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Scale Effects and Correlations in Nonequilibrium Convective Heat Transfer

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The effect of chemical nonequilibrium on the dependence of heat flux on physical scale is illustrated for the case of simultaneous gas-phase and surface-catalyzed-atom recombination. Altitude-velocity regimes in which one can expect appreciable chemical nonequilibrium effects on the heat flux and its scale dependence are displayed and combined with trajectory information for representative hypersonic vehicles. Approximate but rather general correlation equations are suggested for the nonequilibrium boundary-layer regime.

Nomenclature

c_p = specific heat of mixture

D_{12} = atom-molecular binary diffusion coefficient

G = $(\delta^2/D_{12})/\tau$, gas-phase recombination rate parameter

H = $r_D \cdot \Delta h_{chem,\ eq}/\Delta h_f$

h = altitude

k_R = termolecular, homogeneous atom recombination rate constant

k_w = first-order rate constant for heterogeneous atom recombination[8, 28]

Le_f = Lewis number $\equiv D_{12}/[\lambda_f/(\rho c_{p,f})]$

m = exponent in the power-law relation $q''\partial\delta^m$, Eq. (4)

n = total number density or $4 + d \ln\epsilon_w/d \ln T_w$

Nu = $q''/[\lambda_f(T_e - T_w)/\delta]$

p = local pressure

Pr_λ = Prandtl number for heat conduction = $(\mu/\rho)/[\lambda/(\rho c_p)]$

Pr_D = Prandtl number for diffusion = $(\mu/\rho)/D_{12}$

q'' = energy transfer rate per unit area of solid

r_D = recovery factor for chemical energy [Le_f for conductivity cell, $(Le_f)^{0.6}$ for stagnation point boundary layer]

R_B = nose radius of body

St_D = local Stanton number for atom transport

T = absolute temperature

u = component of gas velocity parallel to surface

V_∞ = velocity of vehicle with respect to undisturbed atmosphere

W = $k_w\delta/D_{12}$ = catalytic parameter

α = mass fraction of atoms

β = inviscid velocity gradient at nose

γ = recombination coefficient

δ = plate spacing or boundary-layer thickness

ϵ_w = total hemispheric emittance

λ = thermal conductivity of mixture

μ = dynamic viscosity of mixture

ν = kinematic viscosity of mixture; μ/ρ

ξ = $[G(1 + H)]^{1/2}$

ρ = mass density of mixture

σ = Stefan-Boltzmann radiation constant

τ = recombination relaxation time[25] in gas phase

ϕ = extent of recombination = $(\alpha_e - \alpha_w)/\alpha_e$ ($= \Delta h_{chem}/\Delta h_{chem,\ eq}$)

Δ = operator meaning change in (across conductivity cell or boundary layer)

$0(\ )$ = order of magnitude symbol

Subscripts

chem = chemical contribution

D = pertaining to atom-molecule diffusion

e = at hot boundary or outer edge of boundary layer

eq = pertaining to local thermochemical equilibrium

f = chemically "frozen," i.e. excluding thermochemical contribution

G = at constant G

W = at constant W

w = at wall (gas/solid interface)

λ = pertaining to molecular conduction

1 = atoms

2 = molecules

∞ = relative to upstream infinity (undisturbed atmosphere)

Introduction

CONCEPTUAL division of the general problem of non-equilibrium convective heat transfer into a transfer coefficient and generalized recovery enthalpy driving force fails to confine the dominant influence of fluid dynamic quantities to the coefficients themselves.[2] As one consequence, the Reynold's number dependence of the energy transport rate can exhibit very unusual behavior, particularly in the "mixed" regime in which strongly exothermic gas-phase and surface-atom recombination reactions are of comparable importance. With regard to the hypersonic re-entry problem, it is perhaps not surprising that little attention had been paid to realistic predictions in this intermediate regime.[3,4] Invariably, such computations are time consuming, difficult to correlate, and, regrettably, of uncertain accuracy. However, several approximate methods have recently been suggested for calculating and correlating nonequilibrium stagnation point heat fluxes in the presence of both gas-phase and surface-catalyzed-atom recombination.[1,2,5-7] In this paper, based on Ref. 1, the author wishes to 1) emphasize the scale effects peculiar to this regime, 2) present a conceptually useful overall picture of the location of these nonequilibrium domains for hypersonic entry bodies, and 3) discuss the implications of these analyses with respect to the development of relatively simple correlation formulas for design work.

When one was interested mainly in re-entry trajectories of the ballistic missile type or only in an upper bound to the convective heat transfer rate, the nonequilibrium atom recombination problem could, essentially, be ignored. But now this problem is certainly not academic, since a large class of manned re-entry bodies will experience peak heating rates in altitude-speed regions where nonequilibrium atom recombination will be the rule, not the exception (see below). Depending on the extent of recombination, available calculations indicate that the peak heat flux could differ by as much as a factor of five.[8-12] Moreover, a controllable trajectory that in some sense has been optimized[13] on the basis of a convective heating rate proportional to, say, $\rho_\infty^{0.5} R_B^{-1/2} V_\infty^{3.15}$ (cf., Ref. 14) may be significantly different from the true optimal trajectory taking due account of nonequilibrium phenomena. It has even been conjectured that if nonequilibrium atom recombination were included in certain design calculations there might exist optimum nose radii for (locally) minimum heat flux[9] somewhat in analogy to the more familiar case of combined convective and radiative heat transfer.[15] These considerations have motivated the present preliminary study of scale effects and possible correlation techniques for heat transfer in the presence of nonequilibrium gas-phase and surface atom recombination. In view of the current state of knowledge in these areas and the large number of parameters involved, it was considered that investigation of a simplified model for a binary gas would be more enlightening at this stage than a brute force attack on the multicomponent boundary-layer equations. For the purposes of the present discussion, the author has exploited a linearized conductivity cell ("film" theory) model of the actual process for which the complete nonequilibrium solution can be written down in closed form. It should be commented here that application of film theory to chemical engineering processes involving mass transfer and/or chemical reaction has a long and successful history.[16,17] Brokaw,[18,19] Hansen,[20] Brian and Reid,[21] and Spalding,[22] among others, recently have suggested this model† as a valuable tool for rapidly estimating the effects of dissociation-recombination on convective heat transfer in situations of aerodynamic interest. But, in carrying this through to the computational stage, a film theory/boundary-layer theory "dictionary" is, of course, required, i.e., a set of prescriptions for translating film theory parameters into their

corresponding observable quantities for convective heat transfer. This correspondence may, in fact, be established by matching film theory results with available boundary-layer solutions for several important limiting cases. In this paper, the general implications of the model will therefore be explored with regard to scale effects. Correlation techniques for hypersonic, high-altitude heat transfer and two conjectures also are examined in the light of this and previous boundary-layer investigations.

Linearized Conductivity Cell Model

The continuum model used here is essentially Broadwell's conductivity cell model[23] but generalized to include first-order atom recombination at a cold surface of arbitrary catalytic activity.[24]‡ Thus, first consider two parallel plates separated by a distance δ, enclosing a layer of partially dissociated diatomic gas through which there is no net mass transfer. The local atom concentration α is postulated to attain its equilibrium value at the hot-plate temperature, and the equilibrium concentration of atoms at the cold-plate temperature is considered negligible by comparison. In addition, thermal diffusion and other secondary transport mechanisms are assumed negligible. For this problem, three important nondimensional parameters emerge, written G, W, H. The parameters G and H are those appearing in Broadwell's study, the first of these being a gas-phase recombination parameter and interpretable as the ratio between the characteristic diffusion time δ^2/D_{12} across the film to the gas-phase recombination relaxation time τ. The parameter H is a measure of the maximum possible chemical enthalpy change $\Delta h_{chem, eq}$ across the cell as compared to the sensible (frozen) enthalpy change Δh_f corresponding to the imposed temperature difference $\Delta T = T_e - T_w$, but it includes, as a multiplier, a recovery factor r_D for chemical energy.§ The additional kinetic parameter $W \equiv k_w \delta/D_{12}$, introduced by finite rate atom recombination at the cold nonablating surface, is defined such that $W = 0$ corresponds to a completely noncatalytic surface (the case treated by Broadwell), and $W \to \infty$ corresponds to the diffusion controlled ("perfectly" catalytic, $k_w \to \infty$) case. Closed-form solutions to the coupled linear system of ordinary differential equations governing the steady-state temperature and concentration fields are obtained readily, from which the heat flux at the cold boundary is then deduced. In terms of the nondimensional parameters G, W, H, the explicit result for the nondimensional heat transfer coefficient Nu, based on the frozen thermal conductivity λ_f and the temperature difference across the film thickness δ, is found to be

$$Nu = 1 + \phi H \qquad (1)$$

where the extent of recombination $\phi(G, W; H)$ is explicitly given by

$$\phi = 1 - \{(1 + W) - (1 + H)^{-1}[1 - \xi \coth \xi]\}^{-1} \qquad (2)$$

with $\xi \equiv [G \cdot (1 + H)]^{1/2}$.

The behavior of the heat transfer coefficient Nu as a function of the two nondimensional chemical kinetic parameters G and W is shown in the isometric drawing, Fig. 1, for the particular choice $H = 9$. It is seen that Nu approaches the plateau value $1 + H$ for either large G or large W, since the extent of recombination is complete ($\phi \to 1$) in either case. On the other hand, for very small values of the chemical kinetic parameters G and W or for $H \to 0$, the heat transfer coefficient Nu approaches its "nonreactive" value, unity. As

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† An excellent critical review of previous nonequilibrium conductivity cell analyses may be found in Ref. 19.

‡ And equivalent, therefore, to a specialization of the recent results of Brokaw,[19] Brian and Reid,[21] and Chung.[25]

§ H plays the same role in this problem as the product of the Prandtl and Eckert numbers in the constant property compressible Couette flow problem.[26] It is the ratio of the maximum possible thermochemical contribution to the energy transport driving force to the thermal contribution.[2]
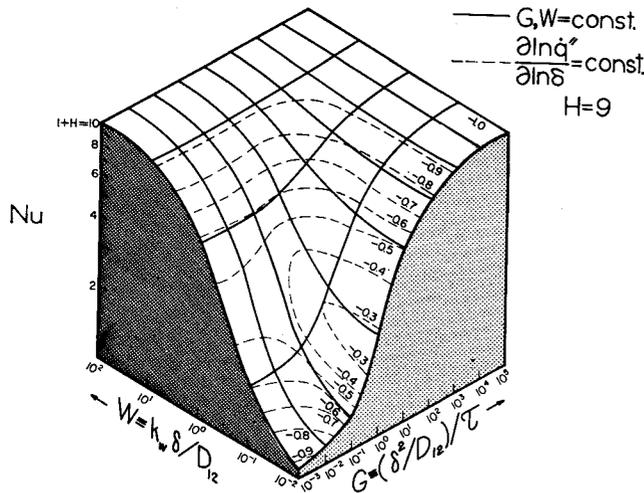
Fig. 1 Dependence of heat transfer coefficient Nu on the chemical kinetic parameters G and W; $H = 9$

one might expect from the existence of generalized recovery enthalpies,[2, 24] the conductivity cell model also exhibits the property

$$\frac{\dot{q}''}{(\lambda_f/c_{p,\,f})\cdot(\Delta h/\delta)\cdot[1 + (r_D - 1)(\Delta h_{\text{chem}}/\Delta h)]} = Nu_{\text{nonreact}} = 1 \tag{3}$$

However, this does not in itself constitute a solution, since Δh and Δh_{chem} depend on the chemical kinetic parameters G and W through the extent of recombination ϕ (see below).

Scale Effects Implied by the Model

Now consider the effect of a change in scale or, in the case of the conductivity cell model, a change in the film thickness δ, leaving all other quantities (and hence H) unchanged. From the definition of the heat transfer coefficient Nu, the energy transfer rate $\dot{q}''$ will change in accord with

$$m \equiv \frac{\partial \ln \dot{q}''}{\partial \ln \delta} = -1 + \frac{\partial nG}{\partial \ln \delta} \cdot \left(\frac{\partial \ln Nu}{\partial \ln G}\right)_W + \frac{\partial \ln W}{\partial \ln \delta} \cdot \left(\frac{\partial \ln Nu}{\partial \ln W}\right)_G \tag{4}$$

where the logarithmic derivative m will be recognized as the exponent appearing in a local power-law representation of the form $\dot{q}'' \propto \delta^m$.

In view of the film thickness dependencies $G \propto \delta^2$ and $W \propto \delta$, Eq. (4) becomes

$$m = -1 + 2(\partial \ln Nu/\partial \ln G)_W + (\partial \ln Nu/\partial \ln W)_G \tag{5}$$

where the geometric interpretation of the partial derivatives is clear with reference to Fig. 1 (which, indeed, has logarithmic scales). Superimposed on the $Nu(G, W; 9)$ surface are dashed contours of constant m which have been constructed with the aid of the following explicit relations, readily derived from Eqs. (1) and (2):

$$(\partial Nu/\partial W)_G = H \cdot (1 - \phi)^2 \tag{6}$$

$$(\partial Nu/\partial G)_W = \tfrac{1}{2}H \cdot (1 - \phi)^2 \cdot (1/\xi)(d/d\xi)(\xi \coth \xi) \tag{7}$$

The form of the $Nu(G, W; H)$ surface drawn in Fig. 1 as well as Eqs. (6) and (7) suggests that, as the value of the chemical enthalpy potential parameter H increases, the chemical contribution to m [cf., Eq. (4)] also increases and can become comparable to unity in absolute value.[||] Indeed, in the limit

$H \to \infty$, the component m approaches $-1 + (1 + W)^{-1}$ for all G. This indicates that, for small W but sufficiently large H, broad domains of m near zero will exist on the log G–log W plane. In the more familiar extreme $H \to 0$, the value of m clearly approaches -1 for all G, W, i.e., the heat flux becomes inversely proportional to the film thickness. Consequently, for any finite value of H of interest, it is instructive to consider the actual variation of m along a line of constant $W/G^{1/2}$ passing through some salient operating point (G, W). Under a contemplated change in the film thickness ($\delta \to \delta'$), both chemical kinetic parameters G and W would change but in such a way that the new operating point (G', W') would lie along this line. If δ' were smaller (say) than δ, then the heat flux at (G', W') indeed would be larger than at (G, W); however, the heat flux sensitivity to the contemplated change in δ can be very much less than proportional to δ^{-1} over an intermediate part of this line (increasing toward δ^{-1} only for sufficiently small, or large, δ). Thus the film theory model offers a convenient method of rapidly estimating the magnitude of the departures from $\dot{q}'' \propto \delta^{-1}$ which might be expected in practice. It also is seen that the physical existence of islands of $m > 0$ (for nonequilibrium convective heat transfer in the absence of radiation) is doubtful.

These results are translated most readily to the case of laminar boundary-layer flow at the forward stagnation region of blunt-nosed bodies.[#] Comparing the foregoing film theory results with the axisymmetric stagnation point results given in Ref. 28 for chemically frozen boundary-layer flow but arbitrary catalytic activity immediately leads to the identifications

$$\delta \to [0.763(\beta/\nu_e)^{1/2}(Pr_{\lambda,\,f})^{0.4}]^{-1} \tag{8}$$

$$r_D \to (Le_f)^{0.6} \tag{9}$$

$$W \to k_w \rho_w / [0.763(\beta \rho_e \mu_e)^{1/2}(Pr_D)^{-0.6}] \tag{10}$$

whereas the gas-phase recombination rate parameter G is clearly related to the corresponding parameter of Ref. 29, with the notable difference that G must, in general, include the degree of dissociation α_e at the outer edge of the film. Since the stagnation point inviscid velocity gradient β appearing in Eq. (8) depends inversely on the nose radius R_B, it is seen that $G \propto R_B$, whereas $W \propto R_B^{1/2}$. In this case, following the arguments of the preceding section, the dependence of heat flux on nose radius may differ markedly from the familiar $R_B^{-1/2}$ behavior predicted by laminar boundary-layer theory for the nonreactive (or $\phi = 1$) case. Thus, a reduction in nose radius by a factor of four, say, need not be associated with doubling the heat flux ($m = -1$) but could, *in principle*, be accompanied by no change in the heat flux ($m = 0$). It is therefore of interest to investigate the spectrum of exponents m which might be encountered in practice.

Nonequilibrium Regimes in Hypersonic Re-Entry[1]

One can make rapid estimates of the magnitudes of G, W, and H encountered in atmospheric re-entry by collectively drawing on the work of Refs. 8–10, 12, 29, and 30. A certain amount of perspective can be gained by first constructing contours (level lines) of constant G, W, and H on the altitude-velocity plane, on which typical re-entry trajectories then can be superimposed. In practice, it is useful to be able to "stack" these drawings in such a way that all level lines can be seen at once; however, this cannot be attempted here. Instead, individual sketches of the relevant contour maps are given in Figs. 2–4. Because of the methods of construction, these are expected to be quantitatively correct only in the range

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[||] The nature of the dependence of m on both the extent of recombination ϕ and the chemical enthalpy potential parameter H is perceived readily in the chemically frozen flow limit, $G \to 0$, for then m can be written as $m = -1 + (1 - \phi)\cdot[\phi H/(1 + \phi H)]$.

[#] A nonequilibrium Couette flow model of the type investigated by Broadwell,[23] Clarke,[27] and Chung[25] would be required for locations on the body at which viscous dissipation must be accounted for.

$10 \leqslant V_\infty \leqslant 30$ kft/sec and $100 \leqslant h \leqslant 300$ kft, but they should be qualitatively correct outside this range. Figure 2 is obtained from a crossplot of Whalen's calculations[30] of a gas-phase recombination parameter, whereas Fig. 3 derives from the calculations of Goulard[8] for chemically frozen flow at 200 and 250 kft with a wall temperature of 700°K. Numerical values on each set of contours correspond to a body with 1-ft nose radius,** and the recombination coefficient γ has been chosen at the intermediate value 10^{-2}. (Thus, in practice, a factor of 10^2 in either direction is possible, depending upon whether the nose material is a very good or a very poor atom recombination catalyst.) Estimates of the chemical enthalpy potential parameter H were derived from crossplots of Grier's and Sand's calculations[9] of the maximum possible heat flux reduction associated with a completely noncatalytic ($\phi = 0$) wall. Numerical values in this case pertain to the choice $T_w = 1000°K$, but H could be higher in practice if higher surface temperatures are allowed (e.g., of order 10 for high-temperature ceramic nose materials). Superimposed on these contour maps are three representative trajectories, corresponding respectively to ballistic sallellite (S) entry,[31] intercontinental ballistic missile (ICBM) re-entry,[31] and a boost-glide hypersonic vehicle (BGV) re-entry.[30] The point on each trajectory
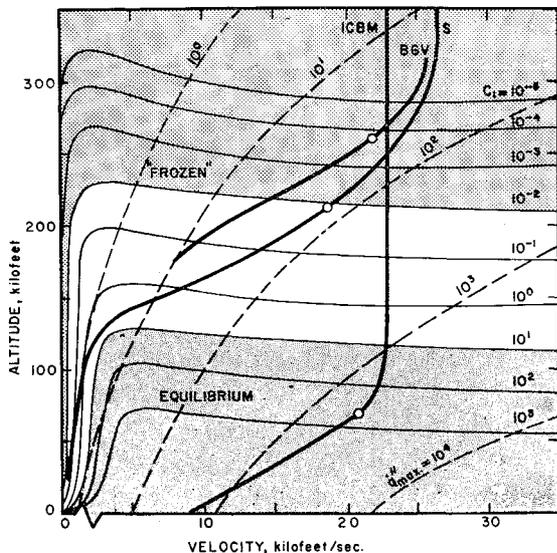
Fig. 2   **Contour map of gas-phase recombination parameter**[30] **on the altitude-velocity plane ($R_B = 1$ ft)**

at which the product $\rho_\infty^{0.5} V_\infty^{3.15}$ passes through a maximum is marked with an open circle. (This would be the point of peak convective heat flux, $\dot{q}''_{max}$, to a cold wall in the case of complete recombination with $r_D \approx 1$.) Figures 2 and 3 also include dashed contours of constant maximum laminar convective heat flux ($\dot{q}''_{max}$) to a strongly cooled surface, as calculated from the Detra-Hidalgo correlation.[14]

Before commenting on the implications of these drawings, several important limiting factors should be mentioned. First, there are altitude limitations[10] set by the breakdown of boundary-layer theory ($h \approx 250$ kft for $R_B \approx 1$ ft) and the process of shock layer dissociative relaxation (which, in the velocity range of interest, may be important as low as 200 kft cf., Refs. 10 and 32–34). Second, it should be remembered that equilibrium radiation heat transfer to the surface[35] will begin to contribute significantly (>10%) to the total stagnation point heat flux for the region roughly characterized by $\dot{q}''_{max} > 10^3$ Btu/ft²-sec on Figs. 2 and 3. Finally, at supersatellite velocities, ionization phenomena must be accounted for in calculating both convective and radiative heat flux.[36, 37]

** Using the facts that $G \propto R_B$ and $W \propto R_B^{1/2}$ values corresponding to any other nose radius are constructed readily from Figs. 2 and 3.
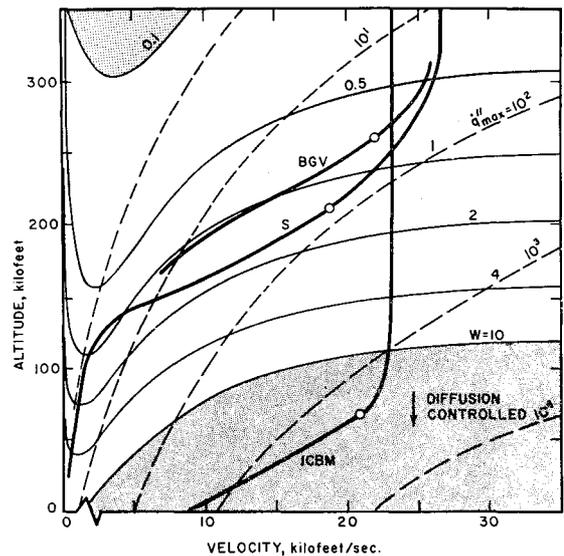

Fig. 3   **Contour map of the catalytic parameter** W **on the altitude-velocity plane ($R_B = 1$ ft, $T_w = 700°K$, $\gamma = 10^{-2}$)**

Bearing these limitations in mind, however, the following general features can be extracted from simultaneous consideration of Figs. 2–4:

1) Unless effective nose radii very much larger than 1 ft are contemplated,†† $\dot{q}''_{max}$ for satellite and glide vehicle reentry typically occurs in the near-frozen ($G \ll 1$) regime‡‡ at values of the chemical enthalpy parameter H which can exceed 2.0 and in regions where equilibrium radiative heat transfer from the shock layer can be neglected. Thus, surface catalytic activity can be very important for such entry vehicles, particularly those with appreciable aerodynamic lift. Since Fig. 3 shows that in this range the catalytic parameter W is of order unity for $\gamma = 0(10^{-2})$, one could, in principle, realize either $\phi \approx 0$ or $\phi \approx 1$, depending upon whether a catalytic ($\gamma \to 1$) or noncatalytic ($\gamma \to 0$) surface were used. In the absence of appreciable dissociation relaxation effects in the shock layer, the case $\phi \approx 0$ would correspond to heat fluxes as small as $\frac{1}{3}$ or $\frac{1}{4}$ of $\dot{q}''_{max}$. The consequences of this behavior
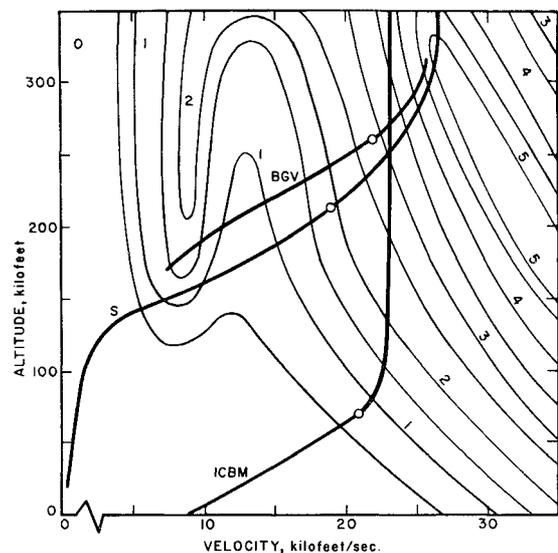

Fig. 4   **Contour map of chemical enthalpy potential parameter** H **on the altitude-velocity plane ($T_w = 1000°K$)**

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†† In accord with crossflow theory, a hypersonic delta wing at large angle of attack will behave like a series of two-dimensional, flat-faced stagnation regions ("strips") with very large effective nose radii (toward the position of maximum span).

‡‡ A tendency that is accentuated by the use of high surface temperatures.[10, 12]

for radiation-cooled entry vehicles§§ are discussed in some detail in Refs. 38 and 39. ‖‖

2) For manned parabolic entry, $\dot{q}''_{max}$ probably will occur in the domain[12] $24 < V_\infty < 35$ kft/sec, $150 < h < 240$ kft, the lower right-hand corner of which is in the range of nonnegligible equilibrium radiative heat flux. But this entire domain is in the range of maximum H ($\approx$ 4 to 5 for $T_w = 1000°$K), intermediate G, and intermediate W (for $\gamma = 10^{-2}$). Thus, considerable departures from a $R_B^{-1/2}$ laminar heat flux/nose radius dependence are possible (e.g., it is not reasonable to expect $R_B^{-0.2}$, which outwardly resembles a turbulent sonic point heat flux correlation.[40] This also may be of interest in certain aerothermoelastic problems in which the nose radius dependence of the heat input plays an important role in determining stress levels, or even static stability, of leading edge structures.[41]

3) $\dot{q}''_{max}$ for ICBM re-entry occurs in the regime of near-equilibrium flow in the boundary layer ($\phi \approx 1$). Regardless of the nose radius, in this region of the h-V_∞ plane H is relatively small, so that surface catalytic activity is not likely to be as important on both counts. Peak heat fluxes for such bodies are larger in absolute value (by some 1 to 2 orders of magnitude) than those corresponding to satellite and boost-glide vehicle re-entry, and, moreover, radiative heat input cannot, in general, be completely neglected.

Correlations in Nonequilibrium Convective Heat Transfer[2]

The nonequilibrium heat transfer correlation formula that would appear most likely to succeed for a laminar, axisymmetric stagnation point boundary-layer flow is of the general form suggested in Ref. 28:

$$\dot{q}'' = 0.763 \left(\frac{\rho_w\mu_w}{\rho_e\mu_e}\right)^{0.1} (\beta\rho_e\mu_e)^{1/2}(Pr_{\lambda,f})^{-0.6}\cdot\Delta h \times$$
$$\left\{1 + \phi\,[(Le_f)^{0.6} - 1]\frac{\Delta h_{chem,\,eq}}{\Delta h}\right\} \quad (11)$$

where in this case the extent of recombination ϕ is not only a function of the catalytic parameter W(i.e., $\mathfrak{C}$ of Refs. 28 and 38) but also depends on the gas-phase recombination parameter## G and somewhat on the chemical enthalpy driving force parameter H as well [cf., Eq. (2)]. Actually, the most important effect of ϕ is not[13] contained in its explicit appearance in the (bracketed) nonunity Lewis number "correction" term*** but is to be found instead in establishing the magnitude of the total enthalpy difference $\Delta h \equiv h_e - h_w$ across the boundary layer, since

$$\Delta h = (h_e - h_{f,w}) - (1 - \phi)\Delta h_{chem,\,eq} \quad (12)$$

As an interim measure for approximating the extent of recombination, $\phi(G, W; H)$, this writer had suggested use of a simple "combining rule" having the requisite limiting behavior[2, 44]

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§§ If ceramic nose caps or leading edges are considered for operation at temperatures of the order of 2500° to 3000°K, then one cannot, in general, neglect the equilibrium degree of dissociation $\alpha_{eq}(T_w;\ p_e)$ as compared with α_e, cf., Refs. 38 and 39.

‖‖ The scale dependence of the steady-state temperature T_w of an aerodynamically heated/radiation-cooled element of surface is readily found to be[39] $\partial \ln T_w/\partial \ln \delta = m/n$, where m is defined by Eq. (4) and was discussed previously, and n is the power of T_w at which the radiative flux $\epsilon_w\sigma T_w^4$ increases with temperature level, i.e., $n \equiv 4 + d\,(\ln\epsilon_w)/d(\ln T_w)$.

A simple correlation for the effect of wall temperature on the effective value of G for nonequilibrium boundary layer heat transfer to noncatalytic walls recently has been suggested by Inger.[42]

*** The existence of such "correction" terms (for $r_D \neq 1$) reveals that $\Delta h_f + r_D\Delta h_{chem}$ (and not Δh) is the true energy transport driving force[2] at a stagnation point.

$$1 - \phi(G, W; H) \cong [1 - \phi(G, 0; H)]\cdot[1 - \phi(0, W; H)] \quad (13)$$

where $\phi(G, 0;\ H)$ could be estimated from existing computer solution for noncatalytic walls,[12, 29] and $\phi(0, W; H)$ is, in fact, independent of H and simply given by $W/(1 + W)$.[3, 28] Since, to good accuracy, $1 - \phi(G, 0;\ H)$ can be identified††† with the quantity $(\dot{q}''_{eq} - \dot{q})/(\dot{q}''_{eq} - \dot{q}''_f)$ even for averaged Lewis numbers appreciably different from unity,[2] Eq. (13) may be written in the form

$$\frac{\dot{q}''_{eq} - \dot{q}''}{\dot{q}''_{eq} - \dot{q}''_{f,\,min}} \cong \left(\frac{\dot{q}''_{eq} - \dot{q}''}{\dot{q}''_{eq} - \dot{q}''_f}\right)_{noncatalytic} \times$$
$$\left(\frac{\dot{q}''_{eq} - \dot{q}''}{\dot{q}''_{eq} - \dot{q}''_{f,\,min}}\right)_{frozen} \quad (14)$$

Interestingly enough, this simple combining rule represents Eq. (2) for all G, W to better than 12.5% for values of H up to 25, with maximum percentage departures occurring at G, $W = 0(1)$. It also represents the suggested interpolation formula of Ref. 6 to better than 18%. With regard to these differences, it should be remembered that Inger's approximate prediction[7] of $1 - \phi(G, 0;\ H)$ can itself depart from the numerical results of Ref. 29 by some 25%.

In view of the limited size of the existing dictionary of "mixed" flow, binary gas, nonequilibrium solutions,‡‡‡ interpolation measures of the types recently suggested[1, 2, 5-7] are not indefensible. However, additional effort and ingenuity will, in the future, have to go into the correlation of accurate computer solutions for nonequilibrium flow, so that these methods and conjectures can be tested and many of the spot calculations encountered in the aerothermochemistry literature can be tied together into an intelligible pattern for design use. In this connection, it will be particularly interesting to learn whether, by considering the relevant gas-phase and wall recombination rate parameters to be, respectively,

$$\frac{k_R(T_w)\cdot\alpha_e n_w^2}{(\rho_e u_e St_{D,f})^2/(\rho_e\mu_e)}, \qquad \frac{k_w\rho_w}{\rho_e u_e St_{D,f}} \quad (15)$$

values of ϕ determined strictly for stagnation point flow can be applied successfully to downstream regions where viscous dissipation effects remain small§§§ and where the boundary layer may be either laminar or turbulent. This is known to be a reasonable approximation for predicting atom concentration (α_w) and heat transfer distributions in chemically frozen boundary-layer flow[46, 48] and has, essentially, been used tentatively for estimating gas-phase atom recombination effects in laminar boundary layers.[49, 50]

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††† This relation can be used conveniently to establish the correspondence between gas-phase rate parameters used by various investigators.[1, 5, 7, 12, 29, 42]

‡‡‡ To the writer's knowledge, the only numerical solution of this type available in the open literature is that of Scala,[3] which corresponds to the single flight condition $h = 100$ kft, $V_\infty \approx 20$, 100 fps with $T_w \approx 450°$K. However, this "point" cannot be readily fitted into the simple scheme previously mentioned, since Scala predicts $\phi \approx 0.2$ even for frozen boundary-layer flow over a catalytically inactive ($\gamma = 0$) surface, owing to the inclusion of thermal diffusion in his calculations. In the present formulation, thermal diffusion would introduce an additional term into Eq. (1).

§§§ Inviscid nonequilibrium effects may be assessed conveniently using arguments recently set forth by Inger.[45]

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