Diffusion in the Laminar Boundary Layer with a Variable Density

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The problem of isothermal diffusion in a variable molecular-weight binary gas mixture is considered for the case when the process occurs in a laminar boundary layer. Viscosity and diffusion coefficient are assumed constant. Solutions are given for both forced and free convection at large Schmidt numbers and large mass transfer rates toward the surface. Use of the molar average velocity considerably simplifies the results. These results suggest that the constant density solution in terms of mole fractions, evaluated at free stream conditions, may be a good approximation for variable density. This technique, improved by an approximate correction derived herein, is shown to agree reasonably well with the results of exact numerical solutions of the boundary layer equations.

In general, solutions of the laminar boundary layer equations for problems involving diffusion, where $v_w \neq 0$, are obtained only with difficulty. Because of the large number of parameters connected with these problems, one approach has been to obtain fairly general asymptotic solutions of these equations (*1* to *5*). Such asymptotic solutions have been very useful, since in many cases the results prove to be valid over wide ranges of the parameters. In this paper, effort is directed toward the solution of the momentum, continuity, and diffusion equations for several limiting isothermal situations where the density is composition dependent. Presumably such solutions are of particular interest with regard to binary diffusion in gases where the species have different molecular weights. For in perfect gas mixtures the diffusivity is essentially constant, while viscosity variations are normally overshadowed by density changes. Furthermore, the effect of a varying density cannot be ascertained by evaluating the constant density solution of equations (*2* to *4*) at an average density, since such a procedure causes effects of density to cancel from both the continuity and diffusion equations.

The development here proceeds in two stages. First, it is shown how the forced convection problem is solved for large Schmidt numbers using a mass fraction formulation. This exact result is compared with an approximate variable density correction obtained earlier, and it is indicated how this correction may be used for problems involving variable surface conditions when $v_w = 0$. Attention is then focused on the formulation of the high Schmidt number problem in terms of mole fractions, as has been done by Stewart (*5*). It is shown that this kind of formulation also leads to simplified results for free convection at large Schmidt numbers, and for both forced and free convection with large mass transfer rates toward the surface. In light of these results, and with the aid of an approximate variable density correction derived in the appendix, a calculation technique is suggested for problems of forced convective diffusion in gaseous systems having a variable density. This technique is shown to agree reasonably well with numerical calculations for systems differing widely in molecular weight.

MASS FRACTION ANALYSIS

The problem considered is that of binary diffusion in a perfect gas mixture. The viscosity and diffusion coefficient are assumed to be constant. Since the mixture behaves ideally

$$\rho = \frac{pM}{Rt} \tag{1}$$

For steady laminar boundary layer flows, the conservation equations for mass, momentum, and diffusion become

$$\frac{\partial \rho_1 u_1}{\partial x_1} + \frac{\partial \rho_1 v_1}{\partial y_1} = 0 \tag{2}$$

$$\rho_1\left(u_1\frac{\partial u_1}{\partial x_1} + v_1\frac{\partial u_1}{\partial y_1}\right) = \frac{\partial^2 u_1}{\partial y_1^2} + U_1\frac{dU_1}{dx_1} \tag{3}$$

$$\rho_1\left(u_1\frac{\partial W}{\partial x_1} + v_1\frac{\partial W}{\partial y_1}\right) = \frac{1}{N_{Sc}}\frac{\partial}{\partial y_1}\left(\rho_1\frac{\partial W}{\partial y_1}\right) \tag{4}$$

Definition of the dimensionless variables is given in the nomenclature. The use of Equation (1) and the introduction of the new variable $S = \ln M/M_\infty$ permit Equations (2) and (4) to be written as

$$\frac{\partial u_1}{\partial x_1} + \frac{\partial v_1}{\partial y_1} + \frac{1}{N_{Sc}}\frac{\partial^2 S}{\partial y_1^2} = 0 \tag{5}$$

$$u_1\frac{\partial S}{\partial x_1} + v_1\frac{\partial S}{\partial y_1} = \frac{1}{N_{Sc}}\frac{\partial^2 S}{\partial y_1^2} \tag{6}$$

For certain limiting situations where the solution of the momentum equation is quite simple, Equations (5) and (6) can be easily solved. For example, at large Schmidt numbers, except near the point of separation, it can be shown (*12*) that the solution of the momentum equation appropriate within the *diffusion* layer is $u_1 = \beta_1(x_1)y_1$. At the point of separation for high Schmidt numbers, $u = \frac{1}{\mu}\frac{dp}{dx}\frac{y^2}{2}$. For flow past a flat plate at small Schmidt numbers, $u = U$. These limiting relations are all valid for variable density as long as the viscosity is constant. The asymptotic boundary layer situations are of some practical importance, particularly since the solutions obtained in this way are often valid over fairly wide ranges of the parameters.

In order to treat the preceding cases in a unified manner we take $u_1 = M(x_1)y_1^m$, where $M(x_1)$ and m must be chosen appropriately. The presentation here is given for two-dimensional flows. For axially-symmetric flows Mangler's transformation may be used. For three-dimensional flows, modifications suggested by Stewart (*5*) may be incorporated. Thus for high Schmidt numbers (except near the point of separation) $M(x_1) = \beta_1(x_1)$ and $m = 1$, etc. It is assumed that $S/S_w = \theta(\eta)$ where $\eta = y_1/l(x)$. Since $v_{1_w} = -\left.\frac{G}{N_{Sc}}\frac{\partial W}{\partial y_1}\right)_w$ from the surface mass balance, Equation (5) gives the following expression for v.

$$v_1 = -\frac{B\phi\theta'(0)}{N_{Sc}\,l} - \frac{S_w\theta'}{N_{Sc}\,l} + \frac{S_w\theta'(0)}{N_{Sc}\,l} - \frac{dM}{dx_1}\frac{y_1^{m+1}}{m+1} \tag{7}$$

If l is given by

$$l = \frac{1}{M^{\frac{1}{m+1}}}\left\{\frac{(m+2)}{N_{Sc}}\int_{x_{1_0}}^{x_1} M^{\frac{1}{m+1}}\,dx_1\right\}^{\frac{1}{m+2}} \tag{8}$$

then Equation (6) becomes

$$\theta'' = -\theta'[\eta^{m+1} + A\theta'(0)] - S_w\theta'^2 \tag{9}$$

The boundary conditions $\theta(0) = 1$, $\theta(\infty) = 0$ correspond to the case where the surface mass fraction and the ratio $\dot{m}_2/\dot{m}_1$, are held constant. The solution of Equation (9) subject to these conditions yields the quantity $\theta'(0)$, which is related to the surface mass flux.

$$\theta'(0) = \frac{-(M_\infty/M_w)}{\phi\int_0^\infty e^{-\left(\frac{\eta^{m+2}}{m+2} + A\theta'(0)\eta\right)}\,d\eta} \tag{10}$$

Thus $\theta'(0)$ depends on the independent parameters B and M_w/M_∞. If the mass transfer coefficient is defined by

$$-\left.D\frac{\partial W}{\partial y}\right)_w \equiv h_D(W_w - W_\infty)$$

we find

$$h_D = -\frac{D\phi\theta'(0)}{l} \tag{11}$$

If h_{D_0} is the coefficient for the case where $B \rightarrow 0$ and $M_w \rightarrow M_\infty$ then

$$\frac{h_D}{h_{D_0}} = \frac{\phi\theta'(0)}{\theta'(0)_0} \tag{12}$$

The total rate of mass transfer is $\dot{m}_1 = \rho_w h_D(W_w - W_\infty)[1 + GW_w]$; for $\dot{m}_2 = 0$ this becomes $\dot{m}_1 = \rho_w h_D B$. Values of h_D/h_{D_0} as a function of B and M_w/M_∞ are shown in Figure 1 for $m = 1$. The effect of varying density is seen to be strong.

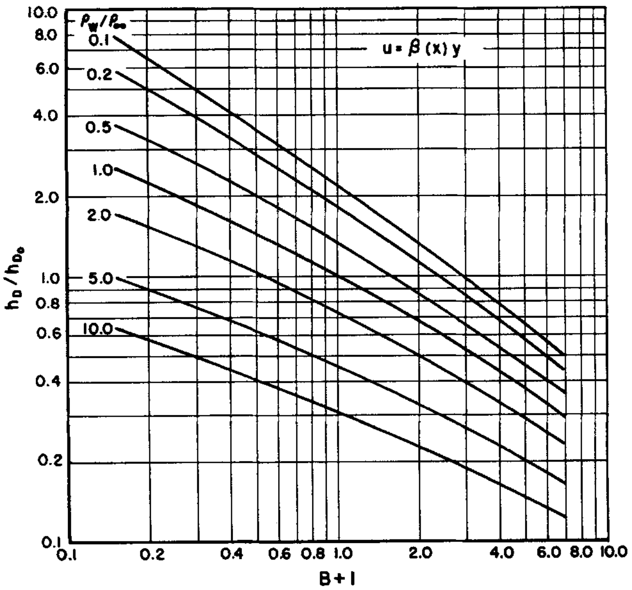

Fig. 1. Effect of ρ_w/ρ_∞ and B on mass transfer coefficients in a laminar boundary layer.

It will be shown below that by working in terms of mole fractions rather than mass fractions it is possible to eliminate the parameter M_w/M_∞ for all of the cases so far considered. For the important case $m = 1$ this has been demonstrated by Stewart (5). Moreover, it will be found that a mole fraction formulation seems to be desirable in many instances.

Equations (5) and (6) can be put into a convenient integral form as shown in Appendix I. The integral method can then be used to obtain an accurate, concise expression for the quantity h_D/h_{D_0} in the case where $B = 0$. This expression is given by

$$\frac{h_D}{h_{D_0}} = \frac{\phi}{\left(1 + \frac{4}{21}S_w\right)^{\frac{1}{m+2}}} \tag{13}$$

This result will be used later in the paper.

Comparison with Approximate Correction: Extension to Variable $W_w(x)$ or $\dot{m}_l(x)$ with $v_w = 0$

The approximate variable density correction of reference 6, which is based on the assumption that u and v in Equation (6) are independent of density, will now be compared to the exact results. In Figure 2 this comparison is made for $B = 0$ and $u = \beta y$. In view of the simplicity and generality of the approximate correction, the agreement is quite reasonable. The maximum error for $0.1 < M_w/M_\infty < 10$ is seen to be about 17% Since the approximate correction is in reasonable agreement with the exact results, this technique will now be extended to situations where the wall mass fraction or mass flux may be prescribed functions of x. Retaining the assumption that u and v in Equation (6) are independent of ρ, and hence of s, it is possible to superimpose solutions to account for the combined effects of variable surface mass fraction or mass flux and variable density. These relations are restricted to very small surface velocities. If the surface mass fraction is specified, the surface mass flux is given by (7)

$$\dot{m}_1\left(\frac{1}{\rho_2} - \frac{1}{\rho_1}\right) = \int_{\xi=0}^{x} h_{D_0}(x,\xi)\,dS_w(\xi) \tag{14}$$

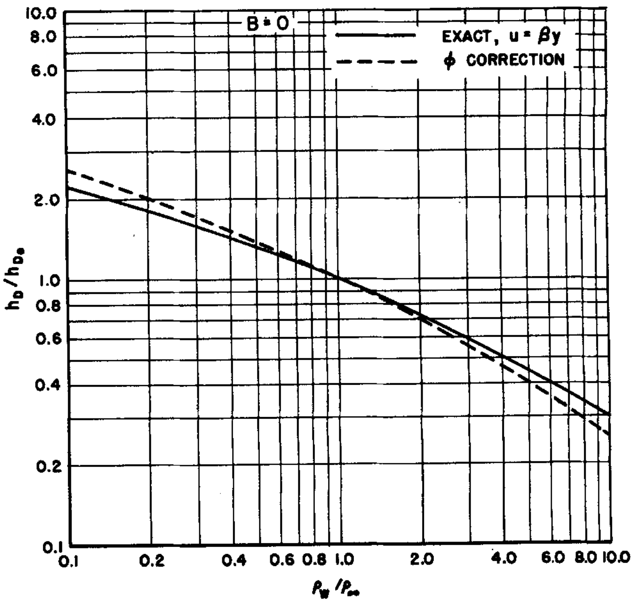

Fig. 2. Comparison between exact results and approximate correction.

where $h_{D_0}(x, \xi)$ is the constant ρ, $v_w = 0$ mass transfer coefficient for the case of a step in surface mass fraction. If the surface mass flux is specified the surface mass fraction can be determined from (*8*)

$$\rho_w \phi (W_w - W_\infty) = \int_{\zeta=0}^{x} \frac{d\dot{m}_1(\zeta)}{h_{D_0}(x, \zeta)} \tag{15}$$

where $h_{D_0}(x, \zeta)$ is the constant ρ, $v_w = 0$ mass transfer coefficient for a step in wall mass flux. Thus, in the case where the surface mass flux is specified, Equation (15) shows that $h_D/h_{D_0} = \phi(x)$, where h_{D_0} is the constant density coefficient for the case of an arbitrary mass flux.

These approximate results are useful since they are not restricted to any particular geometry or Schmidt number. They should also apply for turbulent flow. The essential restriction of these results is to cases where B (or correspondingly, v_w) is small. The requirement is that the effect of B on h_D be small compared to the effect of M_w/M_∞. It can be shown that the permissible range of B values increases with increasing M_w/M_∞.

USE OF MOLE FRACTIONS

As mentioned earlier, it is possible to eliminate the parameter M_w/M_∞ from the exact solutions obtained in the previous section by working in terms of mole fractions. For the case $m = 1$, this has been demonstrated by Stewart (*5*). Similar results will be obtained for the cases $m = 0$, $m = 2$. Use of mole fractions for these cases leads to mass transfer coefficients that are simply the constant density coefficients evaluated at free stream conditions. It will be shown below that this conclusion can be extended to the case of free convection at high Schmidt numbers (a case of little practical interest, since the results would be expected to be valid only for $N_{Sc} > 10$ or so), as well as to the cases of forced and free convection with large mass transfer rates toward the surface. It is also shown that variable density mass transfer coefficients calculated from numerical solutions of the boundary layer equations correlate much better in terms of mole fractions than in terms of the original mass fraction variables.

The mole fraction formulation of isothermal binary diffusion problems involves use of the molar average velocity (*9*) rather than the mass average velocity. This is due to the molar density being independent of composition for perfect gas mixtures. The dimensionless molar velocity components are related to their mass average counterparts by

$$u_1 = u_1^* - \frac{(M_w - M_\infty)}{M\, N_{Re}\, N_{Sc}} \frac{\partial \theta}{\partial x_1} \tag{16}$$

(forced flow)

$$v_1 = v_1^* - \frac{(M_w - M_\infty)}{M\, N_{Sc}} \frac{\partial \theta}{\partial y_1} \tag{17}$$

$$u_2 = u_2^* - \frac{(M_w - M_\infty)}{M\, N_{Gr}^{1/2}\, N_{Sc}} \frac{\partial \theta}{\partial x_2} \tag{18}$$

(free flow)

$$v_2 = v_2^* - \frac{(M_w - M_\infty)}{M\, N_{Sc}} \frac{\partial \theta}{\partial y_2} \tag{19}$$

where $\theta = (x - x_\infty)/(x_w - x_\infty)$.

In the absence of homogeneous chemical reaction, and for isothermal perfect gas mixtures, the continuity and diffusion equations become identical to their constant property forms.

$$\frac{\partial u^*}{\partial x} + \frac{\partial v^*}{\partial y} = 0 \tag{20}$$

$$u^* \frac{\partial \theta}{\partial x} + v^* \frac{\partial \theta}{\partial y} = \frac{1}{N_{Sc}} \frac{\partial^2 \theta}{\partial y^2} \tag{21}$$

Here, appropriate subscripts must be used, depending upon whether the problem is one of forced or free convection. The advantage of retaining the continuity and diffusion equations in their constant property form is compensated for by means of complications in the momentum equations. However, these complications are minimized for boundary layer flows, both forced and free. From the customary order-of-magnitude arguments (*10*), it is easily seen that the last terms of Equations (16) and (18) can be neglected for large Reynolds and Grashof numbers, respectively. The neglect of these terms is completely analogous to the more familiar dropping of axial diffusion compared to axial convection. Thus for laminar boundary layer flows, either forced or free, $u = u^*$ and the pertinent momentum equations become

(forced)

$$\frac{M}{M_\infty}\left(u_1^* \frac{\partial u_1^*}{\partial x_1} + v_1^* \frac{\partial u_1^*}{\partial y_1} \right) = \frac{\partial^2 u_1^*}{\partial y_1^2} + \frac{\left(\dfrac{M_w}{M_\infty} - 1 \right)}{N_{Sc}} \frac{\partial \theta}{\partial y_1} \frac{\partial u_1^*}{\partial y_1} + U_1 \frac{dU_1}{dx_1} \tag{22}$$

(free)

$$\frac{M}{M_\infty}\left(u_2^* \frac{\partial u_2^*}{\partial x_2} + v_2^* \frac{\partial u_2^*}{\partial y_2} \right) = \frac{\partial^2 u_2^*}{\partial y_2^2} + \theta \sin \epsilon + \frac{\left(\dfrac{M_w}{M_\infty} - 1 \right)}{N_{Sc}} \frac{\partial \theta}{\partial y_2} \frac{\partial u_2^*}{\partial y_2} \tag{23}$$

Boundary conditions:

$$y = \infty;\ \theta = 0,\ u_1^* = 1,\ u_2^* = 0$$

$$y = 0,\ x > 0;\ u^* = 0,\ v = -DG^* \left.\frac{\partial x}{\partial y}\right)_w,\ \theta = 1$$

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

For free convection in perfect gas mixtures it may be noted that the effect of variable density is of paramount importance, since the motion is induced by density differences. It will be shown that several solutions to the above equations can be obtained analytically. These solutions all indicate that variable density results can be obtained simply by evaluating properties at the free stream value, provided that a mole fraction formulation is used.

Large Schmidt Numbers

Forced Convection. For large Schmidt numbers, Stewart (*5*) has given the solution to Equations (20), (21), and (22) for forced convection, except near the point of separation. For this situation it is easily shown (*11*, *12*) that only the viscous term in Equation (22) is important, and the solution *in terms of mole fractions* is simply the well-known Lighthill solution modified for the effect of a finite interfacial velocity (*4*, *5*). This solution can be made slightly more general by noting that the cases of a separating flow at large Schmidt number and flow over a flat plate at small Schmidt numbers can be obtained at the same time by writing $u_1 = M(x_1) y_1^m$ and using appropriate values of $M(x_1)$ and m. Thus for flow over a flat plate at low Schmidt numbers, the viscous term in Equation (22) can be neglected and then $u^* = U$ clearly satisfies the momentum equation, so that in this case $M(x_1) = 1$, $m = 0$. For the case of a separating flow at large Schmidt numbers, $u^* = -\rho_\infty U U_x y^2/2\mu$. Taking $\theta = \theta(\eta)$ with $\eta = y_1/l(x)$, where $l(x)$ is given by Equation (8), the diffusion equation becomes

$$\theta'' = -\theta'[\eta^{m+1} + B^*\theta'(0)] \qquad (24)$$

Here $B^* \equiv G^*(x_w - x_\infty)$; this quantity becomes equal to $(x_w - x_\infty)/(1 - x_w)$ for the familiar case of diffusion through a stationary component. The solution is restricted to situations where $\dot{N}_2/\dot{N}_1$ is constant and for a constant surface mole fraction downstream of a step at $x = x_0$. If the mass transfer coefficient h_D^* is defined by $-D\left.\frac{\partial x}{\partial y}\right)_w = h_D^*(x_w - x_\infty)$, then the solution of Equation (24) yields

$$\frac{h_D^*}{h_{D_0}^*} = \frac{1.288}{\int_0^\infty e^{-\left(\frac{\eta^{m+2}}{m+2} + B^*\theta'(0)\eta\right)} d\eta} \qquad (25)$$

where $h_{D_0}^*$ is the coefficient for $B^* = 0$. Values of this integral for $m = 1$ are given in reference 9 along with a graphical representation. Asymptotic forms of the integral are given in Table 1. The total molar rate of transfer of component 1 at the surface is given by

$$\dot{N}_1 = ch_D^*(1 + x_wG^*)(x_w - x_\infty)$$

For $\dot{N}_2 = 0$ this becomes $\dot{N}_1 = ch_D^*B^*$. These results have been obtained previously for constant property systems, where there is no difference between mass and mole fractions. Stewart (5) recognized the importance of the mole fraction formulation for this problem ($m = 1$). However, successful use of the mole fraction formulation goes back to the study of certain one-dimensional problems (9), where it is not necessary to use the momentum equation. As mentioned earlier in the paper, the mass fraction result, Equation (10), may be transformed into Equation (25) by means of relations between mass and mole fractions. Obviously, the result in terms of mole fractions is much to be preferred, since it eliminates the parameter M_w/M_∞. While this result is interesting and significant, the question of the applicability of this result for gas mixture remains, since the analysis is based on the assumption of a large Schmidt number. This question will be considered later in the paper. Although an explicit formula for $(h_D^*/h_{D_0}^*)$ in terms of B^* cannot be obtained from Equation (25), it is interesting to note that Equation (13), which relates h_D/h_{D_0} to M_w/M_∞ for $B = 0$, can be used for this purpose. Thus relating h_D/h_{D_0} to $h_D^*/h_{D_0}^*$ and eliminating M_w/M_∞ in favor of B^*, making use of the fact that $B = 0$ in Equation (13), a very accurate and simple formula for $h_D^*/h_{D_0}^*(B^*)$ is derived.

$$\frac{h_D^*}{h_{D_0}^*} = \frac{1}{B^*}\frac{\ln(1+B^*)}{\left\{1 + \frac{4}{21}\ln(1+B^*)\right\}^{\frac{1}{2+m}}} \qquad (26)$$

This formula represents the results of Equation (25) very well.

Free Convection. At large Schmidt numbers in free convection, the usual coordinate stretching (*12*) applied to Equations (20), (21), and (23) shows that only the viscous and gravitational terms need be retained in the momentum equation in order to calculate the surface mass flux. Thus with a properly defined Grashof number and with use of mole fractions, the variable density equations take their constant property form. As shown in references *4* and *13*, appropriate results for a Newtonian fluid are

$$\frac{h_D^*}{D}\,\frac{1}{(N_{Gr}\,N_{Sc})^{1/4}}\left\{\frac{4}{3(\sin\epsilon)^{1/3}}\int_0^x (\sin\epsilon)^{1/3}\,dx\right\}^{1/4} = b \qquad (27)$$

$$b = 0.54\ (B^* = 0);\ b = 0.407(bB^*)^{1/3}$$

$$\exp\{-0.541(bB^*)^{4/3}\}\ \ (B^* > 3)$$

Although there is doubt about the usefulness of these relations for gas mixtures, it is nevertheless interesting that the use of mole fractions leads to simplified results at large Schmidt numbers for both forced and free convection.

LARGE MASS TRANSFER RATES TOWARD THE SURFACE

Acrivos (3) has shown that for diffusion problems with large interfacial velocities directed toward the surface, the boundary layer equations for both forced and free convection may be solved even for a variable property fluid. His results, given in terms of mass fractions, are particularly simple for the case of constant properties. It will be shown that for both forced and free convection, with constant viscosity and diffusivity, the constant density results apply even for a varying density, provided that the solution is given in terms of mole fractions with the properties evaluated at free stream conditions.

Forced Convection

Following Acrivos, let $u_1^* = U_1(x)F'(\eta)$ and $\theta = \theta(\eta)$ with $\eta = y_1U_1/\left(2\int_0^{x_1} U_1dx_1\right)^{1/2}$. The boundary conditions are

$$\eta = 0:\ F = \frac{B^*\,\theta'(0)}{N_{Sc}},\ F' = 0,\ \theta = 1$$

$$\eta = \infty:\ F' = 1,\ \theta = 0$$

Letting $\theta'(0) \equiv b$ where $b \to \infty$ as $B^* \to -1$, and defining

$$z = b\eta,\ \theta = H(z)$$

$$F = \frac{B^*b}{N_{Sc}} + \frac{\theta(z)}{b}$$

causes Equations (20), (21), and (22) to take the following form for $b \to \infty$.

$$\phi''' + \frac{\phi''}{N_{Sc}}\left\{-B^*\left[\left(\frac{M_w}{M_\infty} - 1\right)H + 1\right] + \right.$$

TABLE 1

Asymptotic values of $\int_0^\infty e^{-\left(\frac{\eta^n}{n} + b\eta\right)} d\eta = I$

$$I = \frac{1}{b}\left[1 - \frac{\Gamma(n)}{b^n}\right] \qquad (b > 3)$$

$$I = \frac{[(2\pi/(n-1)]^{1/2}}{(-b)^{\left(\frac{n-2}{2(n-1)}\right)}}\exp\left[\left(\frac{n-1}{n}\right)(-b)^{\left(\frac{n}{n-1}\right)}\right] \qquad (b < -2)$$

$$I = \frac{\Gamma(1/n)}{n^{\left(\frac{n-1}{n}\right)}} - \frac{b\Gamma(2/n)}{n^{\left(\frac{n-2}{n}\right)}} \qquad (b = 0)$$

$$H'\left(\frac{M_w}{M_\infty}-1\right)\Big\} = 0 \qquad (28)$$

$$H'' + N_{Sc}\left[-\frac{B^*}{N_{Sc}}+\frac{\phi}{b^2}\right]H' = 0 \qquad (29)$$

The boundary conditions are

$$\phi(0) = \phi'(0) = H(\infty) = 0$$

$$\phi' = (\infty) = H(0) = 1$$

It is easily shown that for $b \rightarrow \infty$ $(B^* \rightarrow -1)$

$$b = \sqrt{\frac{N_{Sc}}{(1+B^*)(1+N_{Sc})}} \qquad (30)$$

The Nusselt number becomes

$$\frac{h_D^* L}{D} = \frac{U_1}{\left(\int_0^{x_1} U_1 dx_1\right)^{1/2}} \sqrt{\frac{N_{Re}\, N_{Sc}}{2(1+B^*)(1+N_{Sc})}} \qquad (31)$$

This is just the constant property result in terms of mole fractions evaluated at free stream conditions. It seems reasonable to suppose, then, that the interpolation formula suggested by Acrivos (*3*) to cover the range between $B = 0$ and $B \rightarrow -1$ may be a good approximation for variable density, if the interpolation formula is interpreted as recommended above.

Free Convection

In this case, again following Acrivos, let

$$\eta = \frac{\left(\frac{3}{4}\right)^{1/4} y_2 (\sin\epsilon)^{1/3}}{\left\{\int_0^{x_2} (\sin\epsilon)^{1/3} dx_2\right\}^{1/4}} \text{ and}$$

$$u_2 = F'(\eta)\left(\frac{4}{3}\right)^{1/2} (\sin\epsilon)^{1/3} \left\{\int_0^{x_2} (\sin\epsilon)^{1/3} dx_2\right\}^{1/2}$$

as well as $\theta = \theta(\eta)$. Then introducing $\theta'(0) = b_1$ where $b_1 \rightarrow \infty$ as $B^* \rightarrow -1$, and defining $z_1 = b_1\eta$, $F = \frac{B^* b_1}{N_{Sc}} + \frac{\phi_1(z_1)}{b_1^3}$ and $\theta = H(z_1)$, Equations (20), (21), and (23) become (for $b_1 \rightarrow \infty$)

$$\phi_1''' - \frac{B^*}{N_{Sc}}\left[\left(\frac{M_w}{M_\infty}-1\right)H + 1\right]\phi_1'' + H + \left(\frac{M_w}{M_\infty}-1\right)\frac{H'\phi_1''}{N_{Sc}} = 0 \qquad (32)$$

$$H'' + N_{Sc}\left[\frac{\phi_1}{b_1^4} - \frac{B^*}{N_{Sc}}\right]H' = 0 \qquad (33)$$

The boundary conditions are $\phi(0) = \phi'(0) = \phi'(\infty) = H(\infty) = 0$, $H(0) = 1$. Solving this system for b_1 as $b_1 \rightarrow \infty$ $(B^* \rightarrow -1)$ yields

$$b_1 = \left\{\frac{N_{Sc}^2}{2(1+B^*)(1+N_{Sc})}\right\}^{1/4} \qquad (34)$$

This is again just the constant density result in terms of mole fractions evaluated at free stream conditions. The Nusselt number for this situation becomes

$$\frac{h_D^* L}{D} = \left\{\frac{3}{8}\,\frac{N_{Gr}\, N_{Sc}^2}{(1+B^*)(1+N_{Sc})}\right\}^{1/4} \bullet \frac{(\sin\epsilon)^{1/3}}{\left\{\int_0^{x_2} (\sin\epsilon)^{1/3} dx_2\right\}^{1/4}}$$

Thus for both forced and free convection the simple constant property results are obtained, provided that the free stream density is used. These relations are quite useful, since they are appropriate for moderate Schmidt numbers and since they have been shown to hold reasonably well, at least for constant properties, for relatively small rates of mass transfer.

DISCUSSION

It has been shown that a mole fraction formulation of several problems of isothermal diffusion with a density varying according to the perfect gas law leads to constant property solutions evaluated at free stream conditions. This was seen to be true for both forced and free convection at large Schmidt numbers and at moderate Schmidt numbers with large mass transfer rates toward the surface. These results suggest that in other cases involving diffusion in gas mixtures, the constant property results in terms of mole fractions may be a reasonable approximation, particularly if these results are evaluated at free stream conditions. Using the approximate variable density correction derived in Appendix II, this technique was compared to exact numerical results reported in reference *14* for injection into air of iodine, carbon dioxide, water, helium, and hydrogen, respectively. While a plot of this comparison is not shown because of the different Schmidt numbers involved, agreement was found to be reasonable with maximum errors of about 15%. Finally, by combining Equations (26) and (A_4) an approximate formula can be given for diffusion by forced convection in gaseous systems having a free stream Schmidt number of unity.

$$\frac{h_D^*}{h_{D_0}^*} = \frac{\left\{\frac{\ln(1+B^*)}{B^*}\right\}^{4/3}}{\left\{1+\frac{4}{21}\ln(1+B^*)\right\}^{1/3}} \bullet \left\{\frac{\alpha}{e^\alpha - 1}\right\}^{1/3} \qquad (36)$$

where $\alpha \equiv \frac{M_w}{M_\infty} - 1$. This formula agrees very well with flat plate numerical calculations for constant density when $N_{Sc} = 1$; the effect of geometry is known to be small (*15*). Thus based on the above comparisons with numerical results, Equation (36) should provide good estimates of the quantity $h_D^*/h_{D_0}^*$ for a moderately variable molecular weight if the free stream Schmidt number is near unity.

ACKNOWLEDGMENT

Thanks are due Professors W. E. Stewart, J. P. Hartnett, and A. Acrivos for useful comments and criticism.

NOTATION

A = $B\phi - S_w$
c = molar density
B = $G(W_w - W_\infty)$
B^* = $G^*(x_w - x_\infty)$
D = diffusion coefficient
G = $(1 + \dot{m}_2/\dot{m}_1)/[1 - W_w(1 + \dot{m}_2/\dot{m}_1)]$
G^* = $(1 + \dot{N}_2/\dot{N}_1)/[1 - x_w(1 + \dot{N}_2/\dot{N}_1)]$
h_D = $D(\partial W/\partial y)_w/(W_\infty - W_w)$
h_D^* = $D(\partial x/\partial y)_w/(x_\infty - x_w)$

h_{D_0} = mass transfer coefficient for zero surface velocity and constant ρ

$h_{D_0}(x, \xi)$ = h_{D_0} for the case of a step in W_w at $x = \xi$

$h_{D_0}(x, \zeta)$ = h_{D_0} for the case of a step in $\dot{m}_1$ at $x = \zeta$

$$l(x) = \frac{1}{(M(x))^{\frac{1}{m+1}}} \left[\frac{(m+2)}{N_{Sc}} \int_{x_0}^{x} M(x)^{\frac{1}{m+1}} dx \right]^{\frac{1}{m+2}}$$

M = molecular weight

$\dot{m}_i$ = $i = 1,2$; component surface mass flux

$\dot{N}_i$ = $i = 1,2$; component surface molar flux

N_{Gr} = $\dfrac{L^3 (\rho_\infty - \rho_w)}{v_\infty^2 \rho_\infty} g$

N_{Nu} = $h_D L/D$

N_{Re} = $LU_\infty \rho_\infty/\mu$

N_{Sc} = $\mu/\rho_\infty D$

S = $\ln(\rho/\rho_\infty)$

u = longitudinal velocity component

u_1 = u/U_∞

u_2 = $uL/\nu_\infty N_{Gr}^{1/2}$

u^* = molar-average longitudinal velocity component

u_1^* = u^*/U_∞

u_2^* = $u^* L/\nu_\infty N_{Gr}^{1/2}$

$U_{(x)}$ = local free stream velocity

U_∞ = velocity far from object

U_1 = $U_{(x)}/U_\infty$

v = transverse velocity component

v_1 = $v\, N_{Re}^{1/2}/U_\infty$

v_2 = $v\, L/\nu_\infty N_{Gr}^{1/4}$

v^* = molar-average transverse velocity component

v_1^* = $v\, N_{Re}^{1/2}/U_\infty$

v_2^* = $v^* L/\nu_\infty N_{Gr}^{1/4}$

W = mass fraction of component 1

x = mole fraction of component 1

y_1 = $y\, N_{Re}^{1/2}/L$

y_2 = $y\, N_{Gr}^{1/4}/L$

Greek Letters

α = $M_w/M_\infty - 1$

β = τ_w/μ

ϵ = angle between body force and normal to surface

μ = dynamic viscosity

ρ = mass density

ρ_1 = ρ/ρ_∞

ϕ = $S_w [M_w/M_\infty - 1]$

τ_w = zero mass transfer surface shear stress evaluated at free stream conditions

w = conditions at the surface

∞ = conditions in free stream

$*$ = quantity based on mole fractions

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APPENDIX I

By integrating Equation (6) with respect to y from 0 to δ' (diffusion boundary layer thickness) and combining with Equation (5), the integral diffusion equation is obtained for an ideal solution in terms of S.

$$\frac{d}{dx}\int_0^{\delta'} uS\,dy - D\int_0^{\delta'} \left(\frac{\partial S}{\partial y}\right)^2 dy = D\frac{\partial S}{\partial y}\bigg|_w \left(S_w - B\phi - 1\right) \qquad (A_1)$$

For $v_w = 0$, the following S profile satisfies the first three compatability conditions at the wall and at the edge of the diffusion layer.

$$\frac{S}{S_w} = 1 - \frac{5}{3}\frac{y}{\delta'} + \frac{5}{3}\left(\frac{y}{\delta'}\right)^4 - \left(\frac{y}{\delta'}\right)^5 \qquad (A_2)$$

By combining Equations (A_1) and (A_2) (for $B = 0$) a concise and accurate expression for h_D/h_{D_0} is obtained. The result is

$$\frac{h_D}{h_{D_0}} = \frac{\phi}{\left(1 - \frac{4}{21} S_w\right)^{\frac{1}{2+m}}} \qquad (A_3)$$

APPENDIX II

Modification of Large Schmidt Number Solution for Forced Convection to Include Effects of M_w/M_∞ and B^* at Finite Schmidt Numbers

The solution to the diffusion equation for forced convection at large Schmidt numbers with a variable density has been given by Stewart (5) and discussed in this paper. For constant properties the high Schmidt number solution has been modified so as to give good results at moderate Schmidt numbers even for finite interfacial velocities (15). This modified large Schmidt number solution will be extended here to include effects of a varying density. As in the constant property case, the modification is constructed by correcting the surface shear stress on a flat plate for the effect of a finite interfacial velocity and varying density in a manner which should be reasonable for large Schmidt numbers. Then, hopefully, the results will be useful even for Schmidt numbers of order unity. Taking $M = M_\infty$ in Equation (22), dropping $U\dfrac{dU}{dx}$ (valid for flat plate), substituting $u^* = \beta y$, $v^* = v_w^* - \dfrac{d\beta}{dx}\dfrac{y^2}{2}$ and using the similarity transformation given in Equation (8) with $\dfrac{u^*}{U} = g(\eta)$ gives

$$-\eta^2 g' = N_{Sc} g'' + \theta'(0) g' \left[B^* + \frac{(M_w - M_\infty)}{M_\infty} e^{-h(\eta)} \right] \qquad (B_1)$$

For the boundary conditions $g(0) = 0$, $g(\infty) = 1$ the solution is

$$\frac{1}{g'(0)} = \int_0^\infty exp\left\{ -\frac{1}{N_{Sc}} \left[h(\eta) + \theta'(0)\left(\frac{M_w}{M_\infty} - 1\right) \int_0^\eta e^{-h(t)}\, dt \right] \right\} d\eta \qquad (B_2)$$

For $N_{Sc} = 1$ the integral is easily evaluated to give

$$\frac{\beta}{\beta_0} = \left(\frac{h_D}{h_{D_0}^*}\right)_{N_{Sc} \to \infty} \bullet \left(\frac{\alpha}{e^\alpha - 1}\right) \qquad (B_3)$$

Substituting the corrected shear stress into the expression for h_D^* yields the expression for the corrected mass transfer coefficient when $N_{Sc} = 1$.

$$\left(\frac{h_D^*}{h_{D0}^*}\right)_{N_{Sc}=1} = \left(\frac{h_D^*}{h_{D0}^*}\right)^{4/3}_{N_{Sc}\to\infty} \bullet \left(\frac{\alpha}{e^{\alpha}-1}\right)^{1/3} \quad (B_4)$$

Thus the term $[\alpha/(e^{\alpha}-1)]^{1/3}$ is the predicted variable density correction when $N_{Sc} = 1$. Since the analysis is approximate and the integral clumsy for $N_{Sc} \neq 1$, this correction is suggested for all Schmidt numbers near unity. Use of this correction is made in the Discussion Section of the paper. As in the case of constant properties, it is expected that this correction might apply reasonably well to geometries other than the flat plate.

Manuscript received October 14, 1963; revision received September 14, 1964; paper accepted April 5, 1965. Paper presented at A.I.Ch.E. San Juan meeting.

Interstage Mixing in an Oldshue-Rushton Liquid-Liquid Extraction Column

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Interstage mixing was measured in a 4-in. diam. Oldshue-Rushton column fed with a salt solution at the top and distilled water at the bottom, with the diluted salt solution leaving at the top.

Mixing between stages is relatively slight at low agitator speeds, but increases very rapidly with speed once the turbulent region is reached. Interstage mixing is reported in terms of bulk backflows and also in terms of eddy diffusivities. The amount of interstage mixing is similar to that reported in the literature for rotating disc contactors.

Variations in the horizontal baffle plate design were also studied.

The use of vertical columns rather than mixers-settlers for the continuous extraction of a solute from one liquid into another is quite commonplace. Similar columns are also used as chemical reactors. The efficiency of the column depends mainly on the rate of mass transfer between the phases. However, a number of workers (*2, 5, 8, 10, 11*) have recognized that backmixing or internal circulation may be a major cause of a lowered efficiency in these columns. In fact, just recently Treybal (*9*) proposed a new type of column whose complex internal construction is designed to eliminate interstage mixing.

The degree of interstage mixing that takes place during liquid-liquid extractions is not normally easy to measure. The lowered efficiency that results from backmixing often shows up as a maximum in the curves of extraction efficiency vs. agitator speed. Higher speeds decrease the drop size and therefore increase the surface, and thus, along with the greater turbulence, tend to increase the rate of extraction. On the other hand, higher speeds also increase the interstage mixing; therefore there is often an optimum agitator speed for any given system.

Until now, the actual amount of backflow has not been determined, although Westerterp and Mayberg (*10*) found that an impeller in the top stage caused severe interstage mixing in the top three stages of a rotating disk contactor. Miyauchi et al. (*3, 4*), Eguchi and Nagata (*1*), and Sleicher (*7*) have taken interstage mixing into account by using an eddy diffusivity term in the mass transfer equations. From the actual performance of the column, it is then possible to determine the value of the eddy diffusivity. Strand, Olney, and Ackerman (*8*) and Westerterp and Mayberg (*11*) have directly measured this diffusivity term in a rotating disk contactor.

The approach taken here is to directly measure the amount of interstage mixing in a model, single phase system where no extraction is taking place. In this agitated column the contents of any one stage are assumed to be homogeneous, and concentration changes should then occur in a step-by-step fashion at the horizontal plates separating the stages. The results are explicit, and should directly relate to actual conditions.

EXPERIMENTAL

The Oldshue-Rushton type column (*5*) used for these tests is illustrated in Figure 1. The column consists of a 4-in. I.D. Plexiglas tube. The stainless steel horizontal plates have 2-in. diam. openings and are spaced 2 in. apart. The four ½-in. wide vertical baffles serve to support the horizontal plates. The 2-in. diam., six bladed turbine agitators are manufactured by the Mixing Equipment Company. Teflon steady bearings are used at the top and bottom of the column.

A salt solution is introduced into the top of the column, and distilled water into the bottom. Diluted salt solution is removed from the top. The amount of interstage mixing is determined from the salt concentration at the bottom c_k, the salt concentration of the effluent diluted salt solution c_d, and the distilled water flow F_w, as follows.

The nomenclature illustrated in Figure 1 is used. A salt balance on the top portion of the column above stage n gives

$$c_sF_s + c_n(F_b + F_w) = c_dF_d + c_{n-1}F_b \quad (1)$$

while the overall balance is

$$c_sF_s = c_dF_d \quad (2)$$

Therefore

$$c_n(F_b + F_w) = c_{n-1}F_b \quad (3)$$