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THE INFLUENCE OF PHYSICAL PROPERTY VARIATIONS ON LIQUID-PHASE MASS TRANSFER FOR VARIOUS LAMINAR FLOWS

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Abstract—The combined effect of density, diffusivity and viscosity variations and of the velocity at the interface upon the rate of mass transfer from a rigid surface has been investigated by a perturbation method. The analysis does not consider natural convection, and is restricted to systems of high Schmidt number (lower limit estimated at $Sc = 100$), for which the velocity profile in the diffusion boundary layer is linear. The diffusion equations for three diverse flow geometries, the rotating disk, the flat plate and the falling liquid film, are identical in form at high Schmidt numbers; the effect of the particular geometry is represented by a single parameter, which is characteristic of the limiting slope of the velocity profile near the surface. Application to three typical binary systems indicated that these phenomena can alter the Sherwood number by as much as 30 per cent from its value in the absence of property variations and interfacial velocity. The corrections for variable properties and interfacial velocity may be applicable to a much wider class of solid boundary flows than the three cases considered, and to liquid–liquid systems for which the interface is rigid.

NOMENCLATURE[†]

a,	constant of proportionality between the parallel velocity component and normal distance;
a_0,	constant of proportionality between the parallel velocity component and normal distance for all properties constant at their wall value;
C,	molar concentration, g-moles/cm^3;
D,	diffusion coefficient, cm^2/s, defined by equation (A.6);
$F(\eta)$,	dimensionless radial velocity component for a rotating disk, equation (8);
$f(\eta)$,	dimensionless velocity for flat-plate flow, defined by equation (26);
g,	acceleration of gravity, cm/s^2;
$H(\eta)$,	defined by equation (11), equal to the dimensionless normal velocity for rotating-disk flow for the constant property, zero mass transfer case;
$I_0(\chi)$,	equal to $\int_0^\chi \exp\,[-\,t^3]\,\mathrm{d}t$;
k_c,	mass-transfer coefficient, defined by equation (60), cm/s;
K,	defined by equation (64);
$L(\eta)$,	function describing the effect of density changes on the normal velocity for flat-plate and rotating disk flow, equation (16);
L,	length unit used to make the normal distance dimensionless, cm, equations (7), (25) and (33);
m,	exponent in equation (59), equal to $\frac{1}{2}$ for the flat-plate and rotating-disk, and to $\frac{1}{3}$ for falling-film flow;
M,	molecular weight of the solute;
n,	mass flux of solute relative to stationary observer, g/cm^2 s;
N,	molar flux of solute relative to stationary observer, g-mole/cm^2 s, equal to n/M;
R,	ratio of $\theta'(0)$ to $\theta^{*\prime}(0)$, defined by equation (48);
r,	radial distance on a rotating disk;
S,	ratio of the solvent to solute mass fluxes;

[†] This table does not include the special notation used in the Appendices, which is defined in their accompanying text.

Sc,	Schmidt number, ν/D;
Sh,	Sherwood number, defined by equation (62);
u,	velocity component parallel to surface, cm/s;
U,	mainstream velocity for flat-plate flow, cm/s;
$\mathbf{V}$,	mass average velocity vector of the fluid;
v,	velocity component normal to surface, cm/s;
W,	mass fraction of the diffusing solute;
x,	distance in the direction of flow for a flat plate or falling film, cm;
y,	distance normal to surface, cm.

Greek symbols

α,	constant of proportionality between the dimensionless parallel velocity component and dimensionless normal distance;
β, γ, δ,	cross-product perturbation functions;
Γ,	mass flow rate per unit perimeter, g/cm s;
ϵ_ρ,	density perturbation parameter, defined by equation (3);
ϵ_D,	diffusivity perturbation parameter, defined by equation (4);
ϵ_V,	interfacial velocity perturbation parameter, defined by equation (22);
η,	dimensionless normal distance from the surface, defined for the three cases by equation (7), (25) and (33);
θ,	dimensionless mass fraction, $(W - W_\infty)(W_0 - W_\infty)$;
Λ,	angle of inclination from the vertical of the wall down which the falling liquid film flows;
μ,	viscosity, P;
ν,	kinetic viscosity, cm^2/s;
ρ,	solution density, g/cm^3;
ϕ_1, ϕ_2,	interfacial velocity perturbation functions;
χ,	dimensionless normal distance, defined by equation (39);
Ψ_1, Ψ_2,	diffusivity perturbation functions;
Ω_1, Ω_2,	density perturbation functions;
ω,	rate of rotation of disk, rad/s.

Subscripts

0,	at the surface;
∞,	in the free stream.

Superscripts

$'$,	denotes differentiation with respect to χ;
$*$,	denotes constant properties and zero interfacial velocity.

INTRODUCTION

THIS study presents a perturbation scheme for solving the diffusion equation when the density and diffusivity are known functions of concentration. The method requires that these two properties vary exponentially with mass fraction over the composition range of interest, a limitation which is fortunately followed by many binary liquids.

The diffusivity of a binary liquid system may be a very strong function of composition; a change over reasonable concentration limits by a factor of 2 is not uncommon. Liquid densities, on the other hand, are generally not too sensitive to composition unless extremely large driving forces or solutions of the heavy elements are considered.†

The effect of the velocity generated by the mass-transfer process is accounted for in the same manner as has been presented elsewhere [1–3]. The restriction of high Schmidt number imples that the diffusion boundary layer contains only the linear portion of the velocity profile. The effect of viscosity variation is included by adaption of a simplification due to Schuh [4].

Three different flow geometries are considered: flat-plate flow; rotating-disk flow, which does not require the simplification of boundary-layer theory; and the short-contact-time falling liquid flow which, despite the lack of a true hydrodynamic boundary layer, can be treated by the same method. The approach is believed to be sufficiently general to include laminar flows other than the above-mentioned three.

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† In gases, the situation is just reversed; for a perfect gas mixture, the binary diffusion coefficient is a weak function of composition, but, since the density is proportional to the mean molecular weight, large variations of this property with composition are often encountered.

The diffusion equation can be written as:†

$$\rho \mathbf{V} \cdot \nabla\theta = \nabla \cdot (\rho D \nabla\theta) \qquad (1)$$

or

$$\nabla^2\theta - \left\{\frac{\mathbf{V}}{D} - (W_0 - W_\infty)\left[\frac{1}{\rho D}\,\frac{\mathrm{d}(\rho D)}{\mathrm{d}W}\right]\nabla\theta\right\} \cdot \nabla\theta = 0 \qquad (2)$$

with the definitions

$$\epsilon_\rho = -\,(W_0 - W_\infty)\,\frac{1}{\rho}\,\frac{\mathrm{d}\rho}{\mathrm{d}W} = \ln(\rho_\infty/\rho_0) \qquad (3)$$

$$\epsilon_D = -\,(W_0 - W_\infty)\,\frac{1}{D}\,\frac{\mathrm{d}D}{\mathrm{d}W} = \ln(D_\infty/D_0). \qquad (4)$$

Equation (2) becomes

$$\nabla^2\theta - \left\{\frac{\mathbf{V}}{D} + (\epsilon_\rho + \epsilon_D)\nabla\theta\right\} \cdot \nabla\theta = 0. \qquad (5)$$

It will be assumed that both ϵ_ρ and ϵ_D are independent of composition, or that semi-log plots of ρ and D against W are linear between W_0 and W_∞.

ROTATING-DISK FLOW

Millsaps and Pohlhausen [5] have shown that the steady-state, constant-property energy equation (in the absence of frictional dissipation) depends only upon the distance normal to the surface and is independent of the radius. The constant-property diffusion equation is of the same form and satisfies the same dimensionless boundary conditions; hence it too is one-dimensional. Since the property variations follow the concentration profile, the relation governing variable-property mass transfer from a rotation disk is one-dimensional as well, and from equation (5):

$$\frac{\mathrm{d}^2\theta}{\mathrm{d}y^2} - \left\{\frac{v}{D} + (\epsilon_\rho + \epsilon_D)\frac{\mathrm{d}\theta}{\mathrm{d}y}\right\}\frac{\mathrm{d}\theta}{\mathrm{d}y} = 0. \qquad (6)$$

The following dimensionless quantities are introduced [6a]:

For the normal distance:

$$\eta = y\sqrt{\left(\frac{\omega}{\nu_0}\right)}. \qquad (7)$$

For the radial velocity:

$$u = r\omega\,F(\eta). \qquad (8)$$

Since the density is a function only of composition, and since the latter is independent of radius, the density depends only upon the normal distance. Therefore the over-all continuity equation can be written as:

$$\rho\,\frac{\partial u}{\partial r} + \frac{\rho u}{r} + \frac{\partial}{\partial y}(\rho v) = 0. \qquad (9)$$

Introducing equations (7) and (8) into (9) and integrating between zero and η:

$$v = \frac{\rho_0}{\rho}\,v_0 - 2\sqrt{(\omega\nu_0)}\,\frac{1}{\rho}\int_0^\eta \rho\,F(\eta)\,\mathrm{d}\eta. \qquad (10)$$

Now define the function $H(\eta)$ by:

$$\frac{\mathrm{d}H(\eta)}{\mathrm{d}\eta} = -\,2F(\eta) \qquad (11)$$

and substitute (11) into (10):

$$v = \frac{\rho_0}{\rho}\,v_0 + \sqrt{(\omega\nu_0)}\,\frac{1}{\rho}\int_0^\eta \rho\,\frac{\mathrm{d}H}{\mathrm{d}\eta}\,\mathrm{d}\eta. \qquad (12)$$

Integrating the last term of equation (12) by parts:

$$\frac{1}{\rho}\int_0^\eta \rho\,\frac{\mathrm{d}H}{\mathrm{d}\eta}\,\mathrm{d}\eta = H(\eta) - \frac{\rho_0}{\rho}\,H(0) - \frac{1}{\rho}\int_0^\eta H\,\frac{\mathrm{d}\rho}{\mathrm{d}\eta}\,\mathrm{d}\eta. \qquad (13)$$

Setting

$$v_0 = \sqrt{(\nu_0\omega)}\,H(0), \qquad (14)$$

substitution of equations (13) and (14) into equation (12) yields:

$$v = \sqrt{(\nu_0\omega)}\,H(\eta)\,[1 - L(\eta)] \qquad (15)$$

where

$$L(\eta) = \frac{1}{\rho H(\eta)}\int_0^\eta H(\eta)\,\frac{\mathrm{d}\rho}{\mathrm{d}\eta}\,\mathrm{d}\eta. \qquad (16)$$

Substituting equations (7) and (15) into equation (6), there results:

$$\frac{\mathrm{d}^2\theta}{\mathrm{d}\eta^2} - \left\{\left(\frac{D_0}{D}\right) Sc_0\,H(\eta)\,[1 - L(\eta)] + (\epsilon_\rho + \epsilon_D)\,\frac{\mathrm{d}\theta}{\mathrm{d}\eta}\right\}\frac{\mathrm{d}\theta}{\mathrm{d}\eta} = 0. \qquad (17)$$

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† A derivation of equation (1) and a discussion of its applicability to liquid-phase mass transfer is presented in Appendix A.

At large Schmidt number the greatest portion of the concentration drop occurs quite close to the surface, and the diffusion boundary layer is much thinner than the hydrodynamic boundary layer. In the former region, the radial velocity is satisfactorily represented by the first term of its power-series expansion about $\eta = 0$, or u is proportional to y. Equations (7) and (8) indicate that in dimensionless form this reduction leads to:

$$F(\eta) = a\eta. \tag{18}$$

For the constant-property, zero mass transfer case, Sparrow and Gregg [7] have shown this approximation yields results within 7 per cent of the exact solution at $Sc = 100$.

$H(\eta)$ can be obtained by integration of equation (11) as:

$$H(\eta) = H(0) - a\eta^2. \tag{19}$$

According to the definition of the diffusion coefficient, the interfacial velocity† is

$$v_0 = \frac{-D_0(\partial W/\partial y)_0}{1/(1+S) - W_0} \tag{20}$$

or, in dimensionless form:

$$H(0) = -\frac{\epsilon_V}{Sc_0}\left(\frac{\mathrm{d}\theta}{\mathrm{d}\eta}\right)_0 \tag{21}$$

where

$$\epsilon_V = \frac{W_0 - W_\infty}{1/(1+S) - W_0}. \tag{22}$$

Combining equations (19) and (21) with equation (17), there results:

$$\frac{\mathrm{d}^2\theta}{\mathrm{d}\eta^2} + \left\{\left(\frac{D_0}{D}\right)\left[\alpha Sc_0\eta^2 + \epsilon_V\left(\frac{\mathrm{d}\theta}{\mathrm{d}\eta}\right)_0\right][1 - L(\eta)] - (\epsilon_\rho + \epsilon_D)\frac{\mathrm{d}\theta}{\mathrm{d}\eta}\right\}\frac{\mathrm{d}\theta}{\mathrm{d}\eta} = 0. \tag{23}$$

FLAT-PLATE FLOW

The simplification required to reduce the constant-property diffusion equation to its boundary-layer form involves neglecting $\partial^2\theta/\partial x^2$ compared to $\partial^2\theta/\partial y^2$. Similarly, the physical meaning of the boundary-layer assumptions also permits neglecting $(\partial\theta/\partial x)^2$ compared to $(\partial\theta/\partial y)^2$. With these two simplifications, equation (5) becomes:

$$\frac{\partial^2\theta}{\partial y^2} - \frac{u}{D}\frac{\partial\theta}{\partial x} - \left\{\frac{v}{D} + (\epsilon_\rho + \epsilon_D)\frac{\partial\theta}{\partial y}\right\}\frac{\partial\theta}{\partial y} = 0. \tag{24}$$

The usual dimensionless reduction of the flat-plate equation employs the new variables:

$$\eta = y\sqrt{\left(\frac{U}{\nu_0 x}\right)} \tag{25}$$

and

$$f'(\eta) = u/U. \tag{26}$$

As in the case of the rotating disk, the over-all continuity equation can be integrated to give an expression for v (see Schuh [4]):

$$v = \tfrac{1}{2}\sqrt{\left(\frac{\nu_0 U}{x}\right)}\{\eta f'(\eta) - f(\eta)[1 - L(\eta)]\} \tag{27}$$

where $L(\eta)$ is given again by equation (16) with H replaced by f, and v_0 is:‡

$$v_0 = -\tfrac{1}{2}\sqrt{\left(\frac{\nu_0 U}{x}\right)}f(0). \tag{28}$$

The diffusion equation for the flat plate can now be written as:

$$\frac{\mathrm{d}^2\theta}{\mathrm{d}\eta^2} + \left\{\left(\frac{D_0}{D}\right)Sc_0\frac{f(\eta)}{2}[1 - L(\eta)] - (\epsilon_\rho + \epsilon_D)\frac{\mathrm{d}\theta}{\mathrm{d}\eta}\right\}\frac{\mathrm{d}\theta}{\mathrm{d}\eta} = 0. \tag{29}$$

Within the diffusion boundary layer at high Schmidt numbers, u can be assumed proportional to y, or:

$$f'(\eta) = 4a\eta. \tag{30}$$

Integrating:

$$\frac{f(\eta)}{2} = \frac{f(0)}{2} + a\eta^2. \tag{31}$$

With $f(0)$ from equations (20) and (28), substitution of equation (31) into equation (29) yields equation (23).

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† The $1/(1+S) - W_0$ term in equation (20) presumes the applicability of a Stephan–Maxwell type definition of the diffusion coefficient to a binary liquid. Equation (20) can be derived from equations (A.2–4, 6) of Appendix A.

‡ The restriction that v_0 vary inversely as $\sqrt{x}$ agrees fairly well with the condition of constant mass fraction at the wall [1].

FALLING-FILM FLOW

Following Bird's [8] development for the constant-property case, it will be assumed that diffusion in the x-direction is negligible, and that the y-velocity component is due only to diffusion. With the additional assumption that $(\partial\theta/\partial x)^2 \ll (\partial\theta/\partial y)^2$, equation (5) becomes

$$\frac{\partial^2\theta}{\partial y^2} - \left\{\frac{v}{D} + (\epsilon_\rho + \epsilon_D)\frac{\partial\theta}{\partial y}\right\}\frac{\partial\theta}{\partial y} - \frac{u}{D}\frac{\partial\theta}{\partial x} = 0. \quad (32)$$

A dimensionless distance is defined as:

$$\eta = y\left(\frac{a_0}{\nu_0 x}\right)^{1/3} \quad (33)$$

where

$$a_0 = (g\cos\Lambda)^{2/3}(3\Gamma)^{1/3}\rho_0^{1/3}/\mu_0^{2/3}. \quad (34)$$

In the constant-property case, the velocity parallel to the wall is a parabola with its vertex at the free surface. Close to the wall, however, u can be represented by the linear term alone, or $u = a_0 y$. For the variable-property case considered here, it will be assumed that u is still linear in y, but with a constant of proportionality determined by the magnitude of the density and viscosity variations through the diffusion boundary layer. Thus:

$$u = ay. \quad (35)$$

Contrary to the rotating-disk or flat-plate flows, it is not possible to express the normal velocity in terms of the dimensionless distance η and the correction term $L(\eta)$, as in equations (15) and (27). The effect of variable density on the over-all continuity equation can be expressed by the $L(\eta)$ integral only for those flow situations for which both the constant-property velocity and concentration distributions are functions of the same dimensionless variable η. In the falling-film case, this is not true; the parallel velocity is not a function of x, as indicated by equation (35) with $a = a_0$. The composition, on the other hand, is a function solely of the similarity variable η of equation (33). Since the v-term in equation (32) is identically zero in the absence of mass transfer, the normal velocity with mass transfer will be identified solely with the diffusional velocity, or v_0. This is equivalent to neglecting the effect of compressibility on the over-all continuity equation or to neglecting $L(\eta)$ compared to unity in the rotating-disk and flat-plate derivations.

Substituting equations (20), (33) and (35) into equation (32), the diffusion equation becomes:

$$\frac{d^2\theta}{d\eta^2} + \left\{\left(\frac{D_0}{D}\right)\left[\left(\frac{1}{3}\frac{a}{a_0}\right)Sc_0\eta^2 + \epsilon_V\left(\frac{d\theta}{d\eta}\right)_0\right] - (\epsilon_\rho + \epsilon_D)\frac{d\theta}{d\eta}\right\}\frac{d\theta}{d\eta} = 0. \quad (36)$$

If the geometry-dependent constant for the falling-film system is taken as

$$\alpha = \frac{1}{3}\frac{a}{a_0}, \quad (37)$$

then equation (36) is identical to equation (23) with $L(\eta) = 0$. (No $L(\eta)$ term appears in equation (36) since v has been assumed equal to v_0.)

APPLICATION TO OTHER FLOW GEOMETRIES

The diffusion equations for the three flow geometries have been reduced to equation (23), in which only the numerical value of the parameter α identifies the particular hydrodynamic system. It is reasonable to expect that equation (23) applies to a wider class of laminar flows than those considered here—even to flows which are too complex to permit calculation of the parameter α (or the shear stress at the surface). Only two restrictions are placed upon the flow: that a diffusion boundary layer exist, and that the velocity parallel to the surface in this region be linear in normal distance. These two requirements imply that the constant-property, zero-interfacial-velocity diffusion equation is of the form:

$$\frac{d^2\theta}{d\eta^2} + \alpha^* Sc\eta^2\frac{d\theta}{d\eta} = 0. \quad (38)$$

where η is some dimensionless distance characteristic of the particular flow. Equation (23) is merely an expanded form of equation (38) in which property variations and an interfacial velocity have been considered. Any laminar flow for which the diffusion equation is reducible to equation (38) can be treated by the method outlined here.

In the subsequent analysis, the $L(\eta)$ term in equation (23) (which applies to both rotating-disk and flat-plate flow) will be neglected compared to unity. This simplification is tantamount to assuming that the over-all continuity equation retains its incompressible form despite density variations. The same assumption has already been invoked in deriving equation (36) for the falling film, since the effect of compressibility on the over-all continuity equation is not expressible in terms of $L(\eta)$ for this case. It is shown in Appendix B that neglecting $L(\eta)$ has but a modest effect on the final result. With this assumption, and a new distance variable defined by

$$\chi = \left(\frac{aSc_0}{3}\right)^{1/3} \eta, \tag{39}$$

equations (23) and (36) become:

$$\theta'' + \left\{\left(\frac{D_0}{D}\right)\left[3\chi^2 + \epsilon_V\theta'(0)\right] - (\epsilon_\rho + \epsilon_D)\theta'\right\}\theta' = 0 \tag{40}$$

where the primes denote differentiation with respect to χ. The boundary conditions are:

$$\theta(0) = 1, \qquad \theta(\infty) = 0. \tag{41}$$

Equation (40) is analogous to the variable-property energy equation derived by Acrivos [9].

The transformation of equation (39) relieves the diffusion equation of dependence upon specific values of a and Sc. Equation (40) is independent of the particular geometry and of the Schmidt number (provided the latter is large).

For $\epsilon_\rho = \epsilon_D = \epsilon_V = 0$, equation (40) reduces to

$$\theta^{*\prime\prime} + 3\chi^2\theta^{*\prime} = 0. \tag{42}$$

The solution is

$$\theta^*(\chi) = 1 - I_0(\chi)/I_0(\infty). \tag{43}$$

Equation (43) (or its equivalent) has been derived previously for particular geometries [7–9]

SOLUTION TO THE GENERAL DIFFUSION EQUATION

The diffusivity ratio in equation (40) can be approximated by the following means: integrating equation (4) from $\theta = 1$ to θ there results

$$\frac{D_0}{D} = e^{-\epsilon_D(1-\theta)} \approx 1 - \epsilon_D(1-\theta) + \tfrac{1}{2}\epsilon_D^2(1-\theta)^2 + \ldots. \tag{44}$$

Within the framework of the perturbation analysis, which does not permit large variations of θ from the zero mass transfer, constant-property profile, the series of equation (44) will be carried only through the second-order term and the true concentration profile approximated by θ^* of equation (43). The diffusivity ratio can then be written as

$$\frac{D_0}{D} = 1 - \left(\frac{I_0(\chi)}{I_0(\infty)}\right)\epsilon_D + \left(\frac{1}{2}\frac{I_0^2(\chi)}{I_0^2(\infty)}\right)\epsilon_D^2. \tag{45}$$

Inserting this relation into equation (40), one obtains the following non-linear equation for θ.

$$\theta'' + \left\{[3\chi^2 + \epsilon_V\theta'(0)]\left[1 - \left(\frac{I_0(\chi)}{I_0(\infty)}\right)\epsilon_D + \left(\frac{1}{2}\frac{I_0^2(\chi)}{I_0^2(\infty)}\right)\epsilon_D^2\right] - (\epsilon_\rho + \epsilon_D)\theta'\right\}\theta' = 0. \tag{46}$$

The boundary conditions are given by equation (41).

A solution to equation (46) will be sought as a perturbation expansion of θ in terms of ϵ_ρ, ϵ_D and ϵ_V. With all second-order terms included, such a series can be written as:

$$\begin{aligned}\theta(\chi) = \theta^*(\chi) &+ \Psi_1(\chi)\epsilon_D + \Omega_1(\chi)\epsilon_\rho + \phi_1(\chi)\epsilon_V \\ &+ \Psi_2(\chi)\epsilon_D^2 + \Omega_2(\chi)\epsilon_\rho^2 + \phi_2(\chi)\epsilon_V^2 \\ &+ \beta(\chi)\epsilon_\rho\epsilon_D + \gamma(\chi)\epsilon_\rho\epsilon_V + \delta(\chi)\epsilon_D\epsilon_V.\end{aligned} \tag{47}$$

$\theta^*(\chi)$ obeys the same boundary conditions as $\theta(\chi)$, i.e. those of equation (41). The remaining functions are to be zero at both $\chi = 0$ and $\chi = \infty$.

Upon substituting equation (47) into equation (46) and setting the coefficients of the various powers of $\epsilon_D, \epsilon_\rho, \epsilon_V$, ϵ_D^2, etc., equal to zero, linear differential equations for each of the coefficients of the ϵ's in equation (47) are obtained. These equations can be solved successively to obtain θ^*, ψ_1, Ω_1, $\ldots$ δ in terms of integrals with χ as the upper limit. The integrals, which have been evaluated by machine computations, determine the concentration profile $\theta(\chi)$ for any combination of ϵ_ρ, ϵ_D and ϵ_V. Because the slope at the surface determines the mass-transfer rate, only $\theta'(0)$ is of interest. Expressed as the ratio of the actual slope to that which would exist in the absence of property variations and interfacial velocity, the solution to equation (46) can be written as:

$$R = \frac{\theta'(0)}{\theta^{*\prime}(0)} = 1 + \tfrac{1}{2}\epsilon_\rho + 0{\cdot}262\epsilon_D - 0{\cdot}566\epsilon_V + \tfrac{1}{6}\epsilon_\rho^2 + 0{\cdot}046\epsilon_D^2 + 0{\cdot}407\epsilon_V^2 + 0{\cdot}215\epsilon_\rho\epsilon_D - 0{\cdot}566\epsilon_\rho\epsilon_V - 0{\cdot}232\epsilon_D\epsilon_V. \quad (48)$$

Several interesting qualitative conclusions can be drawn from equation (48). For equal values of the perturbation parameters, ϵ_ρ and ϵ_D, the density variation is approximately twice as important as the diffusivity change. Formally, this is due to the D_0/D term in equation (40). The relative magnitude of the density and diffusivity effects and the positive sign of their first-order perturbation terms can be interpreted physically as follows: The rate of mass transfer normal to the surface can be written as:

$$n = \rho\left[- D\frac{\partial W}{\partial y} + Wv\right]. \quad (49)$$

The bracketed term in the above expression has the units of a velocity; hence, for a fixed value of this term, an increase in density increases the transfer rate.† Equation (48) gives the ratio of the actual composition gradient at the surface to that which would prevail if all properties remained at their surface values. Equation (3) is a measure of the increase in density from the surface towards the free stream. Since a qualitative examination of equation (49) implies that an increase in density over the surface value should increase the transfer rate, the sign on the ϵ_ρ term in equation (48) must be positive to reflect the physical situation.

The positive sign on the ϵ_D term in equation (48) merely confirms the physically obvious conclusion that any increase in the diffusion coefficient will result in higher mass transfer. Since a positive value of ϵ_D, by equation (4), signifies larger diffusivities in the boundary layer than at the wall, then the enhancement of the transfer rate must appear as a positive term in equation (48). However, while the density affects both the diffusive and convective components of the velocity in equation (49), the diffusion coefficient appears only in one term. Therefore, the variation in D will affect the transfer rate only in that region of the boundary layer where the convective component is small, i.e. near the surface. On the average, an increase of diffusion coefficient will not be as effective as an equivalent increase in the total density. The coefficient of ϵ_ρ should be and is larger than that of ϵ_D in equation (48).

The effect of a positive interfacial velocity is to thicken the diffusion boundary layer, thus increasing the resistance to mass transfer above that which would exist if the interfacial velocity were zero. For this reason, the coefficient of ϵ_V in equation (48) is negative.‡

Except for the ϵ_V^2 term, the coefficients of the pure second-order terms are quite small. For extreme values of $\epsilon_\rho = 0{\cdot}5$ and $\epsilon_D = 1$, for example, they are less than 5 per cent of unity. This suggests that the third-order terms will be negligibly small. The cross-product coefficients are relatively large, indicating a significant degree of coupling of the three perturbation constants in equation (40). They are of the same order of magnitude as the lowest first-order coefficient of the perturbation constant they contain; the $\epsilon_\rho\epsilon_D$ and $\epsilon_D\epsilon_V$ coefficients are (in absolute magnitude) nearly equal to each other and to the coefficient of ϵ_D. The coefficient of $\epsilon_\rho\epsilon_V$ is identical to that of ϵ_V, which in turn is close to that of ϵ_ρ.

Considering the effect of each of the three perturbation constants independently, it appears that equation (48) will be in greatest error in estimating the effect of interfacial velocity, since the coefficient of ϵ_V^2 is much larger than that of

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† This is entirely analogous to the flow of a single substance in a duct of unit cross-sectional area, in which the rate at which mass passes a fixed point is the fluid density times the average velocity. If the velocity is maintained constant, the mass flow can be increased simply by increasing the density of the fluid.

‡ The magnitude of this coefficient, 0·566, is identical to that obtained by Merk [2] by a similar perturbation method for a flat plate.

either ϵ_ρ^2 or ϵ_D^2. Hence the range of perturbation constants for which equation (48) is valid would be greatest for ϵ_D and smallest for ϵ_V. Therefore, the two-term approximation to the effect of ϵ_V on R was compared to an exact numerical solution of equation (40) with $\epsilon_\rho = \epsilon_D = 0$:

$$\theta'' + [3\chi^2 + \epsilon_V \theta'(0)]\theta' = 0. \qquad (50)$$

This relation is, as before, subject to the boundary conditions of equation (41). The solution is:

$$-\theta'(0) = [\textstyle\int_0^\infty \exp\{-\chi^3 + \epsilon_V \theta'(0)\chi\}\,\mathrm{d}\chi]^{-1}. \qquad (51)$$

For each value of ϵ_V, equation (51) can be solved by assuming a value of $\theta'(0)$, computing the integral on the right-hand side, and comparing the assumed $\theta'(0)$ with the reciprocal of the calculated integral. When the two agree satisfactorily, $\theta'(0)$ for the particular ϵ_V under consideration is determined.†

The solution of equation (51) is presented graphically in Fig. 1 as $[\theta'(0)/\theta^{*\prime}(0) - 1]$ vs. ϵ_V (solid line), and is compared to the two-term approximation obtained from equation (48) with $\epsilon_D = \epsilon_\rho = 0$.‡ This plot indicates that the perturbation approximation carrying two terms is quite good for $-0{\cdot}4 \leq \epsilon_V \leq 0{\cdot}4$. Therefore, the effect of interfacial velocity on the mass-transfer rate can be evaluated directly from equation (48) for values of the parameter ϵ_V in this region. For $|\epsilon_V| > 0{\cdot}4$, the solid line in Fig. 1 should be used in place of the ϵ_V and ϵ_V^2 terms in equation (48).

Similar independent evaluations of the ϵ_ρ and ϵ_D terms in equation (48) were not obtained. However, rough estimates of the ranges of validity for these two parameters can be obtained by comparison with the result of the ϵ_V analysis. The two-term expansion in ϵ_V fails for $|\epsilon_V| > 0{\cdot}4$, for which the ϵ_V^2 term in equation (48) is 0·065. If this figure is taken as the maximum permissible value for the ϵ_ρ^2 and ϵ_D^2 terms in equation (48) as well, then $|\epsilon_\rho| \lesssim 0{\cdot}6$ and $|\epsilon_D| \lesssim 1{\cdot}2$. These values should be taken only as tentative limits, for they do not include the influence of the cross-product terms, which will be appreciable when any two of the perturbation parameters are large. For this case, the limiting values of ϵ_ρ, ϵ_D and ϵ_V will be smaller than those suggested above, which consider one effect at a time.

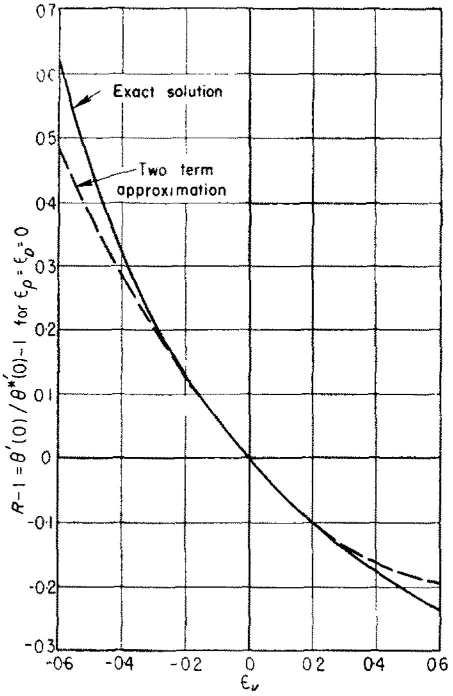

FIG. 1. Comparison of the effect of interfacial velocity as calculated by the exact solution equation (51) and the two-term approximation equation (48) with $\epsilon_\rho = \epsilon_D = 0$.

THE EFFECT OF VARIABLE VISCOSITY

The preceding solution of the diffusion equation requires a linear velocity distribution within the diffusion boundary layer. However, the existence of viscosity variations perturbs this linearity, no matter how large the Schmidt number; equations (18), (30) and (35) represent approximations which improve as viscosity variations decrease.

Analysis of three flow situations has revealed that the sole dependence of the diffusion equation upon the particular flow geometry is contained in the parameter α, which is proportional to the shear stress at the surface. It has

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† For additional discussion concerning equation (50), see [10].

‡ The solid line agrees with the analogous computation of Merk [2] for flat-plate flow.

been shown elsewhere [2, 10] that, in the limit of high Schmidt number, the shear stress at the surface is independent of the interfacial velocity induced by the diffusion process, or α is not a function of ϵ_V. The parameter α is a function of viscosity and density changes across the boundary layer and of α^*, the limiting slope of the dimensionless velocity in the purely hydrodynamic situation (no mass transfer).

Acrivos [9] and Schuh [4] have shown that physical property variations accompanying temperature changes within a thin thermal boundary layer do not affect the shear stress, which behaves as if the properties of the free stream extended directly to the surface. The product of the viscosity and the velocity gradient remains constant, and not the velocity gradient, or

$$\mu \frac{\partial u}{\partial y} = \mu_\infty \left(\frac{\partial u}{\partial y}\right)^{*\infty} \tag{52}$$

where the left-hand side is the actual shear stress and the right-hand term represents the shear stress which would exist at the same point if the free-stream properties extended directly to the surface. This latter term is directly related to α^*, since it describes a constant-property system. Taking the flat plate as an example, the dimensionless form of equation (52) becomes

$$f''(\eta) = 4\alpha^* \sqrt{\left(\frac{\nu_0}{\nu_\infty}\right)} \frac{\mu_\infty}{\mu}. \tag{53}$$

The integrated form of equation (53) is:

$$f'(\eta) = 4\alpha^* \sqrt{\left(\frac{\nu_0}{\nu_\infty}\right)} \int_0^\eta \frac{d\eta}{\mu/\mu_\infty}. \tag{54}$$

This relation, rather than equation (30), is a proper description of the parallel velocity close to the surface of a flat plate in the presence of viscosity or density changes.

If, however, it is assumed that

$$\frac{\mu}{\mu_\infty} \simeq \frac{\mu_0}{\mu_\infty}, \tag{55}$$

equation (54) becomes

$$f'(\eta) = 4\alpha^* \sqrt{\left(\frac{\rho_\infty \mu_\infty}{\rho_0 \mu_0}\right)} \eta. \tag{56}$$

Equation (30) results if α is defined as

$$\alpha = \alpha^* \sqrt{\left(\frac{\rho_\infty \mu_\infty}{\rho_0 \mu_0}\right)}. \tag{57}$$

Schuh has shown that the simplification represented by equation (55) is satisfactory for heat transfer in flat-plate flow with eightfold viscosity variations at a Prandtl number of 10. Equation (55) essentially assumes that the viscosity remains constant at its wall value throughout the diffusion boundary layer and changes abruptly to μ_∞ at the outer edge of this region. The success of this approximation is probably due to the importance of the region extremely close to the wall, where $\mu \simeq \mu_0$. A sketch of the velocity profiles involved is shown in Fig. 2. The lower line is the profile which would result if the bulk viscosity persisted to the surface. The middle curve represents the actual distribution. The approximation of equation (55) leads to the linear profile represented by the dashed line of the figure.

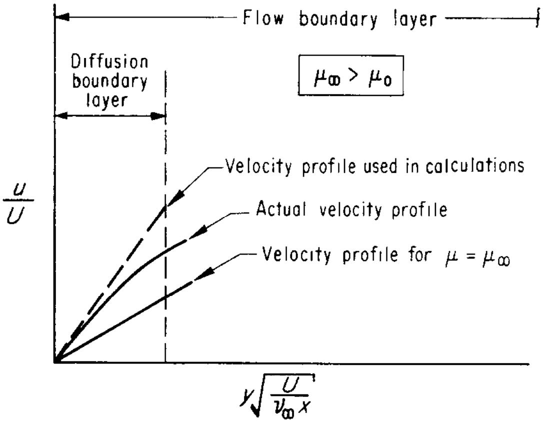

FIG. 2. Schematic velocity profiles within the diffusion boundary layer. Viscosity in free stream greater than at the wall.

Entirely analogous computations on the radial-shear-stress component on a rotating disk again lead to equation (57).

For the falling-liquid film, which is not a boundary-layer flow like the flat plate and rotating disk, the applicability of equation (52) is not immediately evident. However, it can be shown that for arbitrary viscosity and density variations which are restricted to a region close to the wall,

$$\alpha = \alpha^* \left(\frac{\rho_\infty \mu_\infty}{\rho_0 \mu_0}\right)^{1/3} \tag{58}$$

In general, it appears that the ratios of the density–viscosity products are raised to the same power as is the kinematic viscosity in the similarity transformation which defines η [e.g. equations (7), (25) and (33)]. Thus

$$\alpha = \alpha^* \left(\frac{\rho_\infty \mu_\infty}{\rho_0 \mu_0}\right)^{m} \tag{59}$$

where $m = \frac{1}{2}$ or $\frac{1}{3}$ for the cases considered here.

Physically, equations (57) and (58) result from the fact that the shear stress is a gross characteristic of the flow; it depends upon the behavior of the flow field as a whole and is not appreciably affected by variations which are confined to a highly localized region of the system, as is the case with property changes in a very thin diffusion boundary layer.

However, analysis of the effect of variable viscosity and density on laminar pipe flow [11, 12] indicates that equation (59) is not valid for this particular hydrodynamic situation. At high Schmidt (or Prandtl) numbers, the ratio of α to α^* (or the ratio of the actual velocity gradient at the wall to that which would exist for constant-property flow) equals μ_∞/μ_0, irrespective of density changes and the form of the similarity variable used to reduce the diffusion equation to an ordinary differential equation. It should be noted that only equation (59) is inapplicable; it can be shown that the general treatment of the diffusion equation described here and the assumption concerning the equality of the shear stresses at the wall are valid. In order that a diffusion boundary layer exist in a pipe, the active mass-transfer section must be short.

The applicability of equation (59) must, therefore, be restricted to a class of hydrodynamic situations which might be described as free, or external, flows in which the moving fluid is not completely surrounded by a solid surface. In the flat-plate and rotating-disk geometries, the fluid extends to infinity in one direction. In the falling-film system, one boundary of the fluid is a gas–liquid interface, which offers no resistance to slight adjustments in film thickness required by property variations near the wall. In pipe flow, on the other hand, the fluid is completely restricted by the walls of the tube.

THE NET EFFECT OF PROPERTY VARIATIONS AND INTERFACIAL VELOCITY ON THE RATE OF MASS TRANSFER

The mass-transfer coefficient is defined by:

$$N \equiv k_c(C_0 - C_\infty). \tag{60}$$

This definition is chosen because it is directly obtainable from experimental data, i.e. from rate and volumetric concentration measurements. Other definitions of the mass-transfer coefficient have appeared in the literature, involving the use of a diffusive flux (total flux minus the convective contribution at the surface) and the mass-fraction driving force (e.g. [3]). However, the diffusive flux is inconvenient in that it is not immediately related to a material balance involving other parts of the system (for instance, as in the packed-tower-material balance equations), and the use of mass fraction is inconvenient since most equilibrium and analytical data are available as volumetric concentrations. This choice, however, is completely arbitrary, and in no way affects the final result.

For a mass-transfer process characterized by the parameter S, the rate is given by

$$N = -\frac{\rho_0 D_0 (\partial W/\partial y)_0}{M[1 - W_0(1 + S)]}. \tag{61}$$

From equations (60) and (61) and the dimensionless reduction $\eta = y/L$, a local Sherwood number can be obtained as

$$Sh = \frac{[1 - W_0(1 + S)]k_c L}{D_0} = -\left[\frac{C_0 - (\rho_0/\rho_\infty)C_\infty}{C_0 - C_\infty}\right]\left(\frac{d\theta}{d\eta}\right)_0. \tag{62}$$

The appropriate length L can be obtained from equations (7), (25) or (33) for the three cases considered.

The $[1 - W_0(1 + S)]$ term in the Sherwood number appears because of the choice of the total rather than the diffusive flux in the definition of the mass-transfer coefficient. Its incorporation into the Sherwood number follows the common practice in the gas-absorption literature of treating the "log mean partial pressure of the inert gas" (i.e. p_{BM}) term in the same manner. The bracketed term on the right of equation (62) arises from the definition of k_c in terms of the concentration driving force. It disappears if k_c is defined on a mass-fraction driving-force basis, or if there is no density change with composition.

Using equations (3) and (39), equation (62) becomes

$$Sh = -K\left(\frac{\alpha Sc_0}{3}\right)^{1/3}\theta'(0) \tag{63}$$

where

$$K = \frac{C_0 - \mathrm{e}^{-\epsilon_\rho}C_\infty}{C_0 - C_\infty}. \tag{64}$$

Since $\theta^{*\prime}(0) = -1/I_0(\infty) = -1{\cdot}12$, substitution of equations (48) and (59) into equation (63) yields:

$$Sh = \left\{1{\cdot}12\left(\frac{\alpha^* Sc_0}{3}\right)^{1/3}\right\} KR\left(\frac{\rho_\infty\mu_\infty}{\rho_0\mu_0}\right)^{m/3} \tag{65}$$

where the Sherwood number, defined by equation (62), is based on properties at the surface, and K is defined by equation (64). Equation (65) gives the absolute value of the Sherwood number if the hydrodynamic parameter (α^*) of the particular geometry is known. Since the bracketed term in the above relation is the Sherwood number for constant properties and zero interfacial velocity, equation (65) can also be written in a form useful when α^* is not known:

$$\frac{Sh}{Sh^*} = KR\left(\frac{\rho_\infty\mu_\infty}{\rho_0\mu_0}\right)^{m/3}. \tag{66}$$

The effect of variable density, diffusivity and viscosity and of non-zero interfacial velocity is manifest by a deviation of the right-hand side of equation (66) from unity. It should be noted, however, that the factor K in this expression is somewhat arbitrary, inasmuch as it stems from the definition of the mass-transfer coefficient in terms of a concentration driving force. If the weight-fraction potential had been employed, the K would be identically unity. The R term and the ratio of the viscosity-density products, however, are intrinsic to the analysis and do not depend on any arbitrary definitions. For internal or duct flows with short mass-transfer sections, the last term on the right of equations (65) and (66) should be replaced by μ_∞/μ_0.

The characteristic length L of equation (62), the exponent m and the parameter α^* of equation (65) are listed in Table 1 for the three external flows which have been treated in detail.

Table 1. Specific parameters for each flow geometry

Flow geometry	L	m	α^*
Flat plate	$\sqrt{\left(\frac{\nu_0 x}{U}\right)}$	$\frac{1}{2}$	0·083 [6b]
Rotating disk	$\sqrt{\left(\frac{\nu_0}{\omega}\right)}$	$\frac{1}{2}$	0·510 [3, 13]
Falling film	$\left(\frac{\nu_0 x}{a_0}\right)^{1/3}$	$\frac{1}{3}$	$\frac{1}{3}$

a_0 given by equation (34).

NATURAL CONVECTION

There are five places in the system of equations governing the mass-transfer process where the density appears:

(i) In the diffusion equation.
(ii) In the over-all continuity equation.
(iii) Multiplying the convective terms of the equation of motion.
(iv) As an additional buoyancy term in the equation of motion.
(v) Indirectly in the definition of the mass-transfer coefficient.

The foregoing analysis has completely accounted for density variations in (i) amd (v) by the R and K terms of equations (48) and (64). The effect of (iii) results in the appearance of the density ratio in equation (59). Effect (ii) appears in the L integral in equation (16), and the error incurred by neglecting it in the diffusion equation is estimated at ~1 per cent for an extreme case.

For the horizontal flat plate and rotating disk, natural convection will appear only if the bulk fluid is denser than the fluid at the surface. Otherwise, the stratified flow is stable. For other orientations of these two geometries, and for pipe flow, natural convection may occur unless $\epsilon_\rho = 0$.

In general, equations (65) or (66) are strictly applicable only to systems in which the density gradient results in stable stratification. If natural convection is significant, the last term on the right in these two expressions must be modified to include this effect, e.g. as in [11] for pipe flow.

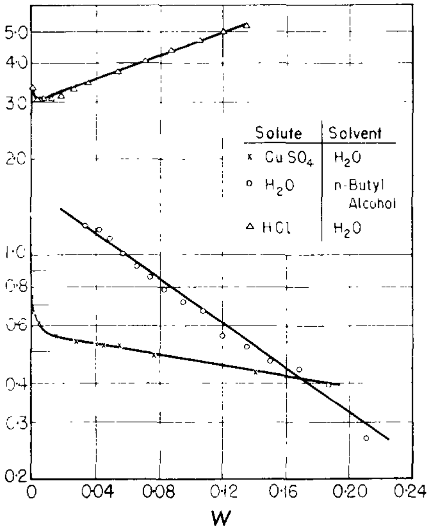

FIG. 3. Diffusivities of three binary liquid systems as a function of composition—$CuSo_4$-H_2O [14]; H_2O-n-butanol [15]; HCl-H_2O [16].

EXAMPLES†

One of the first questions which arises in connection with the previous analysis is this: How well do variations in density and diffusivity in typical binary liquids follow the restricted form represented by equations (3) and (4)? The appropriate data for three systems, chosen because of their relatively large diffusivity variation with composition, are plotted on Figs. 3 and 4. It is evident that the exponential variation of the two properties with mass fraction is reasonably well followed, except for the curvature of the diffusivities of the two inorganic systems at low dilution.

A number of sample calculations are shown in Table 2 for a geometry characterized by $m = \frac{1}{2}$ (e.g. flat plate or rotating disk). The systems considered are:

(a) Solid $CuSO_4 \cdot 5H_2O$ transferring to a free stream of pure water.

(b) $CuSO_4$ transferring from a saturated free stream to a surface at which the copper concentration is reduced to zero (e.g. electrolytic deposition of copper under the conditions of limiting current).

(c) Transfer of water from a water phase saturated with n-butanol (alcohol mass fraction = 0·074) through a rigid interface to an alcohol main stream in which the water content is 0·035 mass fraction.

(d) Transfer of HCl from a surface at which its concentration is 4 molar to a pure water free stream.

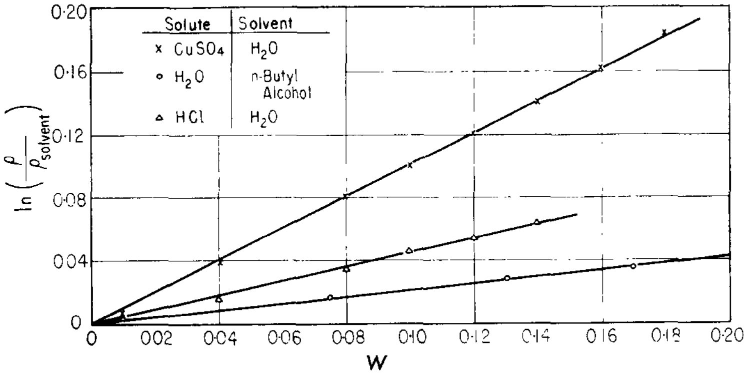

FIG. 4. Densities of three binary liquid systems as a function of composition.

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† All data are from the *International Critical Tables* or the *Landolt-Börnstein Tabelen*, except as noted.

Table 2. Effect of property variations and interfacial velocity on the transfer rate for various systems

System	W_0	W_∞	S	ϵ_ρ	ϵ_D	ϵ_V	R	K	$\left(\frac{\rho_\infty \mu_\infty}{\rho_0 \mu_0}\right)^{1/6}$	$\frac{Sh}{Sh^*}$
a	0·186	0	0·57	−0·18	0·38	0·41	0·83	1	0·84	0·70
b	0	0·186	0	0·18	−0·38	−0·186	1·11	0·84	1·19	1·10
c	0·210	0·035	0·08	−0·04	1·54	0·24	1·29	1	0·98	1·26
d	0·136	0	0	−0·06	−0·53	0·155	0·80	1	0·95	0·76
e	0	0·136	0	0·06	0·53	−0·134	1·30	0·94	1·05	1·28

(e) The reverse of (d) with the same concentration driving force.

The existence of variable properties and interfacial velocity can result in a 30 per cent deviation of the actual rate from the value calculated without considering these effects. A marked dependence upon the direction of transfer is also evident.

CONCLUSIONS

Since the method presented here involves numerous approximations, a summary of the most important ones is in order.

(1) The diffusion coefficient in equation (1), although in general a function of concentration, is not a function of the ratio of the solvent and solute mass fluxes (Appendix A).

(2) The density of the mixture and its diffusion coefficient are simple exponential functions of mass fraction.

(3) The effect of variable density in the over-all continuity equation is neglected (see Appendix B).

(4) Within the diffusion boundary layer, the velocity parallel to the surface varies linearly with normal distance.

(5) The slope of the parallel velocity component near the surface is independent of the interfacial velocity.

(6) The deviation of the slope of the parallel velocity component from its constant-property value can be calculated by assuming that the shear stress behaves as if the free-stream physical properties extended to the surface and that $\mu \simeq \mu_0$.

(7) The ratio D_0/D in equation (40) can be approximated by use of the unperturbed concentration profile [see equation (44) *et seq.*].

(8) The parameters ϵ_ρ, ϵ_D and ϵ_V must be small enough such that the complete second-order perturbation series is a sufficiently accurate approximation to the exact solution of equation (40).

(9) Density gradients must result in stable stratification; natural convection is not considered.

Assumptions (4–6) restrict the analysis to large Schmidt numbers. The question as to what constitutes a sufficiently large Schmidt number depends upon the particular flow geometry; it appears that, in the absence of free convection, no more than a 5–10 per cent error in the absolute value of the gradient at the surface will be incurred at $Sc > 100$ (which includes most binary liquids). The ratio of the actual gradient to that for the zero-mass transfer, constant-property system will be more accurate than the absolute value.

Additional improvements in the calculational methods presented here could be achieved by incorporating the effects of variable density in the over-all continuity equation [$L(\eta)$ of equation (16)] and viscosity variations [the integral of equation (54)]. The present analysis slightly overestimates the effect of viscosity variations and underestimates the consequences of density changes.

Although the analysis has been presented in terms of solid–liquid systems, it should apply to liquid–liquid mass transfer if the interface is rigid and the flow laminar.

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APPENDIX A†

Derivation of the diffusion equation

At steady state the relation describing conservation of a diffusing species in a nonreacting medium can be written as:

$$\nabla \cdot \mathbf{n}_i = 0 \qquad \text{(A-1)}$$

where $\mathbf{n}_i$ is the mass flux of species i relative to a stationary observer and is related to the diffusion velocity $\mathbf{u}_i$ by:

$$\mathbf{n}_i = \rho_i \mathbf{u}_i \qquad \text{(A-2)}$$

where ρ_i is the mass concentration of species i (grams of i/cm^3).

A diffusive flux relative to the mass average velocity is defined by:

$$\mathbf{j}_i = \rho_i(\mathbf{u}_i - \mathbf{V}) \qquad \text{(A-3)}$$

where $\mathbf{V}$ is the mass average or convective velocity of the mixture:

$$\mathbf{V} = \frac{\sum^{i} \rho_i \mathbf{u}_i}{\rho} = \sum^{i} W_i \mathbf{u}_i. \qquad \text{(A-4)}$$

Utilizing these definitions and the over-all continuity equation $[\nabla \cdot (\rho \mathbf{V}) = 0]$, equation (A-1) becomes

$$\rho \mathbf{V} \cdot \nabla W_i = \nabla \cdot \mathbf{j}_i. \qquad \text{(A-5)}$$

The species conservation requirement, equation (A-1) or (A-5), become the "diffusion" equation upon introduction of an appropriate relation for $\mathbf{j}_i$ in terms of a diffusion coefficient. For a binary mixture, the definition of D proposed by Chapman and Cowling [17] is almost universally utilized:

$$\mathbf{j}_i = -\rho D \nabla W_i. \qquad \text{(A-6)}$$

For ideal gases at constant pressure, equation (A-6) is identical to the Maxwell–Stephan diffusion coefficient. Inserting equation (A-6) in equation (A-5),

$$\rho \mathbf{V} \cdot \nabla W_i = \nabla(\rho D \nabla W_i). \qquad \text{(A-7)}$$

The derivation of equation (A-7) emphasizes its dependence upon a particular definition of the diffusion coefficient, i.e. equation (A-6), which was originally proposed from considerations of the kinetic behavior of gases.

By applying the thermodynamic relations:

$$\left.\begin{aligned} &\sum^{i} \bar{V}_i C_i = 1 \\ &\sum^{i} \bar{V}_i \, \mathrm{d}C_i = 0 \end{aligned}\right\} \text{(A-8)}$$

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† The symbols used in Appendix A are essentially those of Bird *et al.* [8]. Subscript i refers to a particular species in the mixture and bold-face type denotes a vector quantity.

where $\bar{V}_i$ is the partial molar volume of species i in the mixture, it can be shown that, for a binary, equation (A-6) can be written as:

$$C_i(\mathbf{u}_i - \mathbf{V}^+) = - D\nabla C_i. \qquad \text{(A-9)}$$

The left-hand side of equation (A-9) is the diffusive flux of i relative to the volume average velocity, which is defined by:

$$\mathbf{V}^+ = \sum^{i} C_i \bar{V}_i \mathbf{u}_i. \qquad \text{(A-10)}$$

Measurements of liquid diffusivities are generally based upon equation (A-9) rather than equation (A-6), although the two relations are equivalent definitions of D. If the volume average velocity is zero, equation (A-9) reduces to Fick's first law:

$$N_i = C_i\mathbf{u}_i = -D\nabla C_i. \qquad \text{(A-11)}$$

Many experimental devices for measuring liquid diffusivities, e.g. capillary or diaphragm cells, approximate processes in which no bulk volume occurs and equation (A-11) is valid. This simplification is exact if the partial molar volumes of the two components in the mixture are equal to the molar volumes of the pure substances (i.e. if there is no volume change on mixing). However, for the highly non-ideal systems for which the methods outlined in this paper have been developed, this is not the case; the diffusion coefficients measured by use of equation (A-11) are not identical to those defined by equation (A-6) and employed in equation (A-7). While this discrepancy is probably small, it may not be negligible. Analysis of diffusion experiments should account for volume changes on mixing by employing equation (A-9) rather than equation (A-11).

APPENDIX B

Error in the solution of the diffusion equation due to neglecting density variations in the over-all continuity equation

Since $d\rho/d\eta = (d\theta/d\eta)(d\rho/d\theta)$, and from equation (3), $d\rho/d\theta = -\rho\epsilon_\rho$, equation (16) becomes:†

$$L(\eta) = -\frac{1}{\rho H(\eta)}\int_0^\eta \rho H(\eta)\epsilon_\rho \frac{d\theta}{d\eta}\, d\eta. \qquad \text{(B-1)}$$

Since only the magnitude of $L(\eta)$ compared to unity is of interest, and since density variations in a liquid are generally quite small (a 25 per cent variation over the boundary layer is greater than is usually encountered), the variation of ρ with η in the integrand equation (B-1) will be neglected, and $L(\eta)$ written as:

$$L(\eta) \simeq -\frac{\epsilon_\rho}{H(\eta)}\int_0^\eta H(\eta)\frac{d\theta}{d\eta}\, d\eta. \qquad \text{(B-2)}$$

Consider the zero-mass-transfer case, for which

$$H(\eta) = -\alpha\eta^2. \qquad \text{(B-3)}$$

Substituting equation (B-3) into equation (B-2) and transforming to the χ-co-ordinate of equation (39), there results:

$$L(\chi) = -\frac{\epsilon_\rho}{\chi^2}\int_0^\chi \chi^2 \frac{d\theta}{d\chi}\, d\chi. \qquad \text{(B-4)}$$

Approximating $d\theta/d\chi$ from the constant-property, zero-mass-transfer solution:

$$\frac{d\theta}{d\chi} = -\frac{\exp(-\chi^3)}{I_0(\infty)}.$$

Equation (B-4) becomes

$$L(\chi) = \frac{\epsilon_\rho}{I_0(\infty)}\frac{1}{\chi^2}\int_0^\chi \chi^2 \exp(-\chi^3)\, d\chi. \qquad \text{(B-5)}$$

The integral in equation (B-5) can be evaluated analytically, and $L(\chi)$ given by:

$$L(\chi) = \epsilon_\rho \kappa(\chi) \qquad \text{(B-6)}$$

where

$$\kappa(\chi) = \frac{1 - \exp(-\chi^3)}{3I_0(\infty)\chi^2}. \qquad \text{(B-7)}$$

The maximum value of the function $\kappa(\chi)$ is approximately 0·25. For a 25 per cent change in density over the boundary layer, $\epsilon_\rho \simeq 0{\cdot}2$, and the additional term, $L(\chi)$, is always less than 5 per cent of unity.

The effect of the function L on the ϵ_ρ coefficient of the perturbation analysis can be obtained by considering the special case of

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† Since the analysis of this effect is identical for a flat plate and a rotating disk, $H(\eta)$ can be replaced by $f(\eta)$ in equation (B-1).

equation (23) (transformed into the χ-coordinate) for which $\epsilon_V = \epsilon_D = 0$:

$$\theta'' + \{3\chi^2[1 - \epsilon_\rho \kappa(\chi)] - \epsilon_\rho \theta'\}\theta' = 0. \quad \text{(B-8)}$$

A truncated expansion for θ can be assumed as

$$\theta = \theta^* + \epsilon_\rho \Omega_1. \quad \text{(B-9)}$$

When equation (B-9) is substituted into equation (B-8) and the coefficients of ϵ_ρ collected and set equal to zero, there results

$$\Omega_1'' + 3\chi^2\Omega_1' = (\theta^{*\prime})^2 + 3\chi^2\kappa(\chi)\theta^{*\prime} \quad \text{(B-10)}$$

which, with the boundary conditions

$$\Omega_1(0) = \Omega_1(\infty) = 0$$

and $\kappa(\chi)$ given by equation (B-7), can be solved to yield

$$\Omega_1'(0) = -0{\cdot}634.$$

If $L(\chi)$ is neglected, the computed value of $\Omega_1'(0)$ is $-0{\cdot}56$. The effect on the other terms containing ϵ_ρ would probably be of the same order of magnitude or less. With $\epsilon_\rho = 0{\cdot}2$, the error introduced by using $\Omega_1'(0) = -0{\cdot}56$ instead of $-0{\cdot}634$ is of the order of 1 per cent, and is considered negligible. Neglecting $L(\chi)$ in equation (23) is equivalent to assuming the flow to be incompressible, except for the $\epsilon_\rho(\mathrm{d}\theta/\mathrm{d}y)$ term in the diffusion equation. In this sense the analysis is equivalent to that usually applied to free convection, in which the effect of variable density is considered only in the buoyancy term.

Zusammenfassung—Mit Hilfe einer Störungsmethode wurde der Einfluss zusammenwirkender Dichte-, Temperaturleitfähigkeits- und Zähigkeitsänderungen sowie der Geschwindigkeit an der Trennfläche auf die Stoffübergangsgeschwindigkeit von einer festen Oberfläche untersucht. Die Analyse umfasst nicht die freie Konvektion und beschränkt sich auf Systeme hoher Schmidt-Zahlen (untere Grenze angenommen zu $Sc = 100$), für welche das Geschwindigkeitsprofil in der Diffusionsgrenzschicht linear ist. Die Diffusionsgleichungen für drei verschiedene Strömungsgeometrien—die rotierende Scheibe, die ebene Platte und den fallenden Flüssigkeitsfilm—sind bei hohen Schmidtzahlen in ihrer Form identisch; der Einfluss der jeweiligen Geometrie ist in einem einzigen Parameter berücksichtigt, der für die Grenzkurve des Geschwindigkeitsprofils nahe der Oberfläche charakteristisch ist. Die Anwendung auf drei typische Binärsysteme ergab für veränderliche Stoffwerte und Geschwindigkeiten an der Trennfläche eine Abweichung der Sherwood-Zahl bis zu 30 Prozent von jenen Werten, die ohne diese Vorgänge gefunden wurden. Die Korrekturen für veränderliche Stoffwerte und Geschwindigkeiten an der Trennfläche sind möglicherweise auf einen viel grösseren Bereich von Strömungen an festen Begrenzungen anwendbar als nur auf die drei hier untersuchten Fälle und auf Flüssigkeit–Flüssigkeit Systeme, deren Trennfläche als starr gelten kann.

Аннотация—Методом возмущений исследовалось совместное влияние одновременного изменения плотности, вязкости, коэффициента диффузии и скорости уноса вещества с твердой поверхности раздела на интенсивность массоотдачи. Влияние естественной конвекции не учитывалось. Анализ был ограничен системами с большими числами Шмидта (не ниже 100), для которых профиль скорости в диффузионном пограничном слое линейный. При больших значениях критерия Шмидта уравнения диффузии оказываются идентичными по форме для трёх различных типов течений: вращающегося диска, плоской пластины и плёнки стекающей жидкости; влияние геометрических факторов представлено отдельным параметром, который характеризуется предельным наклоном профиля скорости у поверхности. Применение метода к трём типичным бинарным системам показало, что указанные выше факторы могут изменять значение критерия Шервуда на 30% от его значения при отсутствии массоотдачи с поверхности раздела. Поправки на изменение физических свойств при наличии скорости на поверхности раздела могут быть распространены, кроме трёх рассмотренных задач, на гораздо более широкий класс потоков вблизи твердой границы, а также на системы жидкость–жидкость с твердой поверхностью раздела.