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A NEW APPROACH TO THE CORRELATION OF BOUNDARY LAYER MASS TRANSFER RATES WITH THERMAL DIFFUSION AND/OR VARIABLE PROPERTIES*

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Abstract—A rational approach to the correlation of boundary layer mass transport rates, applicable to many commonly encountered laminar flow conditions with thermal diffusion and/or variable properties, is outlined. The correlation scheme builds upon already available constant property blowing/suction solutions by introducing appropriate correction factors to account for the additional ("pseudo" blowing and source) effects identified with variable properties and thermal diffusion. Applications of the scheme to the particular laminar boundary layer mass transfer problems considered herein (alkali and transition metal compound vapor transport) indicates satisfactory accuracy up to effective blowing factors equivalent to about one third of the "blow off" value. As a useful by-product of the variable property correlation, we extend the heat-mass transfer analogy, for a wide range of Lewis numbers, to include variable property effects.

NOMENCLATURE

B,	blowing parameters defined by equations (1.2), (3.2), (3.12), (3.13);
C_{mh},	modifying factor, in the mass-heat transfer analogy, equation (3.6);
C_{td},	correlating factor for thermal diffusion, equation (3.12);
$C_{1,vp}$,	correlating factor for variable properties, equation (3.1);
F,	ratio of wall mass transfer rates;
j_i'',	mass flux of species i [$\mathrm{g\,cm^{-2}\,s^{-1}}$];
k,	exponent appearing in heat transfer correlation, equation (3.5);
Le,	Lewis number ($\equiv \rho D c_p/\lambda$);
M,	molecular weight of mixture;
M_i,	molecular weight of species i;
$\dot{m}''$,	mass transfer rate at the wall [$\mathrm{g\,cm^{-2}\,s^{-1}}$];
n,	temperature exponent of diffusion coefficient;
Pe_δ,	Peclet number based on the species boundary layer thickness $\left(Pe_\delta \equiv \dfrac{\bar{v}\delta_m}{D}\right)$;
$\dot{q}''$,	heat flux per unit area;
Re_x,	Reynolds number based on x $\left(\text{i.e., } Re_x \equiv \left(\dfrac{\rho_\infty u_\infty x}{\mu_\infty}\right)\right)$;
Sc,	Schmidt number ($\equiv (\mu/\rho)/D$);
v_s,	suction velocity; equation (2.11a);
v_b,	blowing velocity;
Y_i,	mass fraction of species "i".

Greek symbols

α,	thermal diffusion factor (dimensionless);
α_1,	temperature exponent of specific heat;
β_1, β_2,	exponents defined by equations (A1.11, A1.12);
$\delta_v, \delta_T, \delta_m$,	thickness of the velocity, temperature and species boundary layers, respectively;
ε,	exponent of Lewis number (see equation (3.3));
ε_1,	temperature exponent of thermal conductivity;
ω,	temperature exponent of viscosity.

Subscripts

w,	gas–solid interface (i.e., "wall");
e,	outer edge of thermal boundary layer;
h,	pertaining to heat transfer;
m,	pertaining to mass transfer or species boundary layer edge;
1,	trace species;
2,	"carrier" species (air in present examples);
cp,	constant property case (i.e., incompressible);
vp,	variable property effects included;
eff,	effective quantity;
$*$,	reference quantity (identified here as an average across the species boundary layer);
BL,	a quantity computed numerically from the solution of the full boundary layer equations;
$td + vp$,	in the presence of thermal diffusion and variable property effects;

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td, in the presence of thermal diffusion effects, without variable properties;

tdo, overall quantity referring to the combined source and suction effects of thermal diffusion.

Superscript

$(\bar{\ })$, quantity averaged over the thickness of the species boundary layer.

1. INTRODUCTION

THE HEAT and mass transfer literature includes several alternative algebraic correlations for estimating variable property corrections to laminar boundary layer transfer rates for a wide range of geometries and boundary conditions. While the utility of such algebraic correlations to replace tedious *ab initio* numerical computations is obvious, especially for engineering design purposes, little has been done to develop a general framework for correlating a variety of specific effects, such as those introduced by thermal diffusion and variable properties. In this paper, which treats an important class of laminar boundary layer problems, we show how this can be accomplished by exploiting analogies to already-known problems with "blowing" and/or homogeneous reaction. Although attention will be focused here on the prediction of *mass* transfer rates, our general approach should apply equally well for correlating momentum and energy transfer rates.

The physical problems which motivated this work pertain to salt deposition/corrosion of marine or aircraft gas turbine blades [1], coal fired boiler tubes [2], and the chemical deposition of metallic coatings from vapor phase compounds (CVD) [3]. These applications involve the low-speed boundary layer flow of a multi-component gas mixture over a surface of specified geometry. Often, this gas mixture consists of components of disparate molecular weights, comprising, in the simplest cases, a (pseudo-) binary mixture. Frequently the species containing the elements to be transferred are present in only trace amounts (e.g., a few parts per million). Thus, in the marine gas turbine application, it is of interest to determine the mass deposition rate of corrosive alkali sulfate impurities present as "trace species" in the boundary layer flow of hot combustion product gases over the turbine blades. Alternatively, to deliberately chemically coat a surface with a heavy metal [3] a flow of the corresponding heavy metal halide vapor in a hydrogen and/or inert carrier gas is frequently passed over the heated surface. Deposition of the metal by heterogeneous dissociation/reduction of the halide vapor can then occur *via* a convective diffusion transport mechanism near the hot surface. To embrace the above-mentioned situations we therefore consider forced convection mass transfer rates from a low-speed, laminar boundary layer over a solid wall in the presence of pressure gradients, non-uniform fluid properties and vapor transport *via* thermal (Soret) diffusion [4–6].

In the absence of the above-mentioned coupling effects, "constant property" (*cp*) solutions to the laminar boundary layer equations are relatively simple to obtain for the flow situations outlined above (e.g., see Ref. [7]). Of course, "variable property" effects associated with the inherent temperature dependencies of the gas density, specific heat capacity and the relevant transport coefficients, increase the non-linearity and coupling in the system of equations governing the conservation of mass, momentum, and energy. This, in turn, considerably increases the complexity and computational cost of the numerical solution procedure. In order to summarize the results of such calculations (or expenditure) several correlations have already been devised. These are broadly classified here as those applicable to boundary layer flows with interfacial mass transfer (i.e., "blowing" or "suction") and those for a "solid wall". In the former category, representative correlations are due to Knuth [8], (based on the idea of a reference state), and Gross *et al.* [9]. The latter correlations suggest that in the absence of diffusion-conduction-interaction effects (analogous to the thermal diffusion treated below), the dimensionless momentum and energy transfer rates (normalized with respect to the corresponding laminar or turbulent "solid wall" condition) can be satisfactorily predicted using a function linear in a suitably defined dimensionless "blowing parameter", e.g., [10, 11]:

$$\frac{\dot{q}''_w}{(\dot{q}''_w)_{\text{no blowing}}} \simeq 1 - CB. \tag{1.1}$$

where '*B*', the nondimensional "blowing parameter" is defined as

$$B \equiv \frac{\rho_w v_w}{\rho_e u_e (St_h)_{\text{no blowing}}} \tag{1.2}$$

and the multiplying factor '*C*' is nearly constant at least in the constant property, incompressible case. Also, as pointed out in [10], while the above correlation can also be motivated by film (Couette flow) theory, for constant property laminar boundary layers one can derive such a linear relation only when the extent of blowing ($B > 0$) or suction ($B < 0$) is sufficiently small.

For the "solid wall" cases, on the other hand, variable property effects have been accounted for using either the well-known reference temperature scheme [12] or property-ratio correction factors [13]. In contrast, the underlying basis for the correlation approach presented in this paper is the observation that variable property effects, even for the "solid wall" case, induce blowing or suction-like behavior into the boundary layer. Thus, by suitably defining a nondimensional grouping (in the spirit of the "blowing parameter" suggested by Gross *et al.* [9]), it becomes possible to develop a useful correlation scheme which not only accounts for variable property effects, but also accounts for the mass transport effects of thermal (Soret) diffusion. As will be seen, thermal diffusion also introduces an additional effect, equivalent to a linear pseudo-"source" or "sink" in the species conservation equation. Fortunately, this additional effect is readily included using a simple explicit correction factor, motivated by film theory.†

Actually, considerable attention has already been given to both thermal diffusion and diffusion thermo effects, in connection with the transpiration cooling of hypersonic entry vehicles [14–16]. Although most of this effort was focused on determining the effects of these thermodynamic couplings on the wall mass, momentum, and energy transfer rates, evidently no simple basis for correlating the results of these numerical computations was reported.

2. GOVERNING EQUATIONS AND IMPLICATIONS

For the laminar, binary boundary layer situations described in the previous section, the appropriate differential equations expressing conservation of overall mass, momentum, energy and the trace species of interest are well-known, and may be written in their two-dimensional form:

Overall mass:

$$\frac{\partial}{\partial x}(\rho u)+\frac{\partial}{\partial y}(\rho v)=0; \qquad (2.1)$$

Momentum:

$$\rho u\frac{\partial u}{\partial x}+\rho v\frac{\partial u}{\partial y}=-\frac{\mathrm{d}p}{\mathrm{d}x}+\frac{\partial}{\partial y}\left(\mu\frac{\partial u}{\partial y}\right); \qquad (2.2)$$

Energy:‡

$$\rho u\frac{\partial h_t}{\partial x}+\rho v\frac{\partial h_t}{\partial y}=-\frac{\partial}{\partial y}(\dot q''); \qquad (2.3)$$

Species 1:

$$\rho u\frac{\partial Y_1}{\partial x}+\rho v\frac{\partial Y_1}{\partial y}=-\frac{\partial}{\partial y}(j_1''), \qquad (2.4)$$

where $\dot q''$ and j_1'' are the transverse (y-component) energy and mass fluxes, respectively.

When diffusion–conduction interactions are present, the expressions for the energy and mass fluxes across the boundary layer can be written [6, 16]:

$$\dot q''=-\lambda\frac{\partial T}{\partial y}+RT\frac{M^2}{M_1M_2}\alpha j_1''+(h_1-h_2)j_1'' \qquad (2.5)$$

$$j_i''=-\rho D\left[\frac{\partial Y_i}{\partial y}+\frac{\alpha Y_i(1-Y_i)}{T}\frac{\partial T}{\partial y}\right],\ i=1,2. \qquad (2.6)$$

In equation (2.5), the first term represents the Fourier heat conduction while the second is due to the diffusion-thermo (or Dufour [17]) effect, mentioned earlier. The mass flux of each species in the binary mixture, as given by equation (2.6), includes the concentration gradient contribution (i.e., Fick diffusion) and another due to the temperature gradient (i.e., thermal (Soret [18]) diffusion). Although diffusion and conduction phenomena are generally closely coupled, it is seen from equations (2.5) and (2.6) that when one of the species is present only in trace amounts (i.e., when $Y_1 \ll 1$), the second and third terms in equation (2.5) can be neglected so that Fourier conduction remains the dominant mechanism for energy transfer. Therefore, in the cases being considered herein, the simplified expressions for the energy and mass fluxes take the form:

$$\dot q''=-\lambda\frac{\partial T}{\partial y} \qquad (2.7)$$

$$j_1''=-\rho D\left[\frac{\partial Y_1}{\partial y}+\alpha Y_1\frac{\partial \ln T}{\partial y}\right]. \qquad (2.8)$$

Substituting equations (2.7) and (2.8) into (2.3) and (2.4), respectively, one can re-express the energy and species conservation equations as:

Energy:

$$\rho u\frac{\partial h_t}{\partial x}+\rho v\frac{\partial h_t}{\partial y}=\frac{\partial}{\partial y}\left\{\frac{\lambda}{c_p}\frac{\partial h_t}{\partial y}\right\}; \qquad (2.9)$$

Species:

$$\rho u\frac{\partial Y_1}{\partial x}+\rho v\frac{\partial Y_1}{\partial y}=\frac{\partial}{\partial y}\left\{\rho D\left[\frac{\partial Y_1}{\partial y}+\alpha Y_1\frac{\partial \ln T}{\partial y}\right]\right\}. \qquad (2.10)$$

By carrying out the indicated differentiations on the right hand side of equation (2.10), one can rearrange the species equation to make it resemble the familiar "constant property + homogeneous reaction" form:

$$\rho u\frac{\partial Y_1}{\partial x}+\rho(v-v_s)\frac{\partial Y_1}{\partial y}=\rho D\frac{\partial^2 Y_1}{\partial y^2}+\dot r'''_{1,\mathrm{eff}}, \qquad (2.11)$$

where we have introduced the definitions:

$$v_s\equiv\frac{1}{\rho}\left[\frac{\partial(\rho D)}{\partial y}+\rho D\alpha\frac{\partial \ln T}{\partial y}\right] \qquad (2.11a)$$

and

$$\dot r'''_{1,\mathrm{eff}}\equiv\left\{\frac{\partial}{\partial y}\left(\rho D\alpha\frac{\partial \ln T}{\partial y}\right)\right\}Y_1. \qquad (2.11b)$$

The above form of the species equation reveals that the variable property effect associated with the (ρD) product produces a suction-like effect on the species transport, whereas thermal diffusion contributes both a suction-like term as well as a source-like term.

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†Although the reciprocal ("diffusion thermo"-) effect (contribution of concentration gradients to the heat flux) can be neglected for the particular boundary layer situation treated in this paper, its influence on the heat transfer rate could also be correlated in a fashion similar to that adopted below.

‡The dependent variable for energy is taken to be the stagnation enthalpy h_t, given by $h+(u^2/2)$. Note that in the present situations the mass-averaged specific heat of the mixture, $\sum_{i=1}^{2} Y_i c_{p_i}$, is approximately equal to c_{p_2}, since $Y_1 \ll 1$, for the trace species. The advantage of this form of the energy equation (2.3) is that the compression work term, $u(\mathrm{d}p/\mathrm{d}x)$, does not explicitly appear. The viscous dissipation term, however, has been neglected in equation (2.3) since only low Mach number flows will be considered here.

The combined effect of both these phenomena on the species mass transport is described by equation (2.11) in terms of the overall pseudo-suction velocity v_s and the pseudo-source strength per unit volume, $\dot{r}'''_{1,\mathrm{eff}}$. In connection with the latter, it is interesting to note that the effect of thermal diffusion is similar to that of a distributed, homogeneous, first-order chemical reaction occurring within the boundary layer, with an effective specific rate constant given by†

$$K \equiv \frac{1}{\rho}\left\{\frac{\partial}{\partial y}\left(\rho D\alpha\frac{\partial \ln T}{\partial y}\right)\right\}. \tag{2.12}$$

One observes from equations (2.11a) and (2.11b) that the above-mentioned effects can easily be reversed depending upon the sign of the thermal diffusion factor, α, and the temperature gradient, $\partial T/\partial y$. Consider, for instance, a trace species that is heavier than the carrier gas. In such cases α is usually positive. Now, if $\partial T/\partial y$ was also positive, as for a "cold wall", one can conclude from equation (2.11a) that a "suction" (not "blowing") effect would prevail within the species boundary layer, tending to increase the mass transfer rate to the wall. On the other hand, the influence of $\dot{r}'''_{1,\mathrm{eff}}$ is slightly more complicated. The product of density and diffusivity, for a gas, can be taken to increase with temperature according to the proportionality $\rho D \sim T^{n-1}$ (where, typically, $n > 1$, being exactly 3/2 for "hard-sphere" molecules, from kinetic theory considerations [4]). Also, the thermal diffusion factor may be treated as a constant (for simplicity) in this argument, even though in reality (see below) it is weakly temperature dependent [5]. Using these facts, one can immediately express the pseudo-source term by the proportionality:

$$\dot{r}'''_{1,\mathrm{eff}} \sim \left[(n-2)T^{n-3}\left(\frac{\partial T}{\partial y}\right)^2 + T^{n-2}\frac{\partial^2 T}{\partial y^2}\right]. \tag{2.13}$$

Now, because the temperature exponent of the diffusivity, n, is generally less than 2, the first term in the above proportionality will always be negative. Also, since $\partial^2 T/\partial y^2$ is negative across the boundary layer over a "cold wall", one concludes that thermal diffusion would actually set up a first-order homogeneous "sink" (not "source") for the depletion of the trace species concentration. This leads to a reduction in the mass transfer rate to the wall. In contrast, the case of a "hot wall" (i.e., when $\partial T/\partial y < 0$ and $\partial^2 T/\partial y^2 > 0$), would be expected to cause a first-order homogeneous "source" to prevail, increasing wall mass transfer rates, when $\alpha > 0$. Clearly, the above trends would be reversed when $\alpha < 0$, as for trace species lighter than the carrier gas. Table 1 summarizes these effects of variable properties and thermal diffusion.† It is to be noted that while the influence of $\dot{r}'''_{1,\mathrm{eff}}$ on mass transfer rates is analytically predictable, as shown above, the question of whether v_s would be strong enough to result in a *net* suction or blowing within the boundary layer cannot be as simply answered. Since the problem being considered involves no real suction or blowing at the wall (i.e., the momentum equation is subject to the usual "no-slip condition" in the present "solid wall" case), the forced convective velocity field is fully determined by the coupled momentum and energy equations alone (i.e., equations (2.2) and (2.9)). The one-way coupling between these equations and the species equation (i.e., equation (2.11)) then dictates the magnitudes of the imposed velocity components u and v supplied to the species equation. Thus, a competition is set up between these and v_s. It will be seen in the next section that the predicted influence of v_s is often dominated by the imposed forced convection field, itself influenced by variable property effects (which are usually important whenever thermal (Soret) diffusion is important).

Table 1. Effects of variable properties and thermal diffusion

	"Cold wall"		"Hot wall"	
	v_s	$\dot{r}'''_{1,\mathrm{eff}}$	v_s	$\dot{r}'''_{1,\mathrm{eff}}$
$\alpha > 0$	Suction	Sink	Blowing	Source
$\alpha < 0$	Suction or blowing	Source	Suction or blowing	Sink

3. A NEW CORRELATION SCHEME

Our general approach focuses attention on the actual mass transfer rate normalized with respect to the rate in the absence of the effect. Thus, variable properties (*vp*) and thermal diffusion (*td*) are treated as effects superimposed upon the known "constant property" (*cp*) solutions, leading to a generalized composite correlation, as described below.

3.1. *Correlation of variable property effects*

In the absence of thermal diffusion, since even variable property effects produce pseudo-suction or blowing within the boundary layer, we seek a correlation in terms of a linear relationship similar in spirit to those successful for cases with "real" wall mass

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†Inferences drawn from recent composition probing of CVD boundary layers [T. O. Sedgwick, Paper No. 231, 152nd Electrochemical Society Meeting, Atlanta, Ga., October 9–14 (1977)] should be corrected for this effect since some of the changes currently attributed to the "chemistry" will in fact be due to non-Fick (thermal) diffusion.

†In many previous studies of thermal diffusion effects on boundary layer transfer rates (e.g., see [15]), in the presence of foreign gas injection at the wall, it was reported that the adiabatic wall temperature was shifted owing to diffusion–conduction interactions alone. Although such shifts in the adiabatic wall temperature can be physically related to the presence of a "source" or "sink" within the boundary layer, these mechanisms do not appear to have been clearly identified or exploited.

transfer. Thus we write:

$$F_{vp} \equiv \frac{\dot{m}''}{(\dot{m}'')_{cp}} = 1 - C_{1,vp} B_{\mathrm{eff},vp} \quad , \tag{3.1}$$

where† $B_{\mathrm{eff},vp}$ is the equivalent of the "blowing parameter" mentioned earlier and $C_{1,vp}$ is a quantity which will be determined so as to provide an acceptable accuracy in predicting the required mass transfer ratio, F_{vp}. Based on a line of reasoning given in Appendix 1 we propose the form:

$$B_{\mathrm{eff},vp} = C_{2,vp}\left\{(Le_e)^{2\varepsilon-1}\left[\left(\frac{1}{\theta_*}\right)^{\beta_1(1-2\varepsilon)} - 1\right]\right\} - (n-1)\left(\frac{\theta_* - \theta_w}{\theta_*}\right), \tag{3.2}$$

where $\varepsilon \approx 0.4$, β_1, n are fluid property value exponents, and

$$\theta_* \equiv \theta_w + \tfrac{1}{2}(1-\theta_w)(Le_{vp})^{\varepsilon} \tag{3.3}$$

$$\theta_w \equiv T_w/T_e, \tag{3.4}$$

and the multiplier $C_{2,vp}$ will, for the present, be determined using already available heat transfer correlations in the manner described below. (This results in the implicit inclusion of pressure gradient effects into the present correlation scheme.) The coefficient $C_{1,vp}$ appearing in equation (3.1) will be treated here as the basic "correlating factor", to be determined ultimately by using independently computed exact numerical solutions to the coupled boundary layer equations for F_{vp} (Appendix 2).

In the literature, numerical solutions to the coupled systems of boundary layer momentum and energy equations (i.e., equations (2.2) and (2.3)), with pressure gradient and variable properties, are available [19]. Simple correlations of these for the wall skin friction and heat transfer rates have also been suggested [13]. Reference [13], for instance, provides the following heat transfer correlation in the case of the boundary layer flow of air over a "solid wall":

$$\frac{\dot{q}''_w}{(\dot{q}'')_{cp}} = \frac{Nu_h}{(Nu_h)_{cp}} = \theta_w^k, \tag{3.5}$$

where the exponent 'k' has been given under both "hot" and "cold" wall conditions, for the flat plate and plane stagnation point cases (see also Table 2). Typical values of 'k' (being 0.07 for a "cold" wall and 0.1 for a "hot" wall) confirm our earlier comment (Section 2) regarding the blowing or suction effect of variable properties being dominated by the actual prevailing transverse convection field. In view of the availability of such heat transfer rate correlations, and future applications, it is desirable to relate the variable property mass transfer correlation being sought here to the heat transfer correlation of equation (3.5).

Table 2. Values of the exponent 'k' appearing in the heat transfer correlation (i.e., equation (3.7)) [13]

Geometry	"Hot" wall ($\theta_w > 1$)	"Cold" wall ($\theta_w < 1$)
Flat plate	−0.01	0
Plane stagnation point	0.1	0.07

In the absence of thermal (Soret) diffusion, since the species Lewis number governs the relative importance of mass and heat diffusion, we anticipate

$$\frac{\dot{m}''}{(\dot{m}'')_{cp}} = C_{mh}(\theta_w, Le_e)\left[\frac{\dot{q}''}{(\dot{q}'')_{cp}}\right]. \tag{3.6}$$

Combining equations (3.1), (3.5)† and (3.6) we have:

$$F_{vp} \equiv 1 - C_{1,vp}B_{\mathrm{eff},vp} = C_{mh}(\theta_w, Le_e)\theta_w^k. \tag{3.7}$$

Noting that $Le_{vp} = Le_*$ (which need not be unity even when $Le_e = 1$) and imposing the following obvious requirements on C_{mh}:

$$C_{mh}(\theta_w = 1, Le_*) = 1 \tag{3.8a}$$

$$C_{mh}(\theta_w, Le_* = 1) = 1, \tag{3.8b}$$

one can now derive useful algebraic interrelations of the form:

$$C_{2,vp} = (A_1 + A_2 C_{1,vp})/A_3 \tag{3.9}$$

$$C_{mh} = (A_4 + A_5 C_{1,vp})/\theta_w^k \tag{3.10}$$

where the coefficients A_1, A_2, A_3, A_4, A_5 are explicit functions of the parameters θ_w, Le_e and fluid property exponents (cf. Appendix 1). These relations complete one realization of the present correlation scheme, except for the as yet undetermined "correlating factor" $C_{1,vp}$ which multiplies the effective blowing parameter in equation (3.1). The determination of $C_{1,vp}$ for a range of θ_w and Le_e values was achieved in the present analysis by considering various trace species in air flowing over both "cold" ($\theta_w < 1$) and "hot" ($\theta_w > 1$) walls. For each case, a value of $F_{vp}(=F_{BL}$, say) was computed *via* a numerical solution procedure (cf. Appendix 2) for the governing differential equations. Then, these F_{BL} values were used to obtain $C_{1,vp}(\theta_w, Le_e)$ in tabular form *via* the following relation (obtained by combining equations (3.7) and (3.10)).

$$C_{1,vp} = [F_{BL} - A_4]/A_5. \tag{3.11}$$

To facilitate interpolations (for other values of θ_w and Le_e), and perhaps, extrapolations, a simple "best fit" curve is finally suggested. This is discussed in detail in Section 4.

3.2. *Correlation of thermal diffusion effects*

As seen in Section 2, thermal diffusion introduces both a suction (or blowing) type term, as well as a

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†This ratio of the actual mass transfer rate (with variable property effects) to that without, is exactly equal to the corresponding Stanton or Nusselt (Sherwood) number ratio, i.e.,

$$\frac{\dot{m}''}{(\dot{m}'')_{cp}} = \frac{St_m}{(St_m)_{cp}} = \frac{Nu_m}{(Nu_m)_{cp}}.$$

†Alternatively, a variable property *energy* transfer correlation based on the pseudo-blowing notion, could be used here.

linear pseudo-source (or sink) effect into the species boundary layer conservation equation, thereby modifying the mass transfer rate which would prevail in the presence of variable property effects alone. In the present correlation scheme, these effects are first treated separately *via* two independent correction factors which are later combined to yield an overall correlation. In doing this it is visualized that thermal diffusion effects further perturb the already available (see Section 3.1) variable property rates.

To correlate the "suction"-like behavior associated with thermal (Soret) diffusion we proceed in a manner analogous to that already described for variable property effects. Accordingly, this correction is postulated to be of the form:

$$F_{td} = 1 - C_{td} B_{\mathrm{eff},td}, \tag{3.12}$$

and, based on physical considerations detailed in Appendix 3, we propose†

$$B_{\mathrm{eff},td} = -\frac{\alpha_*(\theta_w^{-1}-1)(Le_*)^{\gamma}}{2+(\theta_w^{-1}-1)(Le_*)^{\gamma}}, \tag{3.13}$$

where

$$\alpha_* \equiv \alpha_\infty\left[1+\frac{(\alpha_{-1}/\alpha_\infty)}{T_e\theta_*}\right], \tag{3.14}$$

and starred quantities are evaluated at the temperature $T_e\theta_*$ (equations (3.3), (A1.9), (A1.10)).

The value of the thermal diffusion factor, including its temperature dependence, is evaluated from kinetic theory considerations presented in references [5] and [6], and is curve-fit by the 2-parameter relation:

$$\alpha = \alpha_\infty + \alpha_{-1}T^{-1} = \alpha_\infty\left[1+\frac{(\alpha_{-1}/\alpha_\infty)}{T}\right], \tag{3.15}$$

where α_∞ and α_{-1} are constants pertinent to the species under consideration. α_* is obtained from equation (3.15) by evaluating α at the temperature T_*. Typical estimated values of α_∞ and $\alpha_{-1}/\alpha_\infty$ for mixtures of a number of trace species in air, are given in Table 3. Figure 1 shows the corresponding variation of α with temperature for these species. Predictions were based on the assumed Lennard–Jones 12:6 potential parameters included in Table 3.

The specification of the effective blowing parameter $B_{\mathrm{eff},td}$ as an explicit function of θ_w, Le and α (equations (3.13) and (3.14)) completes the formulation of the thermal diffusion correction factor F_{td}, provided the corresponding sensitivity coefficient C_{td} is determined so as to yield an acceptable accuracy in the prediction of the mass transfer rate. However, before C_{td} can be determined one has to establish an additional correction factor to account for the "source" effect associated with thermal diffusion. This correction is sought here in the form of an explicit expression for the ratio:

Table 3. Trace species/air† estimated values of α_∞ and $-(\alpha_{-1}/\alpha_\infty)$ (cf. equation (3.15)) and corresponding trace species Lennard–Jones 12:6 interaction parameters

Species	α_∞	$-(\alpha_{-1}/\alpha_\infty)$	σ	ε/k
Na_2SO_4	0.7889	481.29	5.00	2221.0
NaCl	0.3534	449.27	4.186	1989.0
NaOH	0.1670	434.92	3.804	1962.0
Na	−0.05697	436.76	3.567	1375.0
$NbCl_5$	0.8342	237.24	5.148	612.7
$MoCl_5$	0.9162	242.22	5.542	638.4
WCl_5	0.9565	242.73	5.540	647.8
HgI_2	1.0056	249.40	5.625	695.6
UI_4	1.2665	341.12	6.239	1217.7

†For air, $\sigma = 3.711$ Å, $\varepsilon/k = 78.6$ K, transition metal pentachloride potential parameters estimated from thermochemical data compiled in Gerasimov *et al.*, NASA TT F-285.

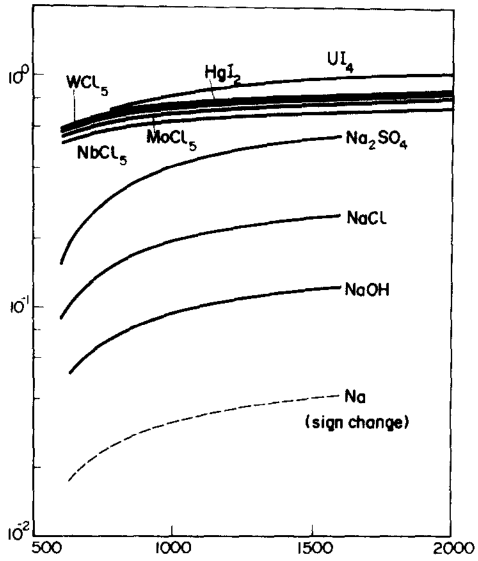

FIG. 1. Variation of the thermal diffusion factor α with temperature, for various trace species-air mixtures.

$$F_s \equiv \dot{m}''/(\dot{m}'')_{\text{no source}}, \tag{3.16}$$

which plays the role of a chemical "reaction factor". Since the suction correction has already been proposed (i.e., F_{td}), it only remains to find the extent by which "source" or "sink" effects might further alter the wall mass transfer rates. Figure 2 illustrates qualitatively the effect of a volumetric "source" or "sink" on the trace species mass fraction profile across the boundary layer. Of course, these effects will in general be competing with the previously mentioned "suction" or "blowing" effect in any given flow situation.

In view of these requirements, it is expedient to again exploit the Couette-type analogy, mentioned in Appendix 1, to provide the following simplified species equation:

$$\overline{\rho D}\,\frac{d^2 Y_1}{dy^2} + \dot{r}_1''' = 0, \tag{3.17}$$

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†Note that in the simultaneous absence of variable property effects and thermal diffusion (i.e., $\theta_w = 1$), $B_{\mathrm{eff},td} = 0$ and one recovers the expected result $F_{td} = 1$. Also, in this limit, $\theta_* = 1$, as required.

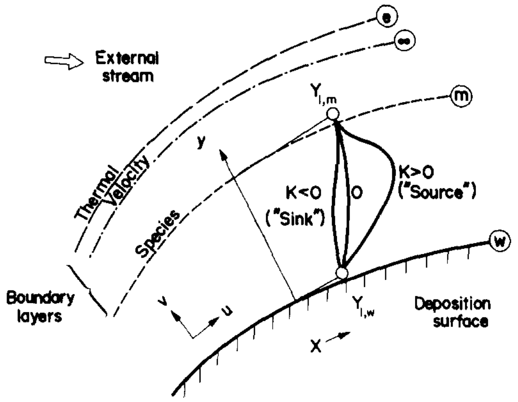

FIG. 2. Schematic of the "source" or "sink" effect of thermal diffusion on the boundary layer mass fraction profiles.

(applicable also to diffusion across a chemically reacting stagnant film). The source $\dot{r}_1'''$ would correspond to a first-order rate law of the form:

$$\dot{r}_1''' \equiv K\rho Y_1, \tag{3.18}$$

where the "specific rate constant", K, is given by equation (2.12). Using the above rate law, the analytical solutions to equation (3.17) are of the form:

"Source" ($K > 0$)

$$Y_1 = A\sin\beta y + B\cos\beta y \tag{3.19}$$

"Sink" ($K < 0$)

$$Y_1 = A'\sinh\beta y + B'\cosh\beta y, \tag{3.20}$$

where

$$\beta = (|K|/D)^{1/2}. \tag{3.21}$$

Note the sinusoidal nature of the "source" solution profiles and the exponential nature of the "sink" solution profiles (cf. the qualitative trends depicted in Fig. 2). Subject to the boundary conditions $Y_1(0) = Y_{1_w}$ and $Y_1(\delta_m) = Y_{1_m}$ one may determine the arbitrary constants A, B or A', B' appearing in equations (3.19) or (3.20). Using these one may then establish the required mass transfer rates (since $\dot{m}'' \sim Y_1'(0)$) both in the presence and absence of the "source" or "sink". In this way one obtains the following expressions for the required correction factor, F_s, depending on whether a "source" or "sink" prevails:

"Source"

$$F_s = \beta\delta_m\left[\frac{Y_{1_m} - Y_{1_w}\cos(\beta\delta_m)}{(Y_{1_m} - Y_{1_w})\sin(\beta\delta_m)}\right]; \tag{3.22}$$

"Sink"

$$F_s = \beta\delta_m\left[\frac{Y_{1_m} - Y_{1_w}\cosh(\beta\delta_m)}{(Y_{1_m} - Y_{1_w})\sinh(\beta\delta_m)}\right]. \tag{3.23}$$

To evaluate $\beta\delta_m \equiv (|K|/D)^{1/2}\delta_m$ in the above expressions it is necessary to consider the average value of K (equation (2.12)) over the species boundary layer thickness, expressed in terms of pertinent variables. Using the estimation procedures given in Appendix 3 we propose:

$$\beta\delta_m = \left\{\frac{\alpha_*\theta_*^{n-1}}{2}\right\}^{1/2}\cdot\left\{\frac{(1-\theta_m)}{\left(\frac{\delta_T}{\delta_m}-1\right)^2}\left(\frac{\delta_T}{\delta_m}-2\right)-(\theta_m-\theta_w)\right.$$
$$\left. + \frac{(n-2)}{2\theta_*}\left[\frac{(1-\theta_m)}{\left(\frac{\delta_T}{\delta_m}-1\right)}+(\theta_m-\theta_w)\right]^2\right\}^{1/2}, \tag{3.24}$$

with the following supplementary relations:

$$\theta_m \cong \theta_w + (1-\theta_w)(Le_*)^{\varepsilon} \tag{3.25}$$

$$\frac{\delta_T}{\delta_m} \cong \frac{1}{(Le_*)^{\varepsilon}}. \tag{3.26}$$

The latter originate from relations given earlier (see equations (3.3) and (A1.8)).

The source correction factor F_s is now completely determined by equations (3.22), (3.23) and the expressions in equations (3.24)–(3.26) for a given θ_w, Le and α. Note that F_s does not contain any unknown "correlating factors", as F_{vp} and F_{td} did.

3.3. *The Composite correlations*

Having independently established the correction factors for the suction and source type behavior of thermal diffusion alone, one can combine them to yield the following useful "overall" multiplicative correlation for thermal diffusion effects:

$$F_{tdo} \equiv \frac{\dot{m}''}{(\dot{m}''_{\alpha=0})_{vp}} = F_{td}F_s \tag{3.27}$$

$$= (1 - C_{td}B_{\text{eff},td})F_s. \tag{3.27a}$$

The determination of the sensitivity coefficient C_{td} (θ_w, Le, α) is carried out in the same manner as that outlined earlier for $C_{1,vp}$.

Finally, in order to correlate the simultaneous effects of both variable properties and thermal diffusion, the following multiplicative "composite" correlation scheme is proposed:

$$F \equiv \frac{\dot{m}''}{(\dot{m}'')_{cp}} = \frac{(\dot{m}'')_{vp}}{(\dot{m}'')_{cp}}\cdot\frac{(\dot{m}'')}{(\dot{m}'')_{vp}} = F_{vp}F_{tdo} \tag{3.28}$$

$$= (1 - C_{1,vp}B_{\text{eff},vp})\cdot(1 - C_{td}B_{\text{eff},td})\cdot F_s. \tag{3.29}$$

In the next section all necessary constants are determined *via* comparisons with exact numerical solutions to the laminar boundary layer equations.

4. RESULTS AND DISCUSSION

To complete the correlation outlined above it is necessary to determine the "correlating factors", $C_{1,vp}$ and C_{td} appearing in the variable property (vp) and thermal diffusion (td) correlations, respectively. The former is a function of the wall temperature ratio,† θ_w, and the trace species Lewis number Le,

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† While $\theta_w \equiv T_w/T_e$ is a convenient variable for discussing variable property and Soret effects, the specific energy variable $\theta_w \equiv h_t/h_{t,e}$ is more convenient in numerically integrating the exact BL energy equation (see Appendix 2). Since we take $c_p \sim T^{\alpha_1}$ (Appendix 1) it is readily seen that $T_w/T_e = (h_{t,w}/h_{t,e})^{1/(1+\alpha_1)}$ for stagnation point flow.

Table 4. Values of constants in equations (4.1) and (4.2) for the "cold" wall and "hot" wall cases

Species	D_0	D_1	E_0	E_1	θ_w-range
Na_2SO_4	1.1864	0.5309	−0.2889	1.4986	$0.3 \leqslant \theta_w \leqslant 0.6$
	0.8124	1.2304	0.1507	0.8679	$0.6 \leqslant \theta_w \leqslant 1.0$
NaCl	1.3890	1.3436	0.0272	1.3130	$0.3 \leqslant \theta_w \leqslant 0.6$
	1.2290	1.5820	0.2149	0.9787	$0.6 \leqslant \theta_w \leqslant 1.0$
NaOH	2.0181	1.5018	0.1997	1.3052	$0.3 \leqslant \theta_w \leqslant 0.6$
	1.9333	1.6648	0.3439	1.0422	$0.6 \leqslant \theta_w \leqslant 1.0$
Na	4.3716	2.2615	0.4943	1.7954	$0.3 \leqslant \theta_w \leqslant 0.6$
	4.1345	2.6593	0.4739	1.8178	$0.6 \leqslant \theta_w \leqslant 1.0$
$NbCl_5$	0.7436	0.8469	−0.1525	0.1806	$1.0 \leqslant \theta_w \leqslant 4.5$
$MoCl_5$	0.6477	0.8234	−0.1469	0.1786	$1.0 \leqslant \theta_w \leqslant 4.5$
WCl_5	0.6374	0.8205	−0.1484	0.1812	$1.0 \leqslant \theta_w \leqslant 4.5$
HgI_2	0.6078	0.8141	−0.1498	0.1818	$1.0 \leqslant \theta_w \leqslant 4.5$
UI_4	0.4601	0.7878	−0.1882	0.1830	$1.0 \leqslant \theta_w \leqslant 4.5$

while the latter also depends upon the relevant thermal diffusion factor α, mainly *via* the product $\alpha(Le)^{c} \cdot (\theta_w^{-1} - 1)$. For specified values of these parameters, $C_{1,rp}$ and C_{td} can be uniquely determined from the relationships given earlier. That is,

$$F_{rp} \equiv \frac{\dot{m}''}{(\dot{m}'')_{cp}} = 1 - C_{1,rp} B_{\mathrm{eff},rp} = C_{mh} \theta_w^k \quad (3.1)$$

$$F_{tdo} \equiv \frac{\dot{m}''}{(\dot{m}'')_{t=0}} = (1 - C_{td} B_{\mathrm{eff},td}) F_s, \quad (3.27a)$$

where the coefficients, blowing parameters and F_s are available from the algebraic expressions given in Section 3. The wall mass transfer rate ratios (i.e., F_{rp} and F_{tdo}) were first computed *via* a complete numerical solution of the system of governing boundary layer differential equations (see Appendix 2 for an outline of the numerical techniques) and representative "eigenvalues" for Na_2SO_4-transport. These solutions were obtained for a variety of trace species in air (covering the molecular weight extremes Na(23) to UI_4(745.6) over a wide range of θ_w-values spanning "cold" to "hot" wall conditions). Using these "exact" results for F_{rp} and F_{tdo} (referred to hereafter as F_{BL}) in equations (3.1) and (3.27a) the "correlating factors" were then determined in tabular form as $C_{1,rp} = C_{1,rp}(\theta_w, Le_e)$ and $C_{td}(\theta_w, Le_e, \alpha_e)$.

For the simplest correlation, one could hope that the pseudo-blowing parameters $B_{\mathrm{eff},rp}$, $B_{\mathrm{eff},td}$ could be defined in such a way that the associated correlating factors $C_{1,rp}$ and C_{td} would be insensitive to Le and wall temperature ratio, over the entire parameter range of interest. However, the magnitude of these ranges necessitated the incorporation of "residual" Le and θ_w dependences into the factors C, according to the simple (two term polynomial) forms:

$$[C_{1,rp}(\theta_w)]_{Le=\text{constant}} = D_0 + D_1 \theta_w \quad (4.1)$$

$$[C_{td}(\theta_w)]_{Le,\alpha=\text{constant}} = E_0 + E_1 \theta_w. \quad (4.2)$$

The values of the resulting constants (D_0, D_1, E_0, E_1) are given in Table 4 for the various species and wall-temperature ratios considered in this study. Note that the coefficients appearing in equations (4.1) and (4.2) are specific to a given binary mixture.

It is remarkable that such simple linear fits are satisfactory for describing all the solutions represented in Table 4. Of course, under conditions such that the source term F_s becomes significantly greater than unity, it is possible that such simple fits would have to be generalized (e.g., using higher order polynomials).†

Having established the required "correlating factors", to use the correlation scheme presented in this paper one goes through the following steps:

S1: For the particular problem being considered establish 'k' from Table 2, or otherwise. Also, evaluate β_1 and β_2 from equations (A1.11) and (A1.12) using known properties of the gas.

S2: Compute the "correlating factor" $C_{1,rp}$ from equation (4.1), using Table 4 and the required θ_w-value.

S3: Using the values of θ_w and Le_e, specified for the problem, compute the variable property correlation ratio F_{rp} from equation (3.7) and the supplementary relations (i.e., equations (3.10) and (A1.15)–(A1.21)).

S4: The thermal diffusion correlation, which consists of a "blowing" part F_{td} and a "source" part F_s can also be simply computed. F_{td} is determined from equation (3.12), using equation (4.2) and Table 4 to supply the required value of C_{td}.

S5: To establish the source correction factor F_s it is necessary to evaluate the quantities α_* and

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† A numerical experiment aimed at testing this hypothesis was conducted by considering "imaginary" trace species with α values an order of magnitude higher than those shown in Fig. 1, for the "hot" wall temperatures. The results revealed values of F_s as high as ten and it was found unjustifiable to continue assuming that the suction and source effects of thermal diffusion are separable, as done in this study. Alternatives more in keeping with the philosophy of the present correlation are presently being investigated for these extreme "hot" wall cases (near the blowoff limit discussed later) and will be reported elsewhere.

Le_* first. α_* is found from equation (3.15) (using Table 3), Le_* from equation (A1.10). These quantities correspond to the reference temperature θ_*, already found in Step 3. Next, from Table 1, establish whether a source or sink prevails and use the above information to evaluate F_s from equations (3.22) or (3.23). The supplementary relations for the various quantities involved in the expression for F_s are provided by equations (3.24)–(3.26).

S6: Knowing F_{vp}, F_{td} and F_s, the "overall" correlation ratio for thermal diffusion alone (i.e., F_{tdo}) and the "composite" ratio for the combined effects of variable properties and thermal diffusion (i.e., F) are obtained from equations (3.27) and (3.29), respectively.

A useful byproduct of the variable property correlation scheme, as formulated in Section 3.1, is the extension of the mass-heat transfer analogy to wall temperature ratios significantly different from unity. As is well known, in the absence of variable properties and diffusion–conduction interactions, if $Le = 1$ then the nondimensional heat and mass transfer coefficients across the boundary layer are equal, provided the respective boundary conditions are similar. The restrictions of constant properties, and unit Lewis number are now relaxed in the analogy given by equation (3.6); that is, C_{mh} is a calculable function of both θ_w and Le_* (cf. equation (3.10), following the procedure of Steps 2 and 3 above). Figure 3 shows the resulting variation of C_{mh} for the various θ_w and Le_e values considered in this study. One notes that when $\theta_w < 1$, $\dot{m}''$ is a smaller fraction of $\dot{m}''_{cp}$ than the corresponding heat transfer ratio. Thus, variable property effects influence mass transfer predictions somewhat more strongly than heat transfer predictions.

To illustrate the success of the present mass transfer correlation scheme we consider here relative errors in the "composite" transfer ratio $F \equiv \dot{m}''/\dot{m}''_{cp}$ accounting, respectively, for variable properties and thermal (Soret) diffusion. Figure 4 shows the deviations in $1-F$ from the corresponding numerically computed boundary layer solution, $1-F_{BL}$, for the transport of metal halide containing vapor species to a "hot" wall ($1.0 < \theta_w < 4.5$). It can be seen from this figure that the values of $1-F$ predicted *via* the present correlation scheme are accurate to better than $\pm 10\%$. Interestingly enough, the corresponding individual correlations for F_{vp} and F_{tdo} $(= F_{td}F_s)$ are even more successful. Similar accuracy was achieved in the "cold" wall cases also (not shown for the sake of brevity). The correlation scheme predicted mass transfer rates which were accurate to within two decimal places.

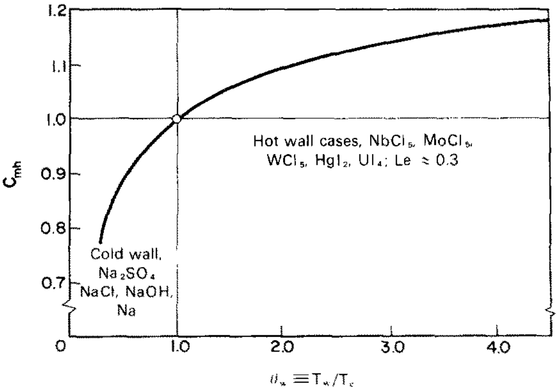

FIG. 3. Variation of $C_{mh}(\theta_w, Le)$ for various species under "hot" and "cold" wall conditions.

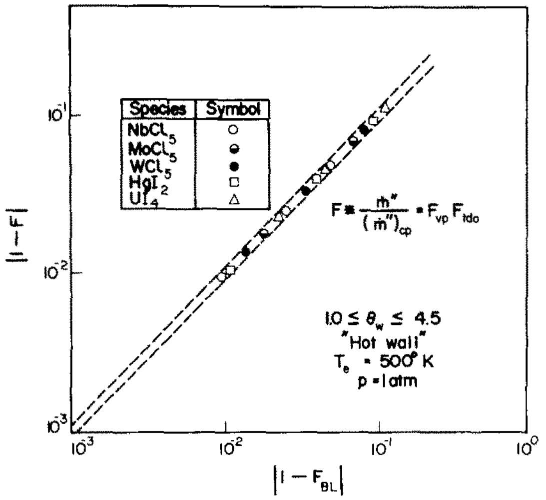

FIG. 4. Comparison of the composite correlation, F, vs the corresponding boundary layer solution, F_{BL} (including variable properties and thermal diffusion), for the "hot" wall case (log–log plot).

As pointed out in Section 1, the species explicitly considered in this study were selected based on their relevance to gas turbine and chemical vapor deposition applications. Accordingly, we considered various sodium salt–air mixtures for the "cold" wall cases, and several heavy metal halide–air (or N_2) mixtures for the "hot" wall cases. Because of molecular weight and size differences we encounter a rather wide variation of the transport coefficients for mass diffusion (i.e., D and α). Consequently, the sodium salt–air mixtures cover a wide range of Lewis numbers (about 0.3 to 0.9) with most of the heavy metal halide–air mixtures having Le values near 0.3. However, these heavy metal halides are characterized by much larger α-values than those of the sodium salt–air mixtures (see also Fig. 1). As a result, it is interesting that the actual $UI_4(g)$ transport rate to a "hot" wall in H_2 (with $\theta_w = 4$) can be reduced to about 50% of that expected from a variable property analysis neglecting thermal (Soret) transport away from the wall.† These results suggest

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† Interestingly enough, variable property effects partially offset those due to Soret transport, with the result that the simultaneous neglect of *both* thermal diffusion and variable properties incurs an error of "only" 18%. Thus, "improved" calculations which include only one effect (e.g., variable properties) will lead to intolerably great errors (*ca.* 50%, cited above).

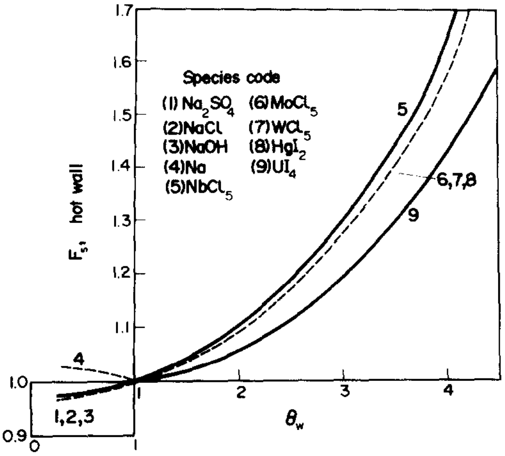

FIG. 5. Variation of the "source" correction factor F_s with wall temperature ratio θ_w for the "hot" and "cold" wall cases.

that the entire area of CVD transport [3] should be reexamined in the light of appreciable thermal (Soret) diffusion [20, 21] as well as the more familiar variable property effects.

Figure 5 shows the wall temperature dependence of the source effect of thermal diffusion (F_s defined by equation (3.16)). Interestingly enough, while the effect of the "sink" (for $\alpha > 0$) is negligibly small for the cold wall cases, in the "hot" wall case the effect of the "source" can be very significant. This trend can be anticipated from the expression for the effective homogeneous rate constant K (equation A3.9), which predicts large values when both the thermal diffusion factors and temperature gradients (i.e., α and θ_w values) are large. The "source" and "sink" effects anticipated due to thermal diffusion were confirmed by the detailed numerical solution of the relevant boundary layer equations. Figure 6 shows typical mass fraction profiles computed for both "cold" ($\theta_w = 0.7$, $Na_2SO_4(g)$-transport) and "hot" ($\theta_w = 4$, $WCl_5(g)$ transport) walls.

In view of the possibility of large "blowing" effects associated with either thermal diffusion and/or variable properties, it is instructive to consider the possible limit of the species boundary layer "blowoff". By the term "blowoff" we mean the condition of zero wall mass transfer rate (despite the presence of a non-vanishing concentration driving force). The present correlation scheme allows one to estimate this "blowoff" condition, explicitly, based on each of the "blowing" influences associated with thermal diffusion and/or variable properties. Thus by formally equating F_{vp} and F_{td_0} to zero equations (3.1) and (3.12) lead to the following boundary layer "blowoff" limits,

$$(B_{\text{eff,bo}})_{vp} = (C_{1,vp})^{-1} \tag{4.3}$$

$$(B_{\text{eff,bo}})_{td} = (C_{td})^{-1}. \tag{4.4}$$

So long as $B_{\text{eff}} < (B_{\text{eff,bo}})$ "blowoff" does not occur and the present correlation scheme is presumed valid. Under the conditions of the present study it was found that blowoff due to either variable properties or thermal diffusion did not occur in any of the cold or hot wall cases considered in this paper. As mentioned earlier, such blowoff limits provide an upper bound for the validity of correlation schemes like the present one.†

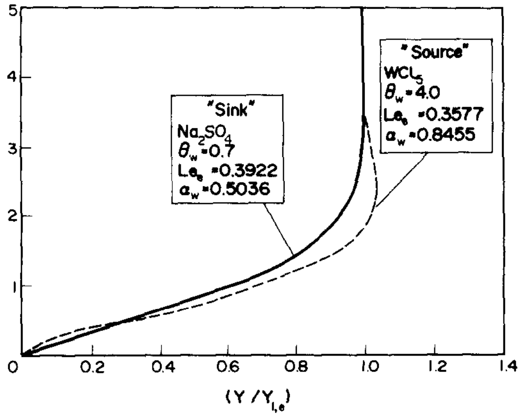

FIG. 6. Numerically computed mass fraction profiles for typical "hot" and "cold" wall cases.

5. CONCLUSIONS

Algebraic relations are proposed to economically summarize the results of a large number of numerical solutions of the coupled laminar boundary layer equations, complicated by the phenomena of thermal (Soret) diffusion and/or variable properties. Specifically, for forced convection laminar boundary layer flow:

(a) In the absence of thermal (Soret) diffusion, the pseudo-"suction" or "blowing" effects of variable properties were identified and successfully correlated with the numerically computed wall mass transport rate.

(b) Using this variable property correlation the heat-mass transfer analogy has also been extended to include the effects of variable properties for a wide range of Lewis numbers and wall temperature ratios.

(c) By separately accounting for the pseudo-suction and source behavior associated with thermal (Soret) diffusion, a successful correlation of thermal diffusion effects on mass transport rates has been developed.

While this scheme has been applied to the correlation/prediction of mass transport rates here, a similar approach could evidently be used for correlation energy and momentum transfer rates. The general procedure we have outlined may be visualized as rationally accounting for special phenomena (e.g. thermal diffusion and variable properties)

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†Calculations based on hypothetical α-values one order of magnitude greater than the present ones yielded mass transfer ratios, F_{td_0}, as small as 10^{-3}, corresponding to the approximate blowoff limit. Note that these remarks do not necessarily imply blowoff with respect to the velocity boundary layer, a condition conventionally discussed.

in terms of appropriate "blowing" and/or source-like effects which make their appearance in the governing conservation equations. These identifiable effects are then superimposed upon the corresponding "constant property"-solid wall boundary layer, for which solutions are readily available in both forced and free convection situations. A similar strategy might be used in the future to correlate the systematic effects of other intervening boundary layer phenomena (viscous dissipation, simple chemical reactions, diffusion-thermo effects, etc.), at least for simple boundary conditions [22].

In retrospect it might be thought that since correlations are certainly not unique, alternate and perhaps simpler-to-use previously proposed "curve fits" (with no particular basis in the underlying conservation equations) would be equally successful and more "practical". However, it is likely that schemes such as that exploited above, motivated by the presence of identifiable new terms in the more general (boundary layer) conservation equations, will be more efficient, and safer to extrapolate, than their more arbitrary counterparts. While the details of implementation will differ from case to case and investigator to investigator, we believe that as a correlation strategy the present approach has considerable potential.

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APPENDIX 1. FORM OF THE VARIABLE PROPERTY EFFECTIVE BLOWING PARAMETER

The following considerations suggest a useful functional form for the effective blowing parameter associated with variable properties (*vp*). Once this functional form is specified, a "library" of specific exact computer solutions can then be used to specify the undetermined coefficients appearing in the "pseudo-blowing" correlation.

In order to satisfy the obvious physical requirement that $F_{vp} \equiv \dot{m}''_{vp}/(\dot{m}'')_{cp}$ should be unity in the absence of variable property effects, it is necessary to define $B_{\mathrm{eff},vp}$ as:

$$B_{\mathrm{eff},vp} \equiv \left[\left(\frac{\bar{v}_{\mathrm{eff}}\delta_m}{D}\right)_{vp} - \left(\frac{\bar{v}_{\mathrm{eff}}\delta_m}{D}\right)_{cp}\right], \qquad \text{(A1.1)}$$

where

$$(\bar{v}_{\mathrm{eff}})_{vp} \equiv \bar{v}_{vp} - (\bar{v}_s)_{vp} \qquad \text{(A1.2)}$$

$$(\bar{v}_{\mathrm{eff}})_{cp} \equiv \bar{v}_{cp}. \qquad \text{(A1.3)}$$

In the above equations note that $\bar{v}$ is the y-component of velocity averaged over the thickness of the transferred species boundary layer, while $(\bar{v}_s)_{vp}$ is the averaged suction velocity produced by variable properties alone (i.e., $(1/\rho)(\partial(\rho D)/\partial y)$, as seen from equation (2.11a)). The motivation for the choice of the grouping $\bar{v}\delta_m/D$, which is a Peclet number based on the species boundary layer thickness (δ_m), comes from approximating the full species equation (i.e., equation (2.11)) by the following Couette-type equation:

$$\rho \bar{v}_B \frac{dY_1}{dy} = \rho D \frac{d^2 Y_1}{dy^2}. \tag{A1.4}$$

The solution of this equation on the domain $0 \leqslant y \leqslant \delta_m$ can be obtained directly in terms of the governing Peclet group, $\bar{v}_B \delta_m / D$. This type of a Couette flow analogy has been widely used for analytically approximating certain boundary layer characteristics (e.g., [8] and [13]).

From equations (A1.1), (A1.2) and (A1.3) we observe that

$$B_{\mathrm{eff},vp} = \Delta(Pe_\delta) - \left(\frac{\bar{v}_s \delta_m}{D}\right)_{vp} \tag{A1.5}$$

where

$$\Delta(Pe_\delta) \equiv (\bar{v}\delta_m/D)_{vp} - (\bar{v}\delta_m/D)_{cp}, \tag{A1.6}$$

and

$$\bar{v}_s = \overline{\frac{1}{\rho}\frac{\partial(\rho D)}{\partial y}}. \tag{A1.7}$$

This "shift" in the Peclet group (i.e., $\Delta(Pe_\delta)$) accounts for the possible "offsetting" of the suction effect of variable properties (mentioned in Section 2) produced by changes in the real normal fluid velocity.

To proceed, we express $\Delta(Pe_\delta)$ and $(\bar{v}_s \delta_m / D)_{vp}$ in terms of more convenient quantities, noting that the terms subscripted 'cp' may be evaluated at 'e', the thermal boundary layer edge. For convenience only, the variable property (or 'vp' subscripted) terms in the effective blowing parameter will be evaluated using a "reference temperature"† (T_*), taken to be the arithmetic average temperature within the species boundary layer, i.e., $T_* \equiv (T_w + T_m)/2$. Now, by approximating the temperature at the species boundary layer edge, T_m, using the relation‡

$$\frac{\delta_m}{\delta_T} \cong \frac{T_m - T_w}{T_e - T_w} \cong (Le_{vp})^\varepsilon, \tag{A1.8}$$

the dimensionless reference temperature is given by equation (3.3) where $\theta \equiv T/T_e$. Also, since the following dimensional argument is valid under typical boundary layer assumptions: $\bar{v} \sim \bar{u}\delta_v/x \sim u_m \delta_v/x \sim u_e \delta_m/x$ and $\delta_m/x \sim (Re_x)^{-1/2}(Sc)^{-\varepsilon}$ we see that $\bar{v}\delta_m/D \sim (Sc)^{1-2\varepsilon}$.

Next, we assume for simplicity that the temperature dependencies of the density, specific heat and transport coefficients can be adequately represented by the simple power-law relations:§ $\rho/\rho_e = \theta^{-1}$; $c_p/c_{p,e} = \theta^{\alpha_1}$; $\mu/\mu_e = \theta^\omega$; $\lambda/\lambda_e = \theta^{\varepsilon_1}$; $D/D_e = \theta^n$.

On this basis the Schmidt and Lewis number ratios (needed below) can be written:

$$\frac{Sc_{vp}}{Sc_{cp}} = \frac{Sc_*}{Sc_e} = \left(\frac{1}{\theta_*}\right)^{\beta_1} \tag{A1.9}$$

$$\frac{Le_{vp}}{Le_{cp}} = \frac{Le_*}{Le_e} = (\theta_*)^{\beta_2}, \tag{A1.10}$$

where

$$\beta_1 \equiv n - 1 - \omega \tag{A1.11}$$

$$\beta_2 \equiv \alpha_1 + n - 1 - \varepsilon_1. \tag{A1.12}$$

Equations (A1.6)–(A1.12) suggest that the "Peclet shift" can be written as:

$$\Delta(Pe_\delta) = C_{2,vp}\left[(Le_e)^{2\varepsilon-1}\left\{\left(\frac{1}{\theta_*}\right)^{\beta_1(1-2\varepsilon)} - 1\right\}\right], \tag{A1.13}$$

where $C_{2,vp}$ is a multiplying factor determined later. In terms of these same quantities the variable property suction term can be expressed:

$$\left(\frac{v_s \delta_m}{D}\right)_{vp} = \left\{\frac{\delta_m}{\rho D}\frac{\partial(\rho D)}{\partial y}\right\}_{vp} \cong (n-1)\left(\frac{\theta_* - \theta_w}{\theta_*}\right). \tag{A1.14}$$

Substituting equations (A1.13) and (A1.14) into equation (A1.1), we finally obtain equation (3.2).

Coefficients relating the factors $C_{1,vp}$, $C_{2,vp}$ *and* C_{mh}

Equations (3.5)–(3.8), when combined with the explicit estimates above, lead to equations (3.9), (3.10), where

$$A_1 \equiv 1 - \theta_w^k \tag{A1.15}$$

$$A_2 \equiv \frac{(n-1)(1/\theta_w - 1)(Le_e)^\varepsilon(\theta_1)^{\beta_2\varepsilon}}{2 + (1/\theta_w - 1)(Le_e)^\varepsilon(\theta_1)^{\beta_2\varepsilon}} \tag{A1.16}$$

$$A_3 \equiv (Le_e)^{2\varepsilon-1}\{(\theta_1)^{\beta_1(2\varepsilon-1)} - 1\} \tag{A1.17}$$

$$A_4 \equiv 1 - \frac{A_1}{A_3}(Le_e)^{2\varepsilon-1}\{(\theta_*)^{\beta_1(2\varepsilon-1)} - 1\} \tag{A1.18}$$

$$A_5 \equiv \left[\frac{(n-1)(1/\theta_w - 1)(Le_e)^\varepsilon(\theta_*)^{\beta_2\varepsilon}}{2 + (1/\theta_w - 1)(Le_e)^\varepsilon(\theta_*)^{\beta_2\varepsilon}}\right] - \frac{A_2}{A_3}(Le_e)^{2\varepsilon-1}\{(\theta_*)^{\beta_1(2\varepsilon-1)} - 1\} \tag{A1.19}$$

$$\theta_* \cong \theta_w + \tfrac{1}{2}(1 - \theta_w)(Le_e)^\varepsilon \tag{A1.20}$$

$$\theta_1 \equiv (\theta_*)_{Le_{vp}=1} \cong \theta_w + \tfrac{1}{2}(1 - \theta_w). \tag{A1.21}$$

For a given wall temperature ratio, θ_w, and Lewis number, Le_e, these interrelations essentially complete one form of the proposed variable property correlation scheme except for the as yet undetermined "correlating factor", $C_{1,vp}$, multiplying the effective blowing parameter.

APPENDIX 2. NUMERICAL SOLUTION PROCEDURE

The system of differential equations governing the compressible, laminar boundary layer problem outlined in Section 2 was solved by first casting the equations into their "incompressible" form *via* the well-known Howarth–Dorodnitsyn–Lees transformations:

$$\xi \equiv \int_0^x \rho_e \mu_e u_e \, dx'$$

$$\eta \equiv \frac{u_e}{(2\xi)^{1/2}} \cdot \int_0^y \rho \, dy'.$$

We then seek "similar" solutions for the non-dimensional momentum, energy and concentration dependent variables: $f(\eta) \equiv (2\xi)^{-1/2}\psi$; $\theta(\eta) \equiv h_t/h_{t,e}$; $Y_i(\eta) \equiv Y_i/Y_{i,e}$.

Upon eliminating the need for the overall mass conservation equation by introducing the stream function ψ, the resulting coupled system of ordinary† differential

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†It is not essential to our approach that the "reference temperature method" be used at this juncture. One may view it as one of several possible methods for motivating an appropriate form for the equivalent blowing parameter appearing in equations (3.1) and (3.13).

‡It can be easily shown through an order of magnitude analysis of the terms in the energy and species equations that ε varies from only 1/3 to 1/2 in the range $0 \leqslant Le \leqslant \infty$. More exact estimates [13] are also available for various specific flow conditions. For the results presented below ε was taken to be 0.4.

§For air in the temperature range $588 < T < 1588$ K and at pressures in the ideal-gas law range (cf. equation (A1.12)) we may take [19] $\alpha_1 = 0.19$, $\omega \approx 0.65$, $\varepsilon_1 \approx 0.85$, $n \approx 1.652$ so that $\beta_1 = 0.002$ and $\beta_2 = -0.008$. Smallness of α_1 eliminates the need to distinguish between *temperature* ratio and *enthalpy* ratio in the low speed boundary layer situations discussed here.

†Primed quantities denote differentiation with respect to the similarity variable η defined above.

Table A2.1. Numerically computed wall eigenvalues for the plane stagnation point flow ($\beta = 1$) of various mixtures

Momentum and energy eigenvalues

θ_w	0.4	0.6	0.8	1.0	2.0	3.0	4.0
$f''(0)$	1.0051	1.1031	1.1755	1.2333	1.4226	1.5408	1.6283
$\theta'(0)$	0.2349	0.1746	0.0940	0	−0.5857	−1.2818	−2.0447

Species eigenvalues†

Species \ θ_w	04.	0.6	0.8	1.0	2.0	3.0	4.0
Na_2SO_4	0.5803	0.6543	0.6929	0.7139			
	0.5682	0.6306	0.6769	0.7139			
NaCl	0.5148	0.5717	0.6081	0.6335			
	0.5017	0.5580	0.5999	0.6335			
NaOH	0.4760	0.5287	0.5651	0.5929			
	0.4685	0.5217	0.5611	0.5929			
Na	0.4240	0.4736	0.5114	0.5422			
	0.4267	0.4759	0.5127	0.5422			
$NbCl_5$				0.7107	0.7283	0.7040	0.6763
				0.7107	0.8308	0.9052	0.9599
$MoCl_5$				0.7356	0.7484	0.7178	0.6849
				0.7356	0.8591	0.9356	0.9918
WCl_5				0.7390	0.7490	0.7148	0.6791
				0.7390	0.8631	0.9398	0.9963
HgI_2				0.7480	0.7558	0.7177	0.6789
				0.7480	0.8733	0.9508	1.0078
UI_4				0.8022	0.8203	0.7659	0.7112
				0.8022	0.9348	1.0169	1.0773

† The two eigenvalues indicated for each species correspond to $\alpha \neq 0$ and $\alpha = 0$ respectively (i.e., with and without thermal diffusion).

equations can be written:

Momentum

$$f''' + \left\{\theta^{n_3} f - n_3 \frac{\theta'}{\theta}\right\} f'' = \beta\theta^{n_3}[(f')^2 - \theta] \qquad \text{(A2.1)}$$

Energy

$$\theta'' - n_1 \frac{(\theta')^2}{\theta} + Pr_e \theta^{n_1} f\theta' = 0 \qquad \text{(A2.2)}$$

Species 1

$$\tilde{Y} Y_1'' + \tilde{Y} Y_1' + \Phi Y_1 = 0, \qquad \text{(A2.3)}$$

where:

$$\tilde{Y} \equiv Sc_e \theta^{n_2} \left\{ f + \frac{\alpha\theta'}{Sc_e \theta^{n_2+1}} \right\} - n_2 \frac{\theta'}{\theta} \qquad \text{(A2.3a)}$$

$$\Phi = \frac{\alpha}{\theta} \left[\theta'' - \left\{ n_2 + 1 + \frac{(\alpha_{-1}/\alpha_\infty)}{\theta T_e + (\alpha_{-1}/\alpha_\infty)} \right\} \frac{(\theta')^2}{\theta} \right] \text{(A2.3b)}$$

$$\begin{aligned} n_1 &\equiv 1 + \alpha_1 - \varepsilon_1 \\ n_2 &\equiv 2 - n \\ n_3 &= 1 - \omega \\ \beta &\equiv \frac{2m}{m+1} \quad (\text{for } u_e \sim x^m). \end{aligned} \qquad \text{(A2.4)}$$

These equations were solved subject to the following simple boundary conditions:

$$\begin{aligned} & f(0) = 0; \quad f'(0) = 0; \quad f'(\infty) = 1 \\ & \theta(0) = \theta_w \text{ (specified constant)}; \quad \theta(\infty) = 1 \end{aligned} \qquad \text{(A2.5)}$$

$$Y_1(0) = 0; \quad Y_1(\infty) = 1. \qquad \text{(A2.6)}$$

Numerical solution of the system of equations (A2.1)–(A2.6) is simplified considerably by the fact that while the momentum and energy fields are strongly coupled they can be solved independently of the normalized trace species mass fraction Y_1. Thus, for each θ_w-value of interest solutions to the coupled, nonlinear system of momentum and energy equations (i.e., equations (A2.1), (A2.2) and (A2.5)) were first found by one computer code and stored. The method of "quasilinearization" [23] was used for the numerical solutions reported here. These solutions were then used as input to another computer code which employed a modified Hamming predictor-corrector method to solve the linear boundary value problem for the trace species concentration Y_1. The numerical solutions obtained for the coupled momentum and energy equations compared well (correct to 4 decimal places) with those of [24]. Our computation time for each solution was about 18 s (on the Yale Computer Center IBM 370/158), for a given θ_w-value. Table A2.1 gives the numerically computed wall eigenvalues for various trace species–air mixtures near a plane stagnation point, for a range of θ_w values.

APPENDIX 3. FORM OF THE THERMAL DIFFUSION PSEUDO-BLOWING PARAMETER AND PSEUDO-SOURCE CORRECTION

Effective blowing parameter associated with thermal (Soret) diffusion

Following the reasoning of Appendix 1, we write the effective "blowing" parameter in the form of a difference in Peclet numbers:

$$B_{\mathrm{eff},td} = \left[\left(\frac{\bar{v}_{\mathrm{eff}} \delta_m}{D} \right)_{td+vp} - \left(\frac{\bar{v}_{\mathrm{eff}} \delta_m}{D} \right)_{vp} \right] \qquad \text{(A3.1)}$$

with

$$(\bar{v}_{\mathrm{eff}})_{td+vp} = \bar{v}_{vp} - (\bar{v}_s)_{td+vp} \qquad \text{(A3.2)}$$

$$(\bar{v}_{\mathrm{eff}})_{vp} = \bar{v}_{vp} - (\bar{v}_s)_{vp}. \qquad \text{(A3.3)}$$

Since equation (2.11a) suggests that $(\bar{v}_s)_{td+vp} = (\bar{v}_s)_{vp} + (\bar{v}_s)_{td}$ one obtains from equation (A3.1), after cancelling terms, the following expression:

$$B_{\mathrm{eff},td} \cong -\left(\frac{\bar{v}_s \delta_m}{D} \right)_{td}. \qquad \text{(A3.4)}$$

The effect of thermal diffusion is included in $(\bar{v}_s)_{td}$, the averaged suction velocity due to thermal diffusion alone.

Moreover, from equation (2.11a), the suction velocity due to thermal diffusion is given by

$$(v_s)_{td} = D\alpha \overline{\frac{\partial \ln T}{\partial y}}. \qquad \text{(A3.5)}$$

It therefore follows that:

$$\left(\frac{\bar{v}_s \delta_m}{D} \right)_{td} \cong \alpha_* \left(\frac{\theta_* - \theta_w}{\theta_*} \right). \qquad \text{(A3.6)}$$

Using the above relation (equation (A3.6)) one may now express the effective blowing parameter associated with thermal diffusion, $B_{\mathrm{eff},td}$ in terms of the pertinent variables in the form of equation (3.13).

Effective Damköhler number associated with pseudo-homogeneous reaction

As discussed in Sections 2 and 3 we anticipate that the pseudo-source effects of thermal (Soret) diffusion can be correlated in terms of a Damköhler group, $\beta\delta_m$, interpretable as the square root of the ratio of a characteristic diffusion time to a characteristic pseudo-chemical reaction time. To implement this idea so that quantitative estimates of the pseudo-source ("reaction" factor) effect, F_s (equations (3.22) and (3.23)) can be obtained, it is necessary to relate $\beta\delta_m$ to the known parameters of our problem. For this purpose the following estimation procedure was tentatively adopted.

Consider first the average value of the pseudo homogeneous rate constant K (over the species boundary layer thickness). From equation (2.12) we have:

$$\bar{K} = \overline{\frac{1}{\rho}\frac{\partial}{\partial y}\left\{\rho D\alpha\frac{\partial \ln\theta}{\partial y}\right\}} \cong \alpha_*\overline{\left\{\frac{1}{\rho}\frac{\partial}{\partial y}\rho D\frac{\partial \ln\theta}{\partial y}\right\}}. \quad \text{(A3.7)}$$

Expanding the right hand side of equation (A3.7) using the fact that $\rho D \sim T^{n-1}$, one obtains:

$$\bar{K} \cong \alpha_* D_* \theta_*^{n-1}\left[\overline{\frac{\partial^2\theta}{\partial y^2}} + \frac{(n-2)}{\theta_*}\left(\overline{\frac{\partial\theta}{\partial y}}\right)^2\right]. \quad \text{(A3.8)}$$

Remembering that the species layer thickness, δ_m, is different from the thermal layer thickness, δ_T, the derivatives appearing in the above equation may be approximated as:

$$\overline{\frac{\partial^2\theta}{\partial y^2}} \cong \frac{1}{2}\left[\left(\frac{\partial^2\theta}{\partial y^2}\right)_m + \left(\frac{\partial^2\theta}{\partial y^2}\right)_w\right] \quad \text{(A3.9)}$$

$$\overline{\frac{\partial\theta}{\partial y}} \cong \frac{1}{2}\left[\left(\frac{\partial\theta}{\partial y}\right)_m + \left(\frac{\partial\theta}{\partial y}\right)_w\right], \quad \text{(A3.10)}$$

with

$$\left(\frac{\partial^2\theta}{\partial y^2}\right)_m \cong \frac{\left(\frac{\partial\theta}{\partial y}\right)_e - \left(\frac{\partial\theta}{\partial y}\right)_m}{\delta_T - \delta_m} \quad \text{(A3.11)}$$

$$\left(\frac{\partial^2\theta}{\partial y^2}\right)_w \cong \frac{\left(\frac{\partial\theta}{\partial y}\right)_m - \left(\frac{\partial\theta}{\partial y}\right)_w}{\delta_m}. \quad \text{(A3.12)}$$

Moreover,

$$\left(\frac{\partial\theta}{\partial y}\right)_e = 0; \quad \left(\frac{\partial\theta}{\partial y}\right)_m \cong \frac{(1-\theta_m)}{\delta_T - \delta_m}; \quad \left(\frac{\partial\theta}{\partial y}\right)_w \cong \frac{\theta_m - \theta_w}{\delta_m}.$$

Combining these estimates, the relevant pseudo-Damköhler number can be written as equation (3.24), which was used in the correlations reported in Section 4 and Fig. 5.

UNE APPROCHE NOUVELLE DU TRANSFERT MASSIQUE EN COUCHE LIMITE AVEC DIFFUSION THERMIQUE ET PROPRIETES VARIABLES

Resume—On degage une approche rationnelle de l'expression du transport massique de couche limite, applicable à de nombreuses conditions d'écoulement laminaire fréquemment rencontrées, avec diffusion thermique et propriétés variables. Le schéma est construit sur les solutions de soufflage/succion avec propriétés constantes, en introduisant des facteurs correctifs appropriés pour tenir compte des effets aditionnels ("pseudo soufflage et source), identifiés avec les propriétés variables et la diffusion thermique. Des applications au problème particulier de transfert massique en couche limite laminaire montrent une précision satisfaisante jusqu'à des facteurs de soufflage de l'ordre du tiers du seuil critique. En application de la corrélation avec propriétés variables, l'analogie des transferts de chaleur et de masse est élargie, pour un grand domaine du nombre de Lewis, en incluant les effets des propriétés variables.

EIN NEUES VERFAHREN ZUR BERECHNUNG DES STOFFÜBERGANGS IN DER GRENZSCHICHT BEI THERMODIFFUSION UND/ODER VARIABLEN STOFFWERTEN

Zusammenfassung—Es wird ein rationelles Verfahren für die Berechnung des Stoffübergangs in der Grenzschicht entworfen, das auf viele allgemein anzutreffende laminare Strömungsbedingungen mit Thermodiffusion und/oder variablen Stoffwerten angewandt werden kann. Das Berechnungsverfahren baut auf bereits bestehenden Verfahren für konstante Stoffwerte bei Ausblasen bzw. Absaugung auf. Dabei werden geeignete Korrekturfaktoren eingeführt, die die zusätzlichen Einflüsse ("pseudo" Ausblasen und Quelle) berücksichtigen, die bei variablen Stoffwerten und Thermodiffusion auftreten. Die Anwendungen des Schemas auf die hier betrachteten besonderen Stoffübergangsprobleme bei laminarer Grenzschicht (Alkali- und Übergangs-Metallgemisch-Dampftransport) zeigen zusriedenstellende Genauigkeit bis zu effektiven Ausblasfaktoren, die etwa einem Drittel des "Abblaswertes" entsprechen. Als nützliches Nebenergebnis des Verfahrens bei variablen Zustandsgrößen erweitern wir die Wärme- und Stoffübergangsanalogie für einen großen Bereich der Lewis–Zahl, um die Einflüsse der variablen Stoffwerte mitzuerfassen.

НОВЫЙ ПОДХОД К КОРРЕЛЯЦИИ СКОРОСТЕЙ ПЕРЕНОСА МАССЫ В ПОГРАНИЧНОМ СЛОЕ ПРИ НАЛИЧИИ ТЕРМИЧЕСКОЙ ДИФФУЗИИ И ПЕРЕМЕННЫХ СВОЙСТВАХ

Аннотация — Предложен практический подход к установлению критериальных зависимостей процесса переноса массы в пограничном слое, который можно использовать во многих обычно встречающихся случаях ламинарного течения при наличии термической диффузии и/или переменных свойств жидкости. Принцип построения зависимостей базируется на имеющихся решениях для вдува/отсоса жидкости с постоянными свойствами, в которые включены соответствующие поправочные коэффициенты для учета влияния переменных свойств жидкости и термической диффузии («псевдовдув» и источник тепла). Предложенный подход в приложении и определенным, рассматриваемым в настоящей работе, задачам переноса массы в ламинарных пограничных слоях (перенос паров соединений щелочных и переходных металлов) дает хорошее совпадение результатов вплоть до значений эффективных коэффициентов вдува, равных 1/3. Кроме того, предлагаемый подход позволяет обобщить аналогию тепломассопереноса в широком диапазоне значений числа Льюиса на случай переменных свойств жидкости.