Simultaneous Energy and Mass Transfer in the Laminar Boundary Layer with Large Mass Transfer Rates Toward the Surface

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The laminar boundary-layer equations are solved asymptotically for simultaneous mass and energy transfer in a variable property binary gas mixture when one component is rapidly transferred toward the surface. Flow is past a surface of arbitrary geometry, and both forced and free convection are studied. Advantage is taken of a mole fraction formulation of the boundary-layer equations, which considerably simplifies the final results. General results are obtained for energy and mass transfer rates when physical properties are arbitrary functions of both temperature and composition. By considering two sets of property variations, representing extremes between which many actual variations lie, it is shown that in many forced convection problems the rates of energy and mass transfer can be expressed in a particularly simple form. The results also show that property variations are generally more important for free convection than for forced convection.

Problems in simultaneous heat and mass transfer have been of considerable contemporary interest. Because of a wide interest in missile cooling and related problems, work has been primarily concerned with mass injection from the surface into the fluid. Processes involving mass transfer toward the surface, on the other hand, have received relatively little attention. Oxidation of surface material or condensation through a noncondensing gas are important examples of this kind of process.

Koh and Harnett (*8*) have given numerical results for constant property simultaneous heat and mass transfer in wedge flows having a Lewis number of unity. Stewart and Prober (*15*) gave results for the same situation which include the effect of Lewis number. Acrivos (*1*) has presented analytical results for isothermal diffusion in laminar boundary-layer flow of a binary mixture past a body of arbitrary geometry. His analysis was performed for one component diffusing through a stagnant component, transfer occurring from the fluid to the surface. Under conditions of asymptotically large interfacial velocities, the boundary-layer equations were solved in a closed form, even when fluid properties vary with composition. For constant properties, the solution has a particularly simple form. Although this simple result is strictly only valid asymptotically, it gives surprising accuracy even for a zero interfacial velocity. Stewart (*14*) has discussed the modification of Acrivos' result for certain heat transfer problems.

The objective of the present investigation is to consider in some detail the effects of variable fluid properties on heat transfer with simultaneous mass transfer toward the surface. In view of the success of Acrivos' isothermal diffusion results with regard to both generality and engineering accuracy, analogous asymptotic results are sought for simultaneous mass and energy transfer with arbitrarily temperature and composition dependent properties. Advantage is taken of the mole fraction formulation of the conservation equations, which leads to greatly simplified results in many cases of practical interest.

USE OF MOLE FRACTIONS

The laminar boundary-layer equations for simultaneous transfer of material and energy in a binary mixture represent the conservation of mass, momentum, species, and energy in a differential volume element under the assumption of large Reynolds number. With few exceptions, transport investigations have been conducted with these equations expressed in terms of mass fraction quantities, for example, mass density, mass average velocity. However, in many instances a formulation of the boundary-layer equations based on molar quantities is more tractable mathematically than the corresponding mass fraction formulation. Recently, Stewart (*13*) and Hanna (*6*) have taken advantage of this approach for certain isothermal diffusion problems. Molar quantities will be used in this investigation, and it will be shown that their use leads to important simplifications in the final results. In order to proceed with a minimum of notational difficulty, dimensionless variables will be used with subscripts 1 and 2, respectively, referring to quantities appropriate for forced and free convection. The continuity, energy, and diffusion equations, Equations (5), (6), and (7), are written without subscripts, since they apply for either forced or free convection when appropriate subscripts are used.

The relationship between mass and molar average velocities is given by Bird, Stewart, and Lightfoot (2). These relations are given here in dimensionless form, where it can be seen that $u = u^*$ and $v = v^*$ when the molecular

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weight is constant:

$$u_1 = u_1^* - \frac{D}{M}\,\frac{(M_w - 1)}{N_{Re}N_{Sc}}\,\frac{\partial X}{\partial x_1} \qquad (1)$$

(Forced convection)

$$v_1 = v_1^* - \frac{D}{M}\,\frac{(M_w - 1)}{N_{Sc}}\,\frac{\partial X}{\partial y_1} \qquad (2)$$

$$u_2 = u_2^* - \frac{D}{M}\,\frac{(M_w - 1)}{N_{Sc}N_{Gr}^{1/2}}\,\frac{\partial X}{\partial x_2} \qquad (3)$$

(Free convection)

$$v_2 = v_2^* - \frac{D}{M}\,\frac{(M_w - 1)}{N_{Sc}}\,\frac{\partial X}{\partial y_2} \qquad (4)$$

Equations (1) to (4) hold for both composition and temperature variations. These equations are similar to those given in reference *6* for isothermal diffusion.

Using the above definitions in the usual continuity, energy and diffusion equations, and eliminating higher-order terms in Reynolds number we obtain the following system of boundary-layer equations in terms of molar quantities:
(Continuity)

$$\frac{\partial cu^*}{\partial x} + \frac{\partial cv^*}{\partial y} = 0 \qquad (5)$$

(Energy)

$$cC_p{}^*\left(u^*\frac{\partial \theta}{\partial x} + v^*\frac{\partial \theta}{\partial y}\right) = \frac{1}{N_{Pr}}\frac{\partial}{\partial y}\left(k\frac{\partial \theta}{\partial y}\right) + \frac{cD}{N_{Sc}}\left[C^*_{p_{x_{w,\theta}}} - C^*_{p_{x_{x,\theta}}}\right]\frac{\partial \theta}{\partial y}\,\frac{\partial X}{\partial y} \qquad (6)$$

(Diffusion)

$$c\left(u^*\frac{\partial X}{\partial x} + v^*\frac{\partial X}{\partial y}\right) = \frac{1}{N_{Sc}}\,\frac{\partial}{\partial y}\left(cD\frac{\partial X}{\partial y}\right) \qquad (7)$$

These equations apply for either forced or free convection when subscripts 1 or 2 are used for u^*, v^*, and y. The last term in Equation (6) accounts for energy transfer by ordinary diffusion. In this analysis we assume a binary perfect gas mixture, no chemical reactions, and radiation or thermodynamic coupling. The body is also assumed not to change shape owing to mass transfer. For axisymmetric flows, Mangler's transformation can be used. Consideration is given to flows at small Mach numbers, although higher Mach number results for the flat plate will be quoted.

The forms of the boundary-layer momentum equation are different for forced and free convection; the appropriate equations are
(Forced)

$$cM\left(u_1^*\frac{\partial u_1^*}{\partial x_1} + v_1^*\frac{\partial u_1^*}{\partial y_1}\right) = \frac{\partial}{\partial y_1}\left(\mu\frac{\partial u_1^*}{\partial y_1}\right) + \frac{cD}{N_{Sc}}\,(M_w - 1)\,\frac{\partial X}{\partial y_1}\,\frac{\partial u_1^*}{\partial y_1} + U_1\frac{dU_1}{dx_1} \qquad (8)$$

(Free)

$$cM\left(u_2^*\frac{\partial u_2^*}{\partial x_2} + v_2^*\frac{\partial u_2^*}{\partial y_2}\right) = \frac{\partial}{\partial y_2}\left(\mu\frac{\partial u_2^*}{\partial y_2}\right) + \frac{cD\,(M_w - 1)}{N_{Sc}}\,\frac{\partial X}{\partial y_2}\,\frac{\partial u_2^*}{\partial y_2} + (1 - cM)\sin\epsilon \qquad (9)$$

Boundary conditions:

$$y_{1,2} = \infty;\quad \theta = 0,\quad X = 0,\quad u_1^* = 1,\quad u_2^* = 0$$

$$y_{1,2} = 0,\quad x > 0;\quad u^*{}_{1,2} = 0,$$

$$v^*{}_{1,2} = -\frac{D_wB^*}{N_{Sc}}\,\frac{\partial X}{\partial y_{1,2}}\bigg|_0,\quad \theta = 1,\quad X = 1$$

$$x = 0,\quad y > 0;\quad u_1^* = 1,\quad u_2^* = 0,\quad \theta = 0,\quad X = 0$$

The $v^*{}_w$ boundary condition is obtained from a mass balance at the wall. The temperature and mass fraction are assumed constant along the surface and in the mainstream.

In the treatment of variable property gas mixtures, Equations (5) to (7) possess certain inherent advantages. These advantages stem from the fact that molar concentration is composition independent for a perfect gas and that molar heat capacity is constant or only slightly variable for mixtures of either monoatomic or diatomic gases. For most gas mixtures, the molar heat capacity tends to vary much less than the mass heat capacity. In addition, the diffusion coefficient and, to a lesser degree, viscosity are nearly independent of composition. With $C_p{}^*$ constant, only the conduction term in the energy equation remains composition dependent, and composition dependences are absent from the continuity and diffusion equations. The momentum equation, however, does not have a constant property form, but at least for isothermal diffusion problems (*6*) this does not seem to be too important, provided that properties are evaluated at free stream conditions. This suggests that simultaneous energy and mass transfer problems may be handled in an approximate way by means of constant property results expressed in molar quantities evaluated at free stream conditions. Results to be obtained here support this conjecture.

SURFACE MASS AND ENERGY BALANCES

The analysis in this paper is concerned with diffusion of one component of a binary mixture through a second component which is impermeable to the surface. The surface mass balance requires that the convective and diffusive fluxes of the stationary component be equal and opposite. This fact has been used in writing the boundary conditions for v^* at $y = 0$. The total molar flux of the diffusing component is given by
(Forced)

$$\dot{N}_1 = -\,(\overline{cD})_w\;B^*\,\frac{\partial X}{\partial y_1}\bigg|_0\,\frac{N_{Re}{}^{1/2}}{L} \qquad (10)$$

(Free)

$$\dot{N}_2 = -\,(\overline{cD})_w\;B^*\,\frac{\partial X}{\partial y_2}\bigg|_0\,\frac{N_{Gr}{}^{1/4}}{L} \qquad (11)$$

For transfer of mass toward the surface, $v^*{}_w$, B^*, and $\dot{N}$ are all negative.

Energy transport from the surface to the fluid in the presence of mass transfer depends on two related factors: the fluid temperature gradient at the wall and the rate of mass transfer. The connection between energy transfer and these two factors is obtained by means of a surface energy balance. Several authors have presented this balance (*4, 9*). Accordingly, the energy balance for a binary mixture with a stagnant component is
(Forced)

$$q_{H_1} = -\,\overline{k}_w\,\frac{\partial \theta}{\partial y_1}\bigg|_0\,\frac{N_{Re}{}^{1/2}\Delta t}{L} + \dot{N}_1\,(h^*{}_w - h^*{}_{sw}) \qquad (12)$$

(Free)

$$q_{H_2} = -\,\overline{k}_w\,\frac{\partial \theta}{\partial y_2}\bigg|_0\,\frac{N_{Gr}{}^{1/4}\Delta t}{L} + \dot{N}_2(h^*{}_w - h^*{}_{sw}) \qquad (13)$$

Hence, their difference is the heat of sublimation or evaporation. Subsequent analysis is aimed at determining the thermal and mole fraction gradients for the case of large rates of mass transfer toward the surface.

FORCED CONVECTION

In seeking a similar solution to Equations (5) to (8), a stream function ψ_1, satisfying continuity, is introduced. That is

$$cu_1^* = \frac{\partial \psi_1}{\partial y_1}, \quad cv_1^* = -\frac{\partial \psi_1}{\partial x_1} \tag{14}$$

Substituting

$$\psi_1 = \left(2 \int_0^{x_1} U_1 \, dx_1 \right)^{1/2} f(\eta_1)$$

where the similarity variable η_1 is given by

$$\eta_1 = \frac{U_1 \int_0^{y_1} c dy_1}{\left(2 \int_0^{x_1} U_1 \, dx_1 \right)^{1/2}} \tag{15}$$

and assuming that the reduced temperature and mole fraction are functions of η_1 alone, we get the following system of equations:
Momentum:

$$\frac{d}{d\eta_1} (\mu c f'') + M f f'' + \frac{c^2 D \, (M_w - 1) \, X' f''}{N_{Sc}} + \left(\frac{2}{cU_1^2} \int_0^{x_1} U_1 \; dx_1 \right) (1 - cMf'^2) \frac{dU_1}{dx_1} \tag{16}$$

Diffusion:

$$\frac{d}{d\eta_1} (c^2 D X') + N_{Sc} f X' = 0 \tag{17}$$

Energy:

$$\frac{d}{d\eta_1} (ck\theta') + N_{Pr} C_p^* f \theta' + N_{Le} \, c^2 D K(\theta) X' \theta' = 0 \tag{18}$$

Primes denote derivatives with respect to η_1. Prandtl, Schmidt, and Lewis numbers are all evaluated at free stream conditions. The accompanying boundary conditions are

$$\eta_1 = 0: \quad f' = 0, \quad f = -\pi b_1, \quad X = 1, \quad \theta = 1$$

$$\eta_1 \to \infty: \quad f' = 1, \quad X = 0, \quad \theta = 0$$

where

$$b_1 = -\left. \frac{dX}{d\eta_1} \right|_0 \quad \text{and} \quad \pi = \frac{c_w^2 D_w B^*}{N_{Sc}}$$

The system of Equations (16) to (18) have no meaning except when the similarity assumptions are satisfied. The momentum Equation (16) reduces to an ordinary differential equation only for certain classes of potential flows, for example, $U(x) \sim x^m$ or $U(x) \sim e^{mx}$, m a constant. However, it will be shown that similarity is indeed preserved for other kinds of potential flows in the limit of large mass fluxes from the bulk of the fluid to the surface.

FORCED CONVECTION

As previously shown by Acrivos (*1*) for isothermal diffusion, if one component of the binary is stagnant, then as $B^* \to -1$, (stating the argument in terms of molar quantities) the rate of mass transfer, and hence $-X'(0)$ to which it is proportional, increases without limit. The above conditions correspond to intensive mass transfer toward the surface.

Following Acrivos, a new function φ_1 is introduced along with coordinate stretching:

$$z_1 = b_1 \eta_1, \; f(\eta_1) = \frac{\varphi_1(z_1)}{b_1} - \pi b_1 \tag{19}$$

This transformation puts the quantity b_1 into the differential equations rather than the boundary conditions. This is convenient for the purpose of seeking a perturbation solution to the equations. Under this transformation, the system (16) to (18) becomes

Momentum:

$$\frac{d}{dz_1} (\mu c \varphi_1'') - M\pi\varphi_1'' + \frac{c^2 D}{N_{Sc}} (M_w - 1) \, X' \varphi_1'' + \frac{1}{b_1^2} \left\{ M\varphi\varphi_1'' + \left(\frac{2}{cU_1^2} \int_0^{x_1} U_1 \, dx_1 \right) (1 - cM\varphi_1'^2) \frac{dU_1}{dx_1} \right\} = 0 \tag{20}$$

Diffusion:

$$\frac{d}{dz_1} \; (c^2 D X') + N_{Sc} \left(\frac{\varphi_1}{b_1^2} - \pi \right) X' = 0 \tag{21}$$

Energy:

$$\frac{d}{dz_1} (ck\theta') - N_{Pr} C_p^* \, \pi\theta' + N_{Le} c^2 D K(\theta) X' \theta' + \frac{N_{Pr} C^*_p \, \varphi_1 \theta'}{b_1^2} = 0 \tag{22}$$

with boundary conditions:

$$z_1 = 0: \quad \varphi_1 = 0, \quad \varphi_1' = 0, \quad X = 0, \quad \theta = 0$$

$$z_1 \to \infty: \quad \varphi_1' = 1, \quad X = 1, \quad \theta = 1$$

Now primes denote derivatives with respect to z_1. For the situation of intensive mass transfer toward the surface, b_1 [$\equiv -X'(0)$] becomes large and $1/b_1^2$ terms become small, thus permitting their deletion in the momentum and energy equations. It will be noted that for this simplification the effect of surface geometry in the momentum equation vanishes. Hence, the results will be applicable to flow past arbitrary geometries.

Integrating Equation (21), we obtain

$$c^2 D X' - c_w^2 D_w + \frac{N_{Sc}}{b_1^2} \int_0^X \varphi_1 \, dX - B^* c_w^2 D_w X = 0 \tag{23}$$

Observing that in the limit as $z_1 \to \infty$, $X \to 1$, and $X' \to 0$, we have upon rearrangement the expression for the reduced wall mole fraction gradient:

$$b_1^2 = \frac{N_{Sc}}{c_w^2 D_w \, (1 + B^*)} \int_0^1 \varphi_1 \, dX \tag{24}$$

Equation (23) can also be made to yield the relation between X and its z_1 derivative. Thus, by allowing $B^* \to -1$, the $1/b_1^2$ term may be dropped, giving

$$X' = \frac{c_w^2 D_w X}{c^2 D} \tag{25}$$

This expression may be then introduced into (20) and (22) to give

$$\frac{d}{dz_1} (\mu c \varphi_1'') + \frac{\pi}{B^*} \varphi_1'' = 0 \tag{26}$$

and

$$\frac{d}{dz_1}(ck\theta') + N_{Le}\, c_w^2 D_w K(\theta)\theta' = 0 \tag{27}$$

where

$$K(\theta) = C^*_{p_{x_\infty}}(\theta)$$

The pure component molar heat capacities are assumed to be known functions of temperature.

Equation (26) is integrated, and the resulting expression is inserted into Equation (24) to yield

$$b_1^2 = \frac{N_{Sc}}{c_w^2 D_w (1 + B^*)\left(1 - e^{\frac{-\beta(0)}{N_{Sc}}}\right)} \int_0^1 \frac{c^2 D}{c_w^2 D_w} \left(1 - e^{\frac{\beta(X)}{N_{Sc}}}\right) dX \tag{28}$$

where

$$\beta(X) = \int_X^1 \frac{cD}{\mu}\frac{dt}{t}$$

By noting that the local temperature gradient vanishes for large z_1, the wall temperature gradient is found from (27):

$$\theta'(0) = -N_{Le}\frac{c_w D_w}{k_w} b_1 \int_0^1 K(\theta)d\theta \tag{29}$$

Transport properties will, in general, be a function of both temperature and composition. Therefore, in order that the integration of (28) be possible, it is necessary to establish the relation between temperature and composition. To this end, the first integral of Equation (27) is combined with Equation (25):

$$\frac{k}{cD}\frac{X}{}\frac{d\theta}{dX} = N_{Le}\int_0^\theta K(t)dt \tag{30}$$

Integration of Equation (30), which can be achieved after variations of properties with temperature and composition have been specified, gives the required relation between temperature and composition (the $\theta - X$ relation). From expressions (28), (29), and (30), the mole fraction and temperature gradients may be computed for arbitrary composition and temperature variation in the properties. By means of these gradients, the energy and mass transferred to the surface may be calculated.

The molar flux rate at the surface has been given by Equation (10); in terms of the quantity b_1, this becomes

$$\dot{N}_1 = \frac{(\overline{cD})_w B^* c_w U_1 b_1 N_{Re}^{1/2}}{\left(2\int_0^{x_1} U_1\, dx_1\right)^{1/2} L} \tag{31}$$

The energy flux is derived from Equation (12) with the aid of (29) to give

$$q_{H1} = \dot{N}_1\left[\overline{C}^*_{p_\infty}\Delta t \int_0^1 K(\theta)d\theta + (h^*_w - h^*_{sw})\right] \tag{32}$$

EFFECTS OF PROPERTY VARIATIONS

In this section the heat and mass fluxes are computed and compared for gases with two different sets of property variations. Comparison of these results will indicate the sensitivity of the solution to property variations. In the interests of generality, rather simple types of property variations are considered. More precise calculations would involve the use of complex expressions for the functional dependence of the transport properties on temperature and composition (*3*). Variations of the properties with pressure are neglected. The two types of variations considered are:

Case 1:

$$c = 1/T,\quad \mu = T,\quad D = T^2,\quad k = k(T, X)$$

Case 2:

$$c = 1/T,\quad \mu = T^{1/2},\quad D = T^{3/2},\quad k = T^{1/2}/M$$

The assumption that the viscosity is a power law function of temperature is known to be a reasonable one (*5*, *11*). For most gases (*10*), the temperature exponent will lie between those of cases 1 and 2. The composition variation of viscosity is generally much less than that of density or conductivity (*5*) and is not considered here.

It is well known (*7*) that the diffusion coefficient is essentially independent of composition. The temperature exponents for the diffusion coefficient in the two cases bracket the values recommended by Slatterly and Bird (*12*) for nonpolar gases.

The variations of c, μ, and D in case 1 permit a simple solution for arbitrary variations of thermal conductivity with temperature and composition. For case 2, the temperature dependence of the conductivity is chosen so that the Prandtl number is independent of temperature. The $1/M$ molecular weight dependence of the conductivity was found to be reasonably valid for the gas pairs: carbon dioxide-air, hydrogen-carbon dioxide, hydrogen-nitrogen, and helium-air. In view of the foregoing discussion, it is expected that the usual types of property variations actually encountered will lie between the extremes of cases 1 and 2.

Case 1

If c^2D = const., $K(\theta) = 1$, and c = const., Equations (28) to (30) are readily integrated. Since Equation (28) is independent of temperature for the given variations, integration may be effected without the aid of (30). The expression for the quantity b_1 becomes
(Case 1)

$$b_1 = \left[\frac{N_{Sc}}{(1 + B^*)(1 + N_{Sc})}\right]^{1/2} \tag{33}$$

Equation (33) is identical in form to an expression for isothermal constant property mass transfer given by Acrivos (*1*).

Case 2

Variations of the form $c = 1/T$, $\mu = T^{1/2}$, $D = T^{3/2}$, and $k = T^{1/2}/M$ are now considered. Variations of this type will require the use of the $\theta - X$ relation, since $T^{-1/2}$ will appear in the integrand of Equation (28). $\beta(X)$ presents no problem, however, as its integrand is independent of temperature. By inserting the property functions into Equation (30) and by performing the integration, the temperature dependence on composition is found:

$$\theta = X^{N_{Le}}\, e^{F(1-X)} \tag{34}$$

where F is defined as

$$F \equiv N_{Le}(1 - M_w)$$

For these particular variations, b_1 is given by
(Case 2)

$$b_1 = \left\{\frac{N_{Sc} T_w}{(1 + B^*)}\int_0^1 \frac{(1 - X^{1/N_{Sc}})\, dX}{[1 + A\, X^{N_{Le}}\, e^{F(1-X)}]^{1/2}}\right\}^{1/2} \tag{35}$$

where $A = T_w - 1$.

The mass and energy fluxes are then obtained from Equations (31) and (32).

Comparison of Cases 1 and 2

The extent to which transport rates for case 1 differ from case 2 is determined by computing the ratio of the energy or the mass fluxes. The quantities $\bar{x}_w$, $\bar{x}_\infty$, $\bar{t}_w$, $\bar{t}_\infty$, $\bar{D}_\infty$, $\bar{\mu}_\infty$, $\bar{C}^*_{pw}$, and $\bar{C}^*_{p\infty}$ are assumed to be the same in both cases 1 and 2. The temperature variation in the pure component heat capacities is also taken to be identical for both cases. With these assumptions and by noting Equations (33) and (35), it is seen that the ratio of the energy or mass fluxes, defined as R, simplifies to

$$R = \frac{\dot{N}_1 \text{ case } 2}{\dot{N}_1 \text{ case } 1} = \left\{ (1 + N_{Sc}) \int_0^1 \frac{(1 - X^{1/N_{Sc}})\, dX}{[1 + A\, X^{N_{Le}}\, e^{F(1-X)}]^{1/2}} \right\}^{1/2} \tag{36}$$

R is a function of N_{Sc}, N_{Le}, T_w, and M_w. Although it is easy to get many approximate analytical expressions for Equation (36) corresponding to different ranges for the parameters, it seems difficult to obtain a single, uniformly valid expression which would apply to all cases. Therefore, we adopt the procedure of presenting some typical numerical results in order to indicate the sensitivity of R to property variations.

Figure 1 is a plot of the ratio R vs. molecular weight ratio at $N_{Pr} = 0.7$ and $N_{Sc} = 2$ for various temperature ratios. As would be expected, the R deviation increases with increasing T_w deviations. Interestingly, the disparity between the solutions for different property variations appears to decrease for large values of the molecular weight ratio M_w.

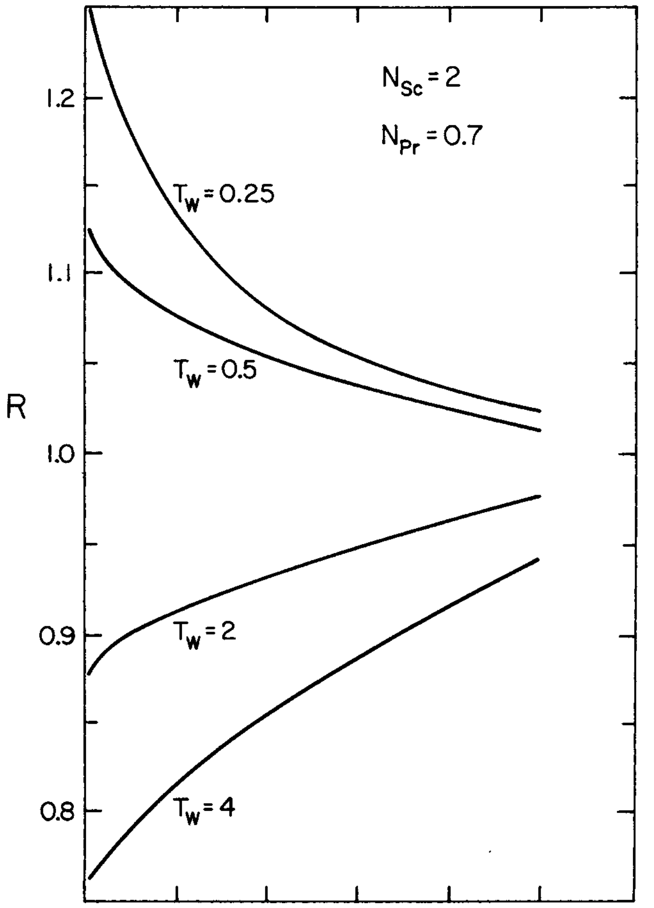

Fig. 1. Effect of property variations on ratio of mass or energy fluxes.

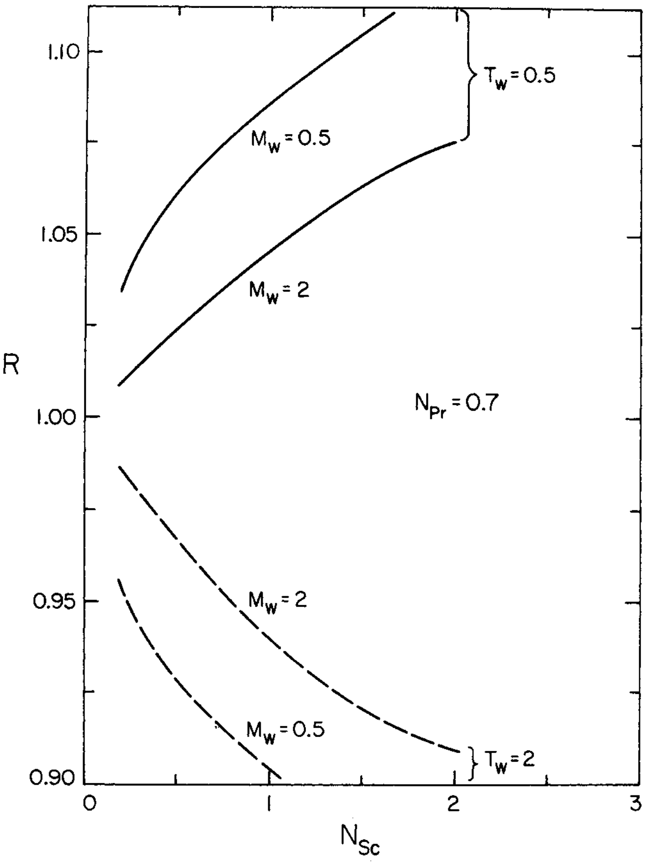

Fig. 2. Effect of Schmidt number on ratio of mass or energy fluxes.

For severe conditions such as $T_w = 0.25$, $M_w = 2$, $N_{Sc} = 2$, and $N_{Pr} = 0.7$, the deviation between the two cases is approximately 15%. The severity of the conditions and the fact that actual property variations would tend to lie between the two cases considered suggest that the simple results of case 1 may apply well for other types of property variations. In fact, Figure 1 shows that the ratio of the result for case 1 to that for case 2 differs from unity by only 7.5% when $T_w = 0.5$ and $M_w = 2$. Figure 2 illustrates the increase in R for increasing Schmidt number.

As mentioned above, Equation (36) can be evaluated numerically or by different approximations for particular ranges of the parameters. However, since the numerical results obtained indicate the effects of variable properties to be relatively small in many problems, it seems useful to indicate some general bounds which show the maximum error involved in the use of the simple case 1 results. Thus, we have, uniformly, for all values of N_{Sc}, N_{Le}, and M_w

$$\begin{aligned} 1/(1 + A)^{1/2} \leq R \leq 1 \quad (A \text{ positive}) \\ 1 \leq R \leq 1/(1 + A)^{1/2} \quad (A \text{ negative}) \end{aligned} \tag{37}$$

Also, it is easy to see that for large values of M_w we obtain the asymptotic formula

$$R \sim \left[1 - 1/2 \left(\frac{1 + N_{Sc}}{N_{Sc}} \right) \frac{A}{F^2} \right]^{1/2} \tag{38}$$

which shows that $R \rightarrow 1$ for large M_w. The general conclusion, then, is that the dominant factor affecting the quantity R is T_w, and that R departs significantly from unity only under rather severe conditions.

Without going into detail, it may be mentioned that an extension of the previous analysis to cover effects of viscous dissipation and diffusion-thermo yields the following results. For case 1 property variations, the mass and energy transport rates are the same as those for constant properties evaluated at free stream conditions for these respective situations. This viscous dissipation result holds only for zero pressure gradient (flate plate flow).

FREE CONVECTION

Attention is now turned to free convection. In this case there is no impressed external flow; the flow is sustained by the density gradient. Thus, we use Equations (5), (6), (7), and (9), with free convection designated by subscript 2 on the appropriate variables.

The free convection, boundary-layer equations are treated in a fashion similar to that for forced flow. The following similarity variables are introduced

$$\eta_2 = \frac{(\sin \epsilon)^{1/3} \int_0^{y_2} c\,dy_2}{\left\{ \frac{4}{3} (1 - c_w M_w) \int_0^{x_2} (\sin \epsilon)^{1/3}\, dx_2 \right\}^{1/4}} \tag{39}$$

$$\psi_2 = \left\{ \frac{4}{3} L\, \overline{\nu}_\infty^{2/3} g^{1/3} \int_0^{x_2} (\sin \epsilon)^{1/3}\, dx_2 \right\}^{3/4} \cdot J(\eta_2)$$

together with the auxiliary variables

$$J(\eta_2) = \frac{\varphi_2(z_2)}{b_2^3} - \pi\, b_2, \quad z_2 = b_2 \eta_2, \quad b_2 = \left. \frac{-dX}{d\eta_2} \right|_0 \tag{40}$$

By using these variables and by taking $T = T(z_2)$, $X = X(z_2)$ causes momentum Equation (9) and the diffusion and energy equations to take the following forms for $b_2 \to \infty$. Subscript 2 refers to the free convection case, and primes denote derivatives with respect to z_2.

(Momentum)

$$\frac{d}{dz_2} (c\mu\varphi_2'') + \frac{\varphi_2''}{N_{Sc}} [Dc^2(M_w - 1)\, X' + c_w^2 D_w M] + (T - M) = 0 \tag{41}$$

(Diffusion)

$$\frac{d}{dz_2} (c^2 D X') + N_{Sc} \left[-\pi + \frac{\varphi_2}{b_2^4} \right] X' = 0 \tag{42}$$

(Energy)

$$\frac{d}{dz_2} (ck\theta') + N_{Pr} C^*_p \left(-\pi + \frac{\varphi_2}{b_2^4} \right) \theta' - N_{Le}\, c^2 D K(\theta) X' \theta' \tag{43}$$

with boundary conditions

$$z_2 = 0{:} \quad \varphi_2 = 0, \quad \varphi_2' = 0, \quad X = 1, \quad \theta = 1$$

$$z_2 \to \infty{:} \quad \varphi_2' = 0, \quad X = 0, \quad \theta = 0$$

Integrating Equation (42) and allowing $B^* \to -1$, we get the relation between X and X' which is found to be identical to Equation (25). This relation, when introduced into the momentum and energy equations, yields

$$\frac{d}{dz_2} (\mu c \varphi_2'') + \frac{c_w^2 D_w}{N_{Sc}} \varphi_2'' + (T_w - 1)\theta - (M_w - 1) X = 0 \tag{44}$$

and

$$\frac{d}{dz_2} (kc\theta') + N_{Le} c_w^2 D_w K(\theta) \theta' = 0 \tag{45}$$

where b_1^{-4} terms have been deleted for $B^* \to -1$. The expression for b_2 resulting from the diffusion equation is

$$b_2 = \left[\frac{N_{Sc}}{c_w^2 D_w (1 + B^*)} \int_0^1 \varphi_2\, dX \right]^{1/4} \tag{46}$$

The integral in Equation (46) is given by

$$\int_0^1 \varphi_2\, dX + P \int_{\psi=0}^1 \alpha\, d\psi \int_{r=1}^{\psi} \frac{\alpha\, dr}{\mu c G r} = \int_{\psi=0}^1 \alpha\, d\psi \int_{s=1}^{\psi} \frac{\alpha\, ds}{\mu c G s} \int_{r=1}^{s} \frac{G\alpha}{r} [(M_w - 1) X - (T_w - 1)\theta]\, dr \tag{47}$$

where

$$\alpha = \frac{c^2 D}{c_w^2 D_w}, \quad G(r) = e^{-\frac{1}{N_{Sc}} \int_1^r \frac{cD}{\mu} \frac{dw}{w}} \tag{48}$$

and

$$P = \frac{- \int_{s=0}^1 \frac{\alpha\, ds}{\mu c G s} \int_{r=s}^1 \frac{G\alpha}{r} [(M_w - 1) X - (T_w - 1)\theta]\, dr}{\int_{r=0}^1 \frac{\alpha\, dr}{\mu c G r}} \tag{49}$$

The surface molar flux becomes

$$N_2 = \frac{(\overline{D_w C_w})\; c_w N_{Gr}^{1/4}\; b_2\, (\sin \epsilon)^{1/3}}{L \left\{ \frac{4}{3} (1 - c_w M_w) \int_0^{x_2} (\sin \epsilon)^{1/3}\, dx_2 \right\}^{1/4}} \tag{50}$$

The quantity b_2 is obtained by means of the combined use of Equations (46) and (47). Since the energy equation is identical to that in forced convection, the $\theta - X$ relation is found by integrating Equation (30). The energy flux is given by Equation (32) with $\dot{N}_1$ replaced by $\dot{N}_2$ as given in Equation (50). Equations (30) and (46) to (50) constitute the solution for free convection with arbitrary property variations.

EFFECTS OF PROPERTY VARIATIONS

The variations to be considered here are similar to those of case 1 in the forced convection problem:

$$c = 1/T, \quad \mu = T, \quad D = T^2, \quad \text{and} \quad k = T/M$$

Owing to the occurrence of the density term in Equation (47), the $\theta - X$ relation must be employed. The problem is to determine $\int_0^1 \varphi_2 dX$. By evaluating Equations (47) to (49) for the indicated property variations, we are led to the following expression for $\int_0^1 \varphi_2 dX$:

$$\int_0^1 \varphi_2 dX = \frac{N_{Sc}}{1 + N_{Sc}} \left\{ \frac{(1 - M_w)}{2} + \frac{(T_w - 1)}{N_{Le}} - (T_w - 1) M_w I \right\} \tag{51}$$

where

$$I = \int_0^1 (1 - z)^{N_{Le}}\, e^{N_{Le}(1 - M_w) z}\, dz \tag{52}$$

The case where M_w is large is of little interest physically (since this would require T_w to be very large in order that the results be applicable), so that the most useful results correspond to either moderate values of $(1 - M_w)N_{Le}$ or large values of N_{Le}. Therefore, the following representations of I are indicated:

$$I = \frac{M_w - 2 + e^{(1-M_w)}}{(M_w - 1)^2}; \quad (N_{Le} = 1) \qquad (53)$$

$$\frac{I}{\dfrac{1 - M_w}{e^{1+2/N_{Le}}}} = \frac{1}{1 + N_{Le}} + E_1;$$

$$0 \leqq E_1 \leqq \frac{(M_w - 1)^2 \; N_{Le}^2}{2(2 + N_{Le})^2(3 + N_{Le}) \left[1 - \left(\dfrac{M_w - 1}{3} \right) N_{Le} \right]}$$

$$[\text{for } |(M_w - 1) \; N_{Le}| < 3] \qquad (54)$$

$$I = \frac{1}{N_{Le}M_w} + E_2; \quad -\frac{1}{N_{Le}^2 M_w^3} \leqq E_2 \leqq 0$$

$$(\text{for} \quad M_w < 3/2) \qquad (55)$$

Also, it is noted that for k independent of M, we get

$$\int_0^1 \varphi_2 dX = \frac{N_{Sc}}{1 + N_{Sc}} \left\{ \frac{(1 - M_w)}{2} + \frac{(T_w - 1)}{N_{Le}(1 + N_{Le})} \right\} \qquad (56)$$

Equations (54) to (56) show that for larger values of N_{Le}, the effects of temperature variations become less important.

Equations (51) to (56) show that the combined effects of molecular weight and temperature variations add or compensate accordingly as the two effects accentuate or diminish the overall density difference. These equations suggest that for certain conditions the surface transfer rates would vanish. This conclusion cannot be drawn, since the entire analysis is based on large rates of transfer.

CONCLUSIONS

When formulated in terms of mole fraction and molar velocities, the variable fluid property transport equations for gas mixtures are of a mathematically more tractable nature than the corresponding mass fraction equations. Simplification hinges upon the fact that in gas mixtures the molar concentration is composition independent, and the molar heat capacity is often constant or nearly so.

Solutions were obtained for the energy and mass fluxes in forced and free convection flows of a binary gas mixture under conditions of large interfacial velocities directed toward the surface. Arbitrary variations of properties with composition and temperatures were considered. It was shown that extremely simple closed form results for forced convection are obtained when the Schmidt number is independent of temperature and varies with composition only through density variations, and if D is equal to T^2. It is known that these conditions correspond reasonably to reality. A second type of property variation, chosen along with the preceding case to bracket most situations, was selected in order to determine the sensitivity of the energy and mass rates to property variations. For situations where

$$\tfrac{1}{4} < T_w < 4 \quad \text{and} \quad \frac{1}{10} < M_w < 10$$

the deviations between the two cases are no more than about 20%. This strongly suggests that the very simple results will give good accuracy in most problems. Use of the variable property asymptotic solution in combination with the zero mass transfer asymptote should prove useful for predicting energy and mass fluxes at values of B^* intermediate between -1 and 0.

The free convection problem is more complicated, and it appears that under normal conditions the effects of property variations are greater in this case.

Although homogeneous chemical reactions were ignored in the analysis, it is clear from the stretched equations that had these terms been considered, they would become small in the limit of large transfer rates toward the surface.

NOTATION

A = $T_w - 1$
b = reduced wall mole fraction gradient, $(dX/d\eta)_w$
B^* = mole fraction mass transfer parameter, $(x_w - x_\infty)/(1 - x_w)$
c = molar concentration/free stream value
C_p^* = molar heat capacity/free stream value
$C^*_{p\infty}(\theta = \overline{C}_p^*{}_{x_\infty,t} / \overline{C}_p^*{}_{x_\infty,t_\infty}$
D = diffusion coefficient/free stream value
F = $N_{Le}(1 - M_w)$
$G(r)$ = defined by Equation (48)
$h^*{}_w$ = vapor molar enthalpy at surface
$h^*{}_{sw}$ = solid or liquid molar enthalpy at surface
k = thermal conductivity/free stream value
$K(\theta)$ = $C_{p*}{}_{x_\infty,\theta}$
L = characteristic length
M = molecular weight/free stream value
N = surface molar flux into the gas stream
N_{Gr} = Grashof number, $L^3 \, (1 - c_w M_w)g/\overline{\nu}_\infty^2$
N_{Le} = Lewis number, $\overline{\rho}_\infty \overline{C}_{p_\infty} \; \overline{D}_\infty/\overline{k}_\infty = N_{Pr}/N_{Sc}$
N_{Pr} = Prandtl number, $\overline{\mu}_\infty \; \overline{C}_{p_\infty}/\overline{k}_\infty$
N_{Re} = Reynolds number, $U_\infty x/\overline{\nu}_\infty$
N_{Sc} = Schmidt number, $\overline{\nu}_\infty/\overline{D}_\infty$
P = defined by Equation (49)
q_H = energy conducted from condensed phase toward interface
R = defined by Equation (36)
t = absolute temperature
T = dimensionless temperature, t/t_∞
u_1 = mass average velocity in x direction$/U_\infty$
u_1^* = molar average velocity in longitudinal direction/ U_∞
u_2 = mass average velocity in x direction $\cdot \, (L/\nu_\infty \, N_{Gr}^{1/2})$
u_2^* = molar average velocity in x direction $\cdot \, (L/\nu_\infty \, N_{Gr}^{1/2})$
U_∞ = free stream velocity
U_1 = local free stream velocity$/U_\infty$
v_1 = mass average velocity in y direction $\cdot \, (N_{Re}^{1/2}/U_\infty)$
v_1^* = molar average velocity in y direction $\cdot \, (N_{Re}^{1/2}/U_\infty)$
v_2 = mass average velocity in y direction $\cdot \, (L/\nu_\infty \, N_{Gr}^{1/4})$
v_2^* = molar average velocity in y direction $\cdot \, (L/\nu_\infty \, N_{Gr}^{1/4})$
x = mole fraction of diffusing component
$x_{1,2}$ = dimensionless axial coordinates
Δx = $x_w - x_\infty$
y_1 = $y \, N_{Re}^{1/2}/L$
y_2 = $y \, N_{Gr}^{1/4}/L$
y = distance normal to the surface
z = stretched coordinate, see Equations (19) and (40)

Greek Letters

α = $c^2 \, D/c_w^2 D_w$

$\beta(X)$ = function defined in Equation (28)
Δt = $t_w - t_\infty$
θ = $(T-1)/(T_w-1)$
ν = kinematic viscosity
μ = viscosity
π = $C_w^2 D_w B^* / N_{Sc}$
η_1 = similarity variable, Equation (15)
η_2 = similarity variable, Equation (39)
φ_1 = stretched variable, Equation (19)
φ_2 = stretched variable, Equation (40)
ϵ = local angle between vertical and normal to body in free convection
ψ = stream function, see Equations (14) and (39)

Subscripts and Superscripts

1 = forced convection
2 = free convection
∞ = free stream value
w = surface value
$\bar{j}$ = denotes dimensional value of the quantity j

LITERATURE CITED

1. Acrivos, Andreas, *AIChE J.*, **6**, 410 (1960).
2. Bird, R. B., W. E. Stewart, and E. N. Lightfoot, "Transport Phenomena," Wiley, New York (1960).
3. Eckert, E. R. G., and R. M. Drake, "Heat and Mass Transfer," McGraw-Hill, New York (1959).
4. Eckert, E. R. G., A. A. Hayday, and W. J. Minkowycz, *Int. J. Heat Mass Transfer*, **4**, 17 (1961).
5. Faulders, C. R., *J. Aero/Space Sci.*, **29**, 76 (1962).
6. Hanna, O. T., *AIChE J.*, **11**, 706 (1965).
7. Hirschfelder, J. O., C. F. Curtiss, and R. B. Bird, "Molecular Theory of Gases and Liquids," Wiley, New York (1954).
8. Koh, J. C. Y., and J. P. Hartnett, *Int. J. Heat Mass Transfer*, **2**, 185 (1961).
9. Lees, L., "Combustion and Propulsion," Third AGARD Colloquium, p. 468, Pergamon Press, New York (1958).
10. Licht, W., and D. Stechert, *J. Phys. Chem.*, **48**, 23 (1944).
11. Schlichting, Herman, "Boundary Layer Theory," 4 ed., McGraw-Hill, New York (1960).
12. Slattery, J. C., and R. B. Bird, *AIChE J.*, **4**, 137 (1958).
13. Stewart, W. E., *ibid.*, **9**, 528 (1963).
14. *Ibid.*, **8**, 421 (1962).
15. Stewart, W. E., and R. Prober, *Int. J. Heat Mass Transfer*, **5**, 1149 (1962).

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Stability Analysis of a Continuous Flow Stirred Tank Reactor with Consecutive Reactions

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The stability of a continuous flow stirred tank reactor with consecutive chemical reactions A→B→C was investigated here for the first time. The system equations were integrated numerically, and parts of the three-dimensional phase space were generated for systems having one and three steady states, respectively.

The surface separatrix was determined by trajectory plotting after extensive computation. The system was also analyzed by Liapunov's second method. Krasovskii's form was used to generate Liapunov functions which proved to be satisfactory but extremely conservative in the estimation of the largest possible regions of asymptotic stability.

The stability of a stirred tank reactor in which a single reaction A → B occurs has been the subject of much research in the last 15 yr. The first definitive analysis of this nonlinear problem was reported by Bilous and Amundson (5) who showed the conditions for the existence of multiple steady states and investigated the transient behavior of typical systems. They demonstrated the utility of phase plane representations of the reactor dynamics and showed how the stability analysis could be carried out by linearization of the system equations.

Since then the literature on reactor stability has grown considerably, due in large part to the contributions of Amundson and co-workers. An overall review of this literature is not appropriate here. However, it should be noted that studies of this subject have evolved three general approaches to the theoretical analysis of stability. These are linearization analysis, direct computation of reactor performance, and application of Liapunov's second method.

The goal of such analysis is to determine whether the operation of a reactor will be stable or unstable as well as the bounds of regions of stable behavior. A region of asymptotic stability (RAS) about a potential steady state point in the phase plane is defined as the set of initial conditions from which the reactor system trajectories will asymptotically approach that steady state. When multiple steady states exist, there will usually be such a region around each stable steady state point, and it is common to define a separatrix as that imaginary line in the phase plane which separates the largest possible RAS's. In this context, much of stability analysis may be thought of as an effort to measure these largest regions of asymptotic stability and thereby to locate the separatrix.

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