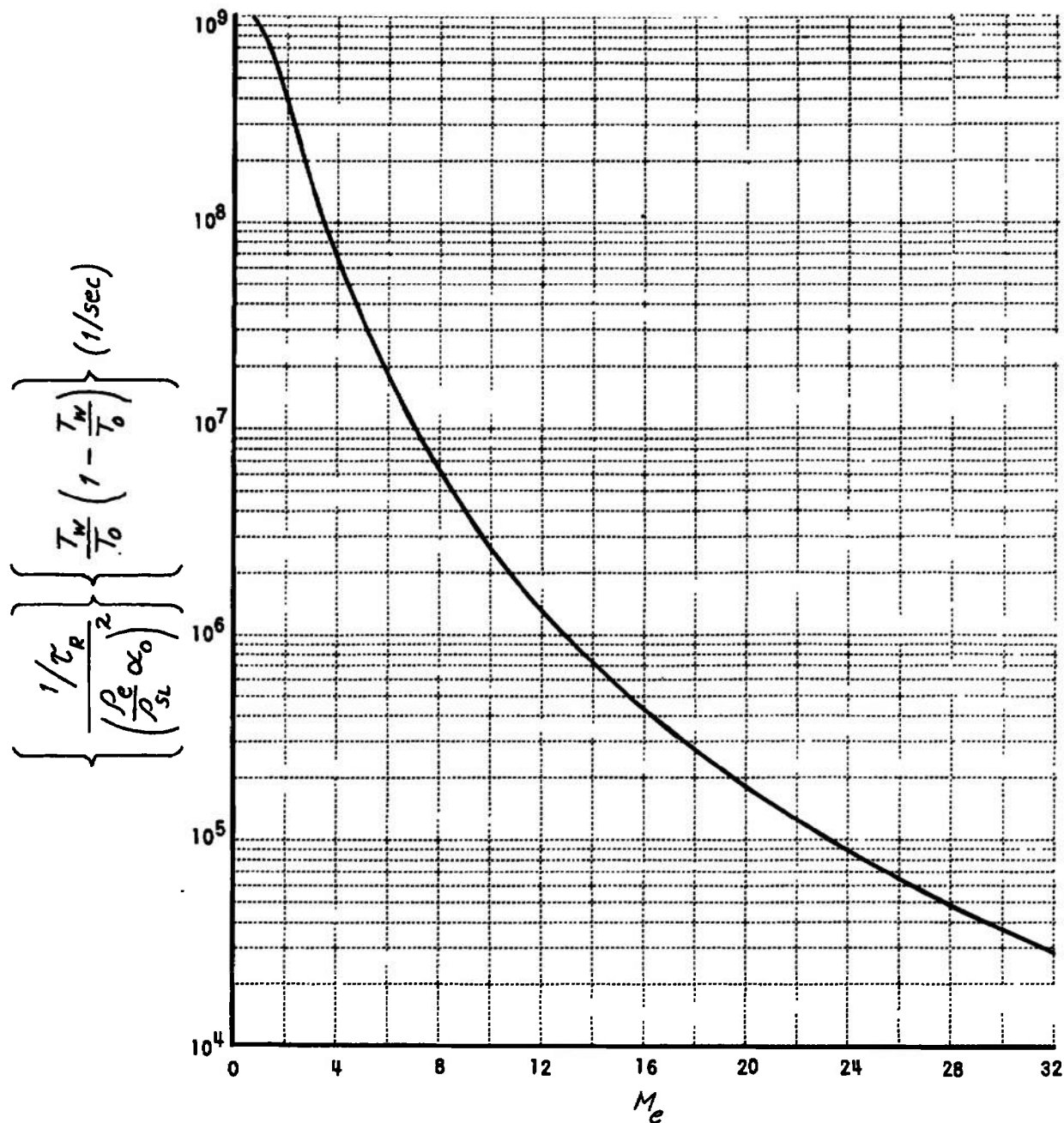


Figure 2 THE CHARACTERISTIC RELAXATION TIME FOR OXYGEN RECOMBINATION
IN A LAMINAR BOUNDARY LAYER

$$\gamma = 1.4 \quad T_w = 300^\circ\text{K}$$

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13. ABSTRACT

An existing theory for predicting the onset of dissociation in a laminar boundary layer is generalized and extended to account for dissociation in the boundary layer and gas-phase recombination near a cold wall. The existing theory shows that dissociation first occurs in a thin layer centered on the maximum temperature in the boundary layer. The present extension shows that for cold walls, there will be a dense layer near the wall with relatively long particle residence times to promote recombination. Hence, at least initially, the reacting boundary layer on a cold wall is characterized by a dissociation layer embedded in the boundary layer and a recombination layer near the wall. The theory is derived without specifying the gas model, and numerical results are given which are based upon a realistic gas model. It is shown that the effects of dissociation and recombination tend to compete, and under certain conditions the effects at the wall tend to cancel.

14.

KEY WORDS

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