Forced Convection in Three-Dimensional Flows: II. Asymptotic Solutions for Mobile Interfaces

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Boundary-layer solutions are given for heat and mass transfer at mobile interfaces. The results are asymptotically valid for small thermal and material diffusivities, or for short exposure times. Phase breakup and coalescence are formally included, but Marangoni effects are not. Effects of rapid mass transfer, chemical reactions, and variable boundary conditions are evaluated. The treatment is a generalization of the penetration and surface-renewal theories.

Presented here is a boundary-layer analysis of heat and mass transfer at mobile interfaces. The transfer coefficients are obtained as explicit functions of the transport properties and surface velocity profiles. The general solutions are then applied to several specific systems. The results should facilitate the analysis and improvement of fluid-fluid contacting operations involving bubbles, sprays, jets, and rippling liquid films. The treatment includes the time dependence of the profiles and should thus be valid for certain turbulent flows as well as laminar ones.

This paper continues the work of Stewart (*1*) on three-dimensional boundary layers and extends the work of Angelo, Lightfoot and Howard (*2*, *3*) on mass transfer at mobile interfaces. It is an improvement of the penetration and surface-renewal theories of Higbie (*4*) and Danckwerts (*5*). It provides a geometrical extension of the diffusion calculations of Ilkovic (*6*) and many others (*2*, *3*, *7* to *21*) in which stretching and contracting interfaces were considered. The latter analyses have clearly demonstrated the importance of surface stretch effects, and these effects are included throughout the present treatment.

Reference *1* may be usefully compared with the present analysis. There, only rigid interfaces were considered, and the systems were at steady state as viewed from an interfacial particle. Here, deforming interfaces are included, but the systems are required to be time dependent as viewed from an interfacial particle. The two treatments thus deal with separate limiting cases, though the methods and results are in many ways analogous.

This treatment is based on the energy and continuity equations (*22*), rewritten for time dependent boundary layers. The following boundary-layer approximations are used:

1. That the conductive and diffusive fluxes are normal to the nearest interfacial element.
2. That the tangential velocity in the thermal and diffusional layers is essentially that of the nearest interfacial element.
3. That the thicknesses of these layers are small relative to the local surface radii of curvature.
4. That the thermal (and diffusional) layers of non-adjacent interfacial elements do not overlap.

The energy and diffusion equations thus simplified are asymptotically valid for small contact times or for small thermal and material diffusivities, α and $\mathcal{D}_{AB}$. The bases of these approximations are discussed under Equations (8) through (13).

For simplicity, this discussion is limited to forced-convection problems, for which separate knowledge or analysis of the velocity profiles can be assumed. Marangoni effects (*23*) and other free-convection flows could be analyzed under the approximations given above, but the equation of motion would then have to be solved simultaneously with the energy and continuity equations.

The first two parts of this paper [up to Equation (17*a*)] give the basic equations and coordinates. The third and fourth parts give general solutions for several types of heat and mass transfer problems. The fifth part (Examples) gives applications to several representative flow situations, with and without chemical reaction.

COORDINATES AND VELOCITIES

Consider the transfer of heat and mass between two fluid phases, one of which may be dispersed in the other. Our attention is focused on the regions near the interfaces, where the gradients of temperature and composition are significant.

It is convenient to analyze the system in coordinates that move and deform with the interfaces. We use the coordinates u, w, and y, where y is the distance to the nearest interfacial element and u and w are surface coordinates of that element. The lines of constant u and w are imbedded in the interfaces, as illustrated in Figure 1, and move tangentially with the interfacial fluid. For mixtures, the tangential motion is the same locally for every species, within the accuracy of approximation 1.

The geometry of the u, w, y coordinates is defined by

$$\mathbf{r} = \mathbf{r}_s(u, w, t) + y\ \mathbf{n}(u, w, t) \qquad (1)$$

which gives the instantaneous position vectors $\mathbf{r}$ of all points u, w, y relative to some datum point. The function $\mathbf{r}_s(u, w, t)$ gives the trajectory of each interfacial element in the system at hand, and the related function $\mathbf{n}(u, w, t)$ gives the instantaneous normal vector to each element, directed into the phase considered. The terms of this equation are illustrated in Figure 2.

To calculate volumes and interfacial areas in these coordinates, we use the base-vector methods of Wills (*24*). The instantaneous volume of the element *dudwdy* (see Figure 2) is

$$dV = \sqrt{g}\ dudwdy \qquad (2)$$

Here $\sqrt{g}$ is the volume of the parallelepiped formed by the base vectors $\partial\mathbf{r}/\partial u$, $\partial\mathbf{r}/\partial w$ and $\mathbf{n} \equiv \partial\mathbf{r}/\partial y$

$$\sqrt{g} = \left| \left[\frac{\partial\mathbf{r}}{\partial u} \times \frac{\partial\mathbf{r}}{\partial w} \right] \bullet \mathbf{n} \right| = \left| \frac{\partial\mathbf{r}}{\partial u} \times \frac{\partial\mathbf{r}}{\partial w} \right| \qquad (3)$$

and varies with u, w, y, and t. The second equality in Equation (3) follows because $\partial\mathbf{r}/\partial u$ and $\partial\mathbf{r}/\partial w$ are always normal to $\mathbf{n}$, though not necessarily normal to each other. The instantaneous area of the interfacial element *dudw* (see Figure 2) is

$$dS = s\ dudw \qquad (4)$$

Here s is the area of the parallelogram formed by the tangential base vectors at the interface

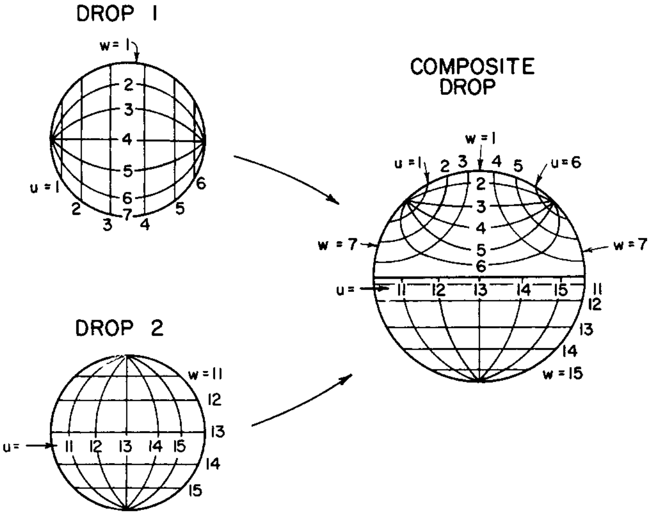

Fig. 1. Schematic illustration of imbedded coordinates in a simple coalescence process.

$$s = \left| \frac{\partial \mathbf{r}_s}{\partial u} \times \frac{\partial \mathbf{r}_s}{\partial w} \right| = \lim_{y \to 0} \sqrt{g} \qquad (5)$$

and varies with u, w, and t. Throughout this paper dS and $dudw$ are regarded as positive quantities.

Fluid velocities $\mathbf{V}$ relative to the datum point can be resolved into two terms as

$$\mathbf{V} = \mathbf{v} + \left(\frac{\partial \mathbf{r}}{\partial t} \right)_{u,w,y} \qquad (6)$$

where $\mathbf{v}$ is the fluid velocity relative to an observer stationed at (u, w, y), and $(\partial \mathbf{r}/\partial t)_{u,w,y}$ is the velocity of the observer relative to the datum.

Taking the divergence of Equation (6), we get (see Appendix A)

$$(\nabla \bullet \mathbf{V}) = (\nabla \bullet \mathbf{v}) + \left(\frac{\partial \ln \sqrt{g}}{\partial t} \right)_{u,w,y} \qquad (7)$$

Thus, the fluid expansion rate $(\nabla \bullet \mathbf{V})$ relative to fixed coordinates is given by the expansion rate $(\nabla \bullet \mathbf{v})$ relative to the u, w, y coordinates, plus the local rate of expansion of the u, w, y coordinate frame. This last term arises from the interfacial deformation and is crucial in the present analysis.

The object of this treatment is to calculate the heat and mass transfer rates in terms of the area function $s(u, w, t)$, or related experimental information. The evaluation of $s(u, w, t)$ is illustrated later for several flow systems.

BOUNDARY-LAYER EQUATIONS

In this section, the conservation equations are reduced to boundary-layer form in the u, w, y coordinates. The key results are given in Equations (15), (17), and (17*a*).

Energy Equations

Consider the time dependent transport of heat from mobile interfaces S into a pure fluid of constant density, heat capacity, and thermal conductivity. The energy equation

$$\frac{DT}{Dt} = \alpha \nabla^2 T \qquad (8)$$

is to be simplified for small values of the thermal diffusivity α.

The simplification depends on order-of-magnitude arguments. If the heat transfer is initiated at time $t = 0$ by an interfacial temperature change ΔT, then a thermal boundary layer will propagate from S into the fluid. The local boundary-layer thickness δ_T at any time t tends to zero with decreasing α. The temperature derivatives in the y direction then become predominant, and approximation 1 becomes valid. Approximations 3 and 4 likewise become valid because of the smallness of δ_T. The term $\alpha \nabla^2 T$ in Equation (8) thereby reduces to $\alpha(\partial^2 T/\partial y^2)_{u,w,t}$ as $\alpha \to 0$, for any finite time t, and the boundary layers on different parts of S (such as the two drops before coalescence in Figure 1) cease to overlap. The same simplifications also hold as $t \to 0$ for any finite value of α.

Approximation 2 demands fuller treatment. We first write out DT/Dt in the u, w, y, t coordinates:

$$\frac{DT}{Dt} = \left(\frac{\partial T}{\partial t} \right)_{u,w,y} + (\mathbf{v} \bullet \nabla T)_{\text{tang}} + (\mathbf{v} \bullet \nabla T)_{\text{norm}} \qquad (9)$$

Expansion of $\mathbf{v}$ in powers of y, and use of the no-slip assumption, gives

$$\mathbf{v}(u, w, y, t) = \mathbf{n}\, v_0(u, w, t) + y\, \mathbf{B}(u, w, t) + \mathbf{O}(y^2) \qquad (10)$$

Here $v_0(u, w, t)$ is the fluid velocity into the given phase due to mass transfer, and the vector $\mathbf{B}(u, w, t)$ is the velocity gradient in the y direction at the interface. The orders of magnitude of the terms in Equation (9) can then be estimated in the middle of the thermal boundary layer:

$$\left(\frac{\partial T}{\partial t} \right)_{u,w,y} \sim \frac{\Delta T}{t} \qquad (11)$$

$$(\mathbf{v} \bullet \nabla T)_{\text{tang}} \sim [\delta_T B_{\text{tang}} + O(\delta_T^2)] \cdot \frac{\Delta T}{L} \qquad (12)$$

$$(\mathbf{v} \bullet \nabla T)_{\text{norm}} \sim [v_0 + \delta_T B_y + O(\delta_T^2)] \cdot \frac{\Delta T}{\delta_T} \qquad (13)$$

Here L is a characteristic length of the system, independent of δ_T.

The term $(\partial T/\partial t)_{u,w,y}$ is essential for time dependent problems, and its order of magnitude in the boundary layer is independent of δ_T. The other terms will therefore be measured relative to this one.

The term $(\mathbf{v} \bullet \nabla T)_{\text{tang}}$ tends to zero with decreasing δ_T, provided that B_{tang} remains finite; this term then vanishes relative to $\partial T/\partial t$. Approximation 2 thus holds in the limit as either $\alpha \to 0$ (for finite t) or as $t \to 0$ (for finite α) if the temperature at (u, w, y) is time dependent. On the other hand, for flow systems with a steady temperature at each point (u, w, y), the term $(\mathbf{v} \bullet \nabla T)_{\text{tang}}$ would be essential; this case was treated in paper I.

The term $(\mathbf{v} \bullet \nabla T)_{\text{norm}}$ contains two potentially significant contributions: that of v_0 and that of B_y. The v_0 contribution has the magnitude $v_0 \Delta T/\delta_T$ and must remain bounded as $\delta_T \to 0$ if $\partial T/\partial t$ is to remain significant. The B_y term is nonvanishing as $\delta_T \to 0$ and must also be retained. The $O(\delta_T^2)$ contribution vanishes as $\delta_T \to 0$ and so can be neglected.

Equation (9) can thus be simplified, for the problems considered here, by using just the y component of Equation (10). The coefficient B_y can be found by inserting Equations (7) and (10) into the continuity equation $(\nabla \bullet \mathbf{V}) = 0$. With the aid of Equation (5) and approximation 3, we then obtain

$$v_y = v_0(u, w, t) - y \frac{\partial \ln s}{\partial t}$$

$$= v_0(u, w, t) - y\, (\nabla \bullet \mathbf{V}_s) \qquad (14)$$

as the one needed velocity component in the thermal boundary layer. The terms $v_0(u, w, t)$ and $y\, \partial \ln s/\partial t$ are the contributions of net mass transfer and of surface stretch, respectively.

If the velocities $\mathbf{V}_s = (\partial \mathbf{r}_s/\partial t)_{u,w}$ of the surface elements are known, the second expression for v_y is convenient. Note that $(\nabla \cdot \mathbf{V}_s)$ contains only tangential derivatives, since $\mathbf{V}_s$ is independent of y.

At first glance, it may appear that Equation (14) is too simple. This simplicity is due to the thinness of the thermal layer and to the fact that both y and $\mathbf{v}$ are measured from the nearest surface element. The surfaces themselves may be in violent motion, as in rippling, splashing, or coalescence, but for our purposes their motion is adequately characterized by the scalar function $s(u, w, t)$.

With these substitutions, Equation (8) takes the form

$$\frac{\partial T}{\partial t} + \left(v_0 - y \frac{\partial \ln s}{\partial t} \right) \frac{\partial T}{\partial y} = \alpha \frac{\partial^2 T}{\partial y^2} \qquad (15)$$

for thin, time dependent, thermal boundary layers. This equation is effectively two-dimensional, since the derivatives with respect to u and w have been suppressed. Integration of this equation at constant u and w will give the thermal history of a given interfacial element and the adjoining fluid elements. Integration with respect to u and w then gives the complete solution, just as integration with respect to z gave the solutions in paper I.

Equations (8) and (15) can be extended to reacting mixtures, and to dissipative systems, by adding a source term $\mathcal{S}/\rho \hat{C}_p$. This extension is compatible with the boundary-layer analysis, provided that $\mathcal{S}$ vanishes at the initial temperature and composition of the fluid. Other types of sources, such as radiation, can be handled by making separate energy analyses for the interior and boundary-layer regions.

Diffusion Equations

For isothermal binary diffusion with constant ρ and $\mathcal{D}_{AB}$, the continuity equation of A is

$$\frac{D\omega_A}{Dt} = \mathcal{D}_{AB} \nabla^2 \omega_A + \frac{r_A}{\rho} \qquad (16)$$

when Fick's first law (22) is assumed. This equation can be simplified in the same manner as Equation (8) to obtain

$$\frac{\partial \omega_A}{\partial t} + \left(v_0 - y \frac{\partial \ln s}{\partial t} \right) \frac{\partial \omega_A}{\partial y} = \mathcal{D}_{AB} \frac{\partial^2 \omega_A}{\partial y^2} + \frac{r_A}{\rho} \qquad (17)$$

in which v_0 is the y component of the fluid mass average velocity $\mathbf{v}$ at the interface.

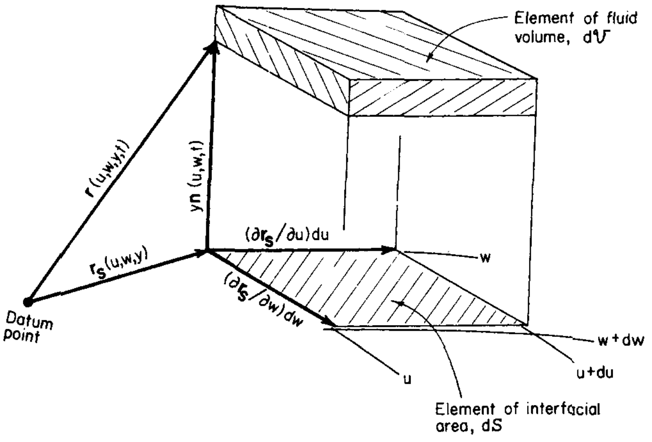

Fig. 2. Boundary-layer coordinates *(u,w,y)* showing enlarged element of area and element of volume. The lines of constant *u* and *w* are imbedded in the interface. The parallelogram *dS* is tangent to the interface at the point *(u,w,O)*.

Alternate Coordinates

If the coordinates t and y of the boundary-layer system are replaced by $\tau = \int_{t_0}^{t} s^2(u, w, t')dt'$ and $\Upsilon = y\, s(u, w, \tau)$ respectively, then Equation (17) becomes

$$\left(\frac{\partial \omega_A}{\partial \tau} \right)_{u,w,\Upsilon} + \frac{v_0}{s} \left(\frac{\partial \omega_A}{\partial \Upsilon} \right)_{u,w,\tau} = \mathcal{D}_{AB} \left(\frac{\partial^2 \omega_A}{\partial \Upsilon^2} \right)_{u,w,\tau} + \frac{r_A}{\rho s^2} \qquad (17a)$$

which is sometimes easier to solve. Thus, if v_0 and r_A are zero, then Equation (17*a*) looks just like Fick's second law, written for a nonflowing semi-infinite system. The nonflow solutions can then be generalized directly by substituting τ and Υ for the time and distance coordinates. The same transformations are applicable to Equation (15).

GENERAL SOLUTIONS

Solutions of Equations (17) and (17*a*) are given here for several types of systems. The corresponding results for heat transfer are also indicated. The geometry and flow conditions are left arbitrary so that the results can be applied to various kinds of contacting equipment.

Rapid Mass Transfer into a Nonreacting Phase

A binary fluid, of uniform composition $\omega_{A\infty}$, is suddenly exposed to another phase containing the same two species. The interfacial composition ω_{A0} and the flux ratio n_{A0}/n_{B0} of the components are considered known and constant. The surface elements u,w may be formed at various times $t_0(u, w)$. The initial and boundary conditions are:

I.C.

$$\omega_A = \omega_{A\infty} \quad \text{at} \quad y > 0 \qquad \text{for} \quad t = t_0(u, w) \qquad (18)$$

B.C. 1:

$$\omega_A = \omega_{A\infty} \quad \text{at} \quad y >> \delta_\omega(u, w) \qquad \text{for} \quad t \geqq t_0(u, w) \qquad (19)$$

B.C. 2:

$$\omega_A = \omega_{A0} \quad \text{at} \quad y = 0 \qquad \text{for} \quad t \geqq t_0(u, w) \qquad (20)$$

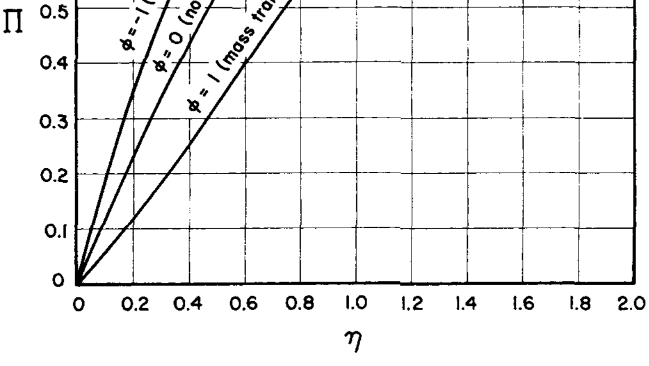

Fig. 3. Boundary-layer composition and temperature profiles according to Equation (34).

TABLE 1. DIMENSIONLESS FUNCTIONS FOR HEAT AND MASS TRANSFER DERIVED FROM EQUATION (35)

ϕ	$\Pi'(0)$	R	θ	ϕ	$\Pi'(0)$	R	θ
+0.00	1.1284	0.0000	1.0000	−0.00	1.1284	−0.0000	1.0000
0.10	1.0575	0.1067	0.9372	−0.10	1.2012	−0.0939	1.0645
0.20	0.9887	0.2282	0.8763	−0.20	1.2759	−0.1769	1.1307
0.30	0.9221	0.3671	0.8172	−0.30	1.3523	−0.2503	1.1985
0.40	0.8576	0.5263	0.7600	−0.40	1.4305	−0.3155	1.2678
0.50	0.7954	0.7093	0.7049	−0.50	1.5104	−0.3735	1.3385
0.60	0.7356	0.9204	0.6519	−0.60	1.5918	−0.4253	1.4107
0.70	0.6782	1.1647	0.6010	−0.70	1.6747	−0.4717	1.4841
0.80	0.6233	1.4483	0.5524	−0.80	1.7589	−0.5132	1.5588
0.90	0.5709	1.7789	0.5059	−0.90	1.8446	−0.5506	1.6347
1.00	0.5211	2.1654	0.4618	−1.00	1.9315	−0.5842	1.7117
1.10	0.4739	2.6191	0.4200	−1.10	2.0196	−0.6146	1.7898
1.20	0.4294	3.1535	0.3805	−1.20	2.1088	−0.6421	1.8689
1.30	0.3875	3.7854	0.3434	−1.30	2.1992	−0.6670	1.9490
1.40	0.3483	4.5356	0.3087	−1.40	2.2905	−0.6897	2.0299
1.50	0.3117	5.4296	0.2763	−1.50	2.3829	−0.7103	2.1118
1.60	0.2778	6.4993	0.2462	−1.60	2.4761	−0.7291	2.1944
1.70	0.2464	7.7845	0.2184	−1.70	2.5703	−0.7463	2.2778
1.80	0.2176	9.3351	0.1928	−1.80	2.6652	−0.7621	2.3620
1.90	0.1912	11.214	0.1694	−1.90	2.7609	−0.7765	2.4468
2.00	0.1672	13.500	0.1482	−2.00	2.8574	−0.7898	2.5323
2.50	0.0790	35.715	0.0700	−2.50	3.3496	−0.8422	2.9685
3.00	0.0324	104.39	0.0287	−3.00	3.8553	−0.8780	3.4167
4.00	0.0035	1302.0	0.0031	−4.00	4.8956	−0.9220	4.3386
∞	0.0	∞	0.0	−∞	∞	−1.0	∞

B.C. 3:

$$\frac{n_{Ay}}{n_{By}} = \frac{n_{A0}}{n_{B0}} \quad \text{at} \quad y = 0 \qquad\qquad \text{for} \quad t \geqq t_0(u, w) \tag{21}$$

The last boundary condition can be satisfied by calculating v_0 from Fick's first law

$$v_0 = -\frac{\mathcal{D}_{AB} \left.\dfrac{\partial \omega_A}{\partial y}\right|_{y=0}}{\left(\dfrac{n_{A0}}{n_{A0} + n_{B0}} - \omega_{A0}\right)} \tag{22}$$

and by evaluating the denominator from the constants of Equations (20) and (21). Equation (17) then takes the form

$$\frac{\partial \omega_A}{\partial t} + \left\{ \frac{-\mathcal{D}_{AB} \left.\dfrac{\partial \omega_A}{\partial y}\right|_{y=0}}{\left(\dfrac{n_{A0}}{n_{A0} + n_{B0}} - \omega_{A0}\right)} - y\frac{\partial \ln s}{\partial t} \right\} \frac{\partial \omega_A}{\partial y} = \mathcal{D}_{AB} \frac{\partial^2 \omega_A}{\partial y^2} \tag{23}$$

which is to be solved under the conditions of Equations (18), (19), and (20).

Since the problem contains no characteristic length or time, we try a combination of variables. A solution is postulated in the form

$$\frac{\omega_A - \omega_{A0}}{\omega_{A\infty} - \omega_{A0}} = \Pi_\omega(\eta_\omega); \quad \eta_\omega = \frac{y}{\delta_\omega(u, w, t)} \tag{24), (25}$$

for times subsequent to the local formation of the interface. At the instant of contact, the boundary-layer thickness δ_ω is zero. With these substitutions, Equations (18) to (20) are reduced to two boundary conditions

$$\Pi_\omega(\infty) = 1; \quad \Pi_\omega(0) = 0 \tag{26), (27}$$

and Equation (23) reduces to

$$\left[\frac{(\omega_{A0} - \omega_{A\infty})}{\left(\dfrac{n_{A0}}{n_{A0} + n_{B0}} - \omega_{A0}\right)} \Pi_\omega'(0) - \eta_\omega \left(\frac{1}{2s^2\, \mathcal{D}_{AB}} \frac{\partial (s\delta_\omega)^2}{\partial t} \right) \right] \frac{d\Pi_\omega}{d\eta_\omega} = \frac{d^2\Pi_\omega}{d{\eta_\omega}^2} \tag{28}$$

in which $\Pi_\omega'(0)$ stands for $d\Pi_\omega/d\eta_\omega$, evaluated at $\eta = 0$. Finally, we eliminate the time variable by setting

$$\frac{1}{2s^2\, \mathcal{D}_{AB}} \frac{\partial (s\delta_\omega)^2}{\partial t} = C_0 \tag{29}$$

$$\frac{(\omega_{A0} - \omega_{A\infty})}{\left(\dfrac{n_{A0}}{n_{A0} + n_{B0}} - \omega_{A0}\right)} \Pi_\omega'(0) = \frac{v_0 \delta_\omega}{\mathcal{D}_{AB}} = C_\omega \tag{30}$$

and the combination of variables is complete. Here C_0 is a numerical constant and can be chosen arbitrarily; we choose $C_0 = 2$ for convenience. The constant C_ω is a dimensionless mass transfer rate, introduced to simplify the integration.

The choice $C_0 = 2$ in Equation (29) leads to the following solution for the boundary-layer thickness:

$$\delta_\omega = \frac{1}{s(u, w, t)} \sqrt{4\mathcal{D}_{AB} \int_{t_0(u,w)}^{t} s^2(u, w, t')\,dt'} \tag{31}$$

The dimensionless coordinate η_ω thus becomes

$$\eta_\omega = \frac{y\, s(u, w, t)}{\sqrt{4\mathcal{D}_{AB} \displaystyle\int_{t_0(u,w)}^{t} s^2(u, w, t')\,dt'}} \tag{32}$$

and Equation (28) takes the form

$$[C_\omega - 2\eta_\omega] \frac{d\Pi_\omega}{d\eta_\omega} = \frac{d^2\Pi_\omega}{d{\eta_\omega}^2} \tag{33}$$

Integration with boundary conditions (26) and (27) gives the dimensionless composition profile

$$\Pi_\omega = \frac{\displaystyle\int_0^{\eta_\omega} \exp(C_\omega Z - Z^2)\,dZ}{\displaystyle\int_0^{\infty} \exp(C_\omega Z - Z^2)\,dZ}$$

$$= \frac{\operatorname{erf}\left(\eta_\omega - \frac{1}{2}C_\omega\right) + \operatorname{erf}\left(\frac{1}{2}C_\omega\right)}{1 + \operatorname{erf}\left(\frac{1}{2}C_\omega\right)} \tag{34}$$

and the dimensionless composition gradient at the interface:

$$\Pi_\omega'(0) = \frac{1}{\int_0^\infty \exp(C_\omega Z - Z^2)dZ}$$

$$= \frac{\frac{2}{\sqrt{\pi}}\exp\left(-\frac{1}{4}C_\omega^2\right)}{1 + \operatorname{erf}\left(\frac{1}{2}C_\omega\right)} \tag{35}$$

These solutions closely resemble Equations (19) and (20) of paper I. Some calculated values are displayed in Figure 3 and Table 1.

The composition gradient $\Pi_\omega'(0)$ can be combined with Fick's first law to obtain the diffusion flux at the interface:

$$j_{A0} = -\rho\mathcal{D}_{AB}\frac{\partial\omega_A}{\partial y}\bigg|_{y=0} = \frac{\rho\mathcal{D}_{AB}}{\delta_\omega}\Pi_\omega'(0)(\omega_{A0} - \omega_{A\infty}) \tag{36}$$

This can also be written in terms of transfer coefficients as

$$j_{A0} = k_\omega\theta_\omega(\omega_{A0} - \omega_{A\infty}) = k_\omega^\bullet(\omega_{A0} - \omega_{A\infty}) \tag{37}$$

Here k_ω is the mass transfer coefficient uncorrected for the velocity v_0, and $k_\omega^\bullet$ is the mass transfer coefficient with this correction included. The correction factor θ_ω, given by $\Pi_\omega'(0)\sqrt{\pi}/2$, is obtainable from Table 1 as a function of the flux ratio

$$\frac{C_\omega}{\Pi_\omega'(0)} = \frac{(\omega_{A0} - \omega_{A\infty})}{\left(\frac{n_{A0}}{n_{A0} + n_{B0}} - \omega_{A0}\right)} \equiv R_\omega \tag{38}$$

or of the dimensionless flux

$$\frac{\sqrt{\pi}}{2}C_\omega = \frac{n_{A0} + n_{B0}}{k_\omega} \equiv \phi_\omega \tag{39}$$

The correction factor becomes appreciable when the net mass flux $(n_{A0} + n_{B0})$ is appreciable; that is, when ϕ_ω exceeds about 0.1 in magnitude. These results are generalizations of those given by Arnold (25) for one-dimensional systems and summarized in reference 22.

To calculate the mass fluxes n_{A0} and n_{B0} for the problem at hand, one first inserts the given values of ω_{A0}, $\omega_{A\infty}$, and n_{A0}/n_{B0} into Equation (38) and calculates R_ω. Then one can either look up θ_ω from the table and use Equation (37), or look up ϕ_ω and use Equation (39). The resulting flux expression can be combined with the specified value of (n_{A0}/n_{B0}) to obtain both n_{A0} and n_{B0}. The uncorrected mass transfer coefficient k_ω can be calculated from

$$k_\omega = \frac{2}{\sqrt{\pi}}\frac{\rho\mathcal{D}_{AB}}{\delta_\omega} \tag{40}$$

if the velocity profiles of the system are known; otherwise a local on mean value of R_ω may be estimated from a mass transfer correlation [see Equations (108) and (109)].

The total rate of diffusion from a finite interfacial region $\mathcal{R}(u, w, t)$ is found by integration of Equation (36) over the surface. The result is

$$w_{A0} - \omega_{A0}(w_{A0} + w_{B0})$$

$$= (\omega_{A0} - \omega_{A\infty})\sqrt{\frac{\rho^2\mathcal{D}_{AB}}{4}}\,\Pi_\omega'(0)\int_{\mathcal{R}}\int \frac{s^2(u, w, t)\,du dw}{\sqrt{\int_{t_0(u,w)}^t s^2(u, w, t')dt'}}$$

$$= (\omega_{A0} - \omega_{A\infty})\sqrt{\rho^2\mathcal{D}_{AB}}\,\Pi_\omega'(0)\int_{\mathcal{R}}\int \frac{\partial}{\partial t}\sqrt{\int_{t_0(u,w)}^t s^2(u, w, t')dt'}\;du dw \tag{41}$$

which can be solved for w_{A0} or w_{B0} when the appropriate value of w_{A0}/w_{B0} is inserted. The right side, with $\partial/\partial t$ removed, gives the total mass of A that has diffused into the fluid from the surface elements currently included in $\mathcal{R}$.

The effects of the interfacial deformation can now be assessed. According to Equations (31) and (36), the local diffusion flux from a rigid interface would be

$$(j_{A0})_{\text{rigid}} = \frac{\rho\mathcal{D}_{AB}(\omega_{A0} - \omega_{A\infty})\,\Pi_\omega'(0)}{\sqrt{4\mathcal{D}_{AB}[t - t_0(u, w)]}} \tag{42}$$

in agreement with the calculation of Arnold (25). The effect of the deformation is to multiply this result by a factor

$$\kappa = \frac{(j_{A0})_{\text{mobile}}}{(j_{A0})_{\text{rigid}}} = \left\{\frac{[t - t_0(u, w)]s^2(u, w, t)}{\int_{t_0(u,w)}^t s^2(u, w, t')dt'}\right\}^{1/2} \tag{43}$$

which is equal to the current value of s at u, w divided by its root-mean-square value up to time t. Thus, the penetration theory underestimates the mass flux if the surface continually expands and overestimates it if the surface continually shrinks. These errors can be very large, as shown in the examples.

This solution can be rewritten for heat transfer by the analogies of Table 2. For binary systems, this implies the neglect of dissipation, thermal expansion, diffusion-thermo effects, and the small term $\Sigma_i(\mathbf{j}_i \bullet \nabla \overline{H}_i/M_i)$ from the energy equations of reference 22. The analogous molar form of the diffusion problem is also included for convenience.

Mass Transfer Between Two Nonreacting Phases

The preceding solution can be extended to two-phase systems by inserting the proper interfacial boundary conditions. The results are valid for small α and $\mathcal{D}_{AB}$ in each phase and negligible interfacial resistance (or resistance proportional to δ_ω).

Two convenient features here are the constancy of the calculated interfacial state and the constant ratios of the boundary-layer thicknesses in the two phases. Thus, for diffusion in two adjacent binary phases, Equation (31) gives

TABLE 2. ANALOGOUS SUBSTITUTIONS† FOR EQUATIONS (16) TO (44) AND (76) TO (80)

Symbols for binary diffusion with constant ρ and $\mathcal{D}_{AB}$:	Symbols for binary diffusion with constant c and $\mathcal{D}_{AB}$:	Symbols for heat transfer with constant ρ, $\hat{C}_p$ and k:
ω_A	x_A	T
$\mathcal{D}_{AB}$	$\mathcal{D}_{AB}$	α
$\rho\,\mathcal{D}_{AB}$	$c\,\mathcal{D}_{AB}$	k
ρ	c	$\rho\,\hat{C}_p$
$n_{A0} + n_{B0}$	$N_{A0} + N_{B0}$	$(n_{A0} + n_{B0})\hat{C}_p$
$j_{A0} = n_{A0} - \omega_{A0}\,(n_{A0} + n_{B0})$	$J_{A0}^{\star} = N_{A0} - x_{A0}\,(N_{A0} + N_{B0})$	q_0
$j_{A\infty} = n_{A0} - \omega_{A\infty}\,(n_{A0} + n_{B0})$	$J_{A\infty}^{\star} = N_{A0} - x_{A\infty}\,(N_{A0} + N_{B0})$	$q_0 + (n_{A0} + n_{B0})\,\hat{C}_p\,(T_\infty - T_0)$
$w_{A0} - \omega_{A0}\,(w_{A0} + w_{B0})$	$\mathcal{W}_{A0} - x_{A0}\,(\mathcal{W}_{A0} + \mathcal{W}_{B0})$	Q
$w_{A0} - \omega_{A\infty}\,(w_{A0} + w_{B0})$	$\mathcal{W}_{A0} - x_{A\infty}\,(\mathcal{W}_{A0} + \mathcal{W}_{B0})$	$Q + (w_{A0} + w_{B0})\,\hat{C}_p(T_\infty - \overline{T}_0)$
$R_\omega = \dfrac{(\omega_{A0} - \omega_{A\infty})}{\left(\dfrac{n_{A0}}{n_{A0} + n_{B0}} - \omega_{A0}\right)}$	$R_x = \dfrac{(x_{A0} - x_{A\infty})}{\left(\dfrac{N_{A0}}{N_{A0} + N_{B0}} - x_{A0}\right)}$	$R_T = \dfrac{(n_{A0} + n_{B0})\,\hat{C}_p\,(T_0 - T_\infty)}{q_0}$
$\phi_\omega = \dfrac{n_{A0} + n_{B0}}{k_\omega}$	$\phi_x = \dfrac{N_{A0} + N_{B0}}{k_x}$	$\phi_T = \dfrac{(n_{A0} + n_{B0})\,\hat{C}_p}{h}$
$\theta_\omega = \dfrac{k_\omega^\bullet}{k_\omega}$	$\theta_x = \dfrac{k_x^\bullet}{k_x}$	$\theta_T = \dfrac{h^\bullet}{h}$
r_A	$R_A - x_A\,(R_A + R_B)$	$\mathcal{S}$
$\mathbf{v}$	$\mathbf{v}^\star$	$\mathbf{v}$
$\Pi_\omega, \eta_\omega, \delta_\omega, C_\omega$	$\Pi_x, \eta_x, \delta_x, C_x$	$\Pi_T, \eta_T, \delta_T, C_T$

† The Soret and Dufour effects are neglected here, and q is defined as the conductive heat flux.

$$\frac{\delta_\omega^{I}}{\delta_\omega^{II}} = \sqrt{\frac{\mathcal{D}^{I}}{\mathcal{D}^{II}}} \tag{44}$$

for each surface location, and a similar relation is obtained for heat transfer via Table 2. These thickness ratios are independent of the position, time, flow conditions, and geometry of the equipment as long as the boundary-layer approximations hold. The interfacial temperature and composition are similarly independent of the same factors.

As an illustration, consider the transfer of solute A between immiscible solvents B and C at a given interfacial temperature and pressure. For comparison with known results, molar units will be used. The contacting begins locally at time $t_0(u, w)$, with initial compositions $x_{A\infty}{}^{I}$ and $x_{A\infty}{}^{II}$ in the two phases (see Figure 4). The interfacial compositions and transfer rate of A are to be calculated, with interfacial resistance neglected.

For small mass transfer rates, the interfacial composition can be found by plotting the equilibrium locus

$$x_{A0}{}^{II} = f(x_{A0}{}^{I}) \tag{45}$$

and the driving force locus for this system

$$\left(\frac{x_{A0} - x_{A\infty}}{1 - x_{A0}}\right)^{II} = -\frac{k_x{}^{I}}{k_x{}^{II}}\left(\frac{x_{A0} - x_{A\infty}}{1 - x_{A0}}\right)^{I} \tag{46}$$

on a phase diagram (see Figure 4 and reference 22). Evaluation of the ratio $k_x{}^{I}/k_x{}^{II}$ from the molar analogs of Equations (40) and (44) gives

$$\left(\frac{x_{A0} - x_{A\infty}}{1 - x_{A0}}\right)^{II} = -\sqrt{\frac{(c^2\,\mathcal{D}_{AB})^{I}}{(c^2\,\mathcal{D}_{AC})^{II}}}\left(\frac{x_{A0} - x_{A\infty}}{1 - x_{A0}}\right)^{I} \tag{47}$$

which is shown as the dotted line in Figure 4. The solution, labeled L on the diagram, can be inserted in the mass transfer formula

$$N_{A0}{}^{I} - x_{A0}{}^{I}\,(N_{A0}{}^{I} + N_{B0}{}^{I}) = k_x{}^{I}\,\theta_x{}^{I}\,(x_{A0}{}^{I} - x_{A\infty}{}^{I}) \tag{48}$$

to compute the solute transfer rate $N_{A0}{}^{I} = -N_{A0}{}^{II}$. For consistency with Equations (46) and (47), this calculation should be made with $N_{B0}{}^{I} = 0$ and $\theta_x{}^{I} = 1$.

For higher mass transfer rates, several procedures are available. One way is to correct Equations (46) and (47) by introducing the factor $\theta_x{}^{I}/\theta_x{}^{II}$ on the right side. The correction factors can be obtained from Table 1 at estimated values of $\phi_x{}^{I}$ and $\phi_x{}^{II}$. Actually, only $\phi_x{}^{I}$ need be estimated, since $\phi_x{}^{II}$ then follows from the condition $N_{A0}{}^{II} = -N_{A0}{}^{I}$ and the ratio $k_x{}^{II}/k_x{}^{I}$ used above:

$$\phi_x{}^{II} = -\phi_x{}^{I}\sqrt{\frac{(c^2\,\mathcal{D}_{AB})^{I}}{(c^2\,\mathcal{D}_{AC})^{II}}} \tag{49}$$

The resulting tentative solution for $N_{A0}{}^{I}$ can be used to produce an improved value of $\phi_x{}^{I}$, and if necessary the calculation cycle can be repeated.

A more direct method is to estimate $\phi_x{}^{I}$, calculate $\phi_x{}^{II}$ as above, and read out $R_x{}^{I}$ and $R_x{}^{II}$ from Table 1. Then rearrangement of the definition of R_x (see Table 2) gives the following tentative interfacial compositions:

$$x_{A0}{}^{I} = \frac{x_{A\infty}{}^{I} + R_x{}^{I}\left(\dfrac{N_{A0}{}^{I}}{N_{A0}{}^{I} + N_{B0}{}^{I}}\right)}{1 + R_x{}^{I}} \tag{50}$$

$$x_{A0}{}^{II} = \frac{x_{A\infty}{}^{II} + R_x{}^{II}\left(\dfrac{N_{A0}{}^{II}}{N_{A0}{}^{II} + N_{C0}{}^{II}}\right)}{1 + R_x{}^{II}} \tag{51}$$

with $N_{B0}{}^{I} = 0$ and $N_{C0}{}^{II} = 0$ for the case at hand. These compositions can be plotted on the phase diagram for various values of ϕ_x^I, as shown in Figure 4, to give a more accurate locus than Equation (47). The correct interfacial composition is then found at the intersection with the equilibrium line (point H in Figure 4); it differs significantly from the approximate solution L found earlier. Finally, the mass transfer rate can be found from the definition of ϕ_x

$$(N_{A0}^I + N_{B0}^I) = k_x^I \, \phi_x^I \tag{52}$$

with a known or predicted value of k_x^I for the given flow situation.

For dispersed-phase contactors, it is convenient to use a mass transfer coefficient $k_{xm}a$ based on a unit volume of the system. Then Equation (48) can be replaced by

$$\begin{aligned} d\mathcal{W}_{A0}^I - x_{A0}^I \, (d\mathcal{W}_{A0}^I + d\mathcal{W}_{B0}^I) \\ = (k_{xm}a)^I \, \theta_x^I \, (x_{A0}^I - x_{A\infty}^I) \, dV \end{aligned} \tag{53}$$

and ϕ_x^I can be expressed as

$$\phi_x^I = \frac{d(\mathcal{W}_{A0}^I + \mathcal{W}_{B0}^I)}{(k_{xm}a)^I \, dV} \tag{54}$$

in which the volume element dV is large compared with the boundary-layer dimensions. The calculation of the interfacial conditions remains as given above.

Many other two-phase problems, such as nonisothermal contacting and diffusion controlled reactions, can be handled by variations of these procedures. The interfacial state will be time independent, as above, provided that no characteristic length, or time constant, appears in the boundary-layer problem.

Absorption with Diffusion Controlled Reaction

Consider the absorption of gas A by a liquid solvent S, to which a reactive solute B has been added. Species A and B combine in an instantaneous irreversible reaction $aA + bB \rightarrow P$. The contacting begins locally at time $t_0(u, w)$ as before. We analyze the process according to Equation (17*a*), considering the concentrations of A, B and P to be small and accordingly neglecting v_0. We also use the substitutions $\rho\omega_A = M_A c_A$ and $\rho\omega_B = M_B c_B$ for comparison with related treatments (*26*) to (*28*).

Since A and B react instantly on contact, the reaction is localized at a moving front $y = y_R(u, w, t)$ which separates the zone containing A from the zone containing B (see Figure 5). The diffusion equations for the reactants are

$$\frac{\partial c_A}{\partial \tau} = \mathcal{D}_{AS} \frac{\partial^2 c_A}{\partial \Upsilon^2} \qquad \left(\begin{matrix} \text{Zone } A, \\ 0 < \Upsilon < s y_R \end{matrix} \right) \tag{55}$$

$$\frac{\partial c_B}{\partial \tau} = \mathcal{D}_{BS} \frac{\partial^2 c_B}{\partial \Upsilon^2} \qquad \left(\begin{matrix} \text{Zone } B, \\ \Upsilon > s y_R \end{matrix} \right) \tag{56}$$

The homogeneous reaction does not appear in these equations since it is localized at $\Upsilon = s y_R$.

The initial and boundary conditions are

$$\text{I.C.:} \quad c_B = c_{B\infty} \quad \text{at} \quad \Upsilon > 0 \quad \text{for} \quad \tau = 0 \tag{57}$$

$$\text{B.C. 1:} \quad c_A = c_{A0} \quad \text{at} \quad \Upsilon = 0 \quad \text{for} \quad \tau \geqq 0 \tag{58}$$

$$\text{B.C. 2:} \quad c_A = 0 \quad \text{at} \quad \Upsilon = s y_R \quad \text{for} \quad \tau \geqq 0 \tag{59}$$

$$\text{B.C. 3:} \quad c_B = 0 \quad \text{at} \quad \Upsilon = s y_R \quad \text{for} \quad \tau \geqq 0 \tag{60}$$

$$\text{B.C. 4:} \quad \frac{\mathcal{D}_{AS}}{a} \frac{\partial c_A}{\partial \Upsilon} = - \frac{\mathcal{D}_{BS}}{b} \frac{\partial c_B}{\partial \Upsilon} \quad \text{at} \quad \Upsilon = s y_R \quad \text{for} \quad \tau \geqq 0 \tag{61}$$

$$\text{B.C. 5:} \quad c_B = c_{B\infty} \quad \text{at} \quad \Upsilon >> s y_R \quad \text{for} \quad \tau \geqq 0 \tag{62}$$

Equation (61) expresses the stoichiometric requirement that a moles of A consume b moles of B.

Equations (55) to (62) are formally similar to the corresponding nonflow problem, which has already been solved (*26*, *27*). The nonflow solution thus can be applied to mobile interfaces if it is written in terms of τ and Υ. This gives the concentration profiles

$$\frac{c_A}{c_{A0}} = 1 - \frac{\operatorname{erf} \eta}{\operatorname{erf} \eta_R} \tag{63}$$

$$\frac{c_B}{c_{B\infty}} = 1 - \frac{\operatorname{erfc} \eta \sqrt{\mathcal{D}_{AS}/\mathcal{D}_{BS}}}{\operatorname{erfc} \eta_R \sqrt{\mathcal{D}_{AS}/\mathcal{D}_{BS}}} \tag{64}$$

in which $\eta = \Upsilon/\sqrt{4\mathcal{D}_{AS}\tau} = y/\delta_{AS}$, and δ_{AS} is given by δ_ω of Equation (31) with B replaced by S. Here η_R, the value of η at the reaction zone, is given implicitly by

$$\begin{aligned} \frac{a \, c_{B\infty}}{b \, c_{A0}} \operatorname{erf} \eta_R \exp \eta_R^2 \\ = \sqrt{\frac{\mathcal{D}_{AS}}{\mathcal{D}_{BS}}} \operatorname{erfc} \sqrt{\frac{\mathcal{D}_{AS}}{\mathcal{D}_{BS}} \eta_R^2} \exp \left(\frac{\mathcal{D}_{AS}}{\mathcal{D}_{BS}} \eta_R^2 \right) \end{aligned} \tag{65}$$

and is thus independent of u, w, and t. The depth of zone A is given by $y_R = \eta_R \delta_{AS}$ and is thus directly proportional to δ_{AS}, the boundary-layer thickness that would exist for absorption of A into the pure solvent.

The instantaneous absorption rate follows from Equation (63) and Fick's first law, written for dilute solutions:

$$N_{A0} = - \mathcal{D}_{AS} \left. \frac{\partial c_A}{\partial y} \right|_{y=0} = \frac{2}{\sqrt{\pi}} \, \frac{c_{A0} \, \mathcal{D}_{AS}}{\delta_{AS}} \, \frac{1}{\operatorname{erf} \eta_R} \tag{66}$$

The effect of the interfacial deformation is contained in the expression for δ_{AS} and can also be expressed by the correction factor κ of Equation (43). Thus the deformation has the same relative effect in the presence or absence of the reaction.

With decreasing initial concentration of B, the reaction location η_R tends to infinity, and the rate approaches that of physical absorption of A by pure S:

$$N_{A0}^{(\text{phys})} = \frac{2}{\sqrt{\pi}} \, \frac{c_{A0} \, \mathcal{D}_{AS}}{\delta_{AS}} \tag{67}$$

Thus the addition of species B speeds up the absorption rate by a factor

$$Ha \equiv \frac{N_{A0}}{N_{A0}^{(\text{phys})}} = \frac{1}{\operatorname{erf} \eta_R} \tag{68}$$

where Ha is the Hatta number, or reaction factor.

Equation (68) was given for stationary interfaces by Danckwerts (*26*) and verified by Sherwood and Pigford (*27*). The following limiting cases of this formula are useful:

$$\frac{N_{A0}}{N_{A0}^{(\text{phys})}} = 1 + \frac{a \, c_{B\infty}}{b \, c_{A0}} \left\{ \begin{matrix} \text{if} & \mathcal{D}_{AS} = \mathcal{D}_{BS} \\ \text{or} & \dfrac{c_{B\infty}}{c_{A0}} << \dfrac{b}{a} \end{matrix} \right\} \tag{68a}$$

$$\frac{N_{A0}}{N_{A0}^{(\text{phys})}} = \left[1 + \frac{a \, c_{B\infty} \, \mathcal{D}_{BS}}{b \, c_{A0} \, \mathcal{D}_{AS}} \right] \sqrt{\frac{\mathcal{D}_{AS}}{\mathcal{D}_{BS}}} \qquad \left\{ \text{if} \ \frac{c_{B\infty}}{c_{A0}} >> \frac{b}{a} \right\} \tag{68b}$$

Danckwerts (26) gave Equation (68*a*) for the equal diffusivity case, and Sherwood and Pigford (27) verified its accuracy over the usual range of diffusivity ratios. Equation (68*b*) was given by Lightfoot (28), who has also compared these asymptotes with Equation (68) and with other mass transfer models. It is remarkable that Equation (68*a*) coincides with the result obtained by Hatta (29) from a stagnant film model.

Absorption with First-Order Homogeneous Reaction

Consider the isothermal absorption of gas A by liquid B in the presence of a homogeneous pseudo first-order reaction $A + B \rightarrow P$. The contacting begins locally at time $t_0(u, w)$ as before. The concentrations of A and P in the liquid are assumed to be small, and the interfacial concentration of A is assumed constant at c_{A0}. Equation (17*a*) then gives

$$\frac{\partial c_A}{\partial \tau} = \mathcal{D}_{AB}\frac{\partial^2 c_A}{\partial \Upsilon^2} - \frac{k_1''' c_A}{s^2} \qquad (69)$$

and the initial and boundary conditions are

I.C. $\quad c_A = 0 \quad$ at $\Upsilon > 0 \quad$ for $\tau = 0 \qquad (70)$
B.C. 1: $\quad c_A \rightarrow 0 \quad$ at $\Upsilon \rightarrow \infty \quad$ for $\tau \geqq 0 \qquad (71)$
B.C. 2: $\quad c_A = c_{A0} \quad$ at $\Upsilon = 0 \quad$ for $\tau \geqq 0 \qquad (72)$

This problem is solvable by setting $c_A = \psi_A \exp(-k_1'''t)$ and by using the Laplace transformation with respect to τ. The concentration profile is

$$\frac{c_A}{c_{A0}} = e^{k_1'''(t_0(u,w)-t)} \operatorname{erfc} \frac{y s(u, w, t)}{\sqrt{4\mathcal{D}_{AB}\int_{t_0(u,w)}^{t} s^2(u, w, t')\,dt'}} + \int_{t_1=t_0(u,w)}^{t_1=t} k_1''' e^{k_1'''(t_1-t)} \operatorname{erfc} \frac{y s(u, w, t)}{\sqrt{4\mathcal{D}_{AB}\int_{t_1}^{t} s^2(u, w, t')\,dt'}}\, dt_1 \qquad (73)$$

The local absorption rate is

$$N_{A0} = c_{A0}\sqrt{\frac{\mathcal{D}_{AB}}{\pi}}\, s(u, w, t) \frac{e^{k_1'''(t_0(u,w)-t)}}{\sqrt{\int_{t_0(u,w)}^{t} s^2(u, w, t')\,dt'}} + c_{A0}\sqrt{\frac{\mathcal{D}_{AB}}{\pi}}\, s(u, w, t) \int_{t_1=t_0(u,w)}^{t_1=t} \frac{k_1''' e^{k_1'''(t_1-t)}\, dt_1}{\sqrt{\int_{t_1}^{t} s^2(u, w, t')\,dt'}} \qquad (74)$$

and the rate of absorption for a surface region $\mathcal{R}(u, w, t)$ is

$$\mathcal{W}_{A0} = c_{A0}\sqrt{\frac{\mathcal{D}_{AB}}{\pi}} \int_{\mathcal{R}}\!\int \frac{s^2(u, w, t)\, e^{k_1'''(t_0(u,w)-t)}}{\sqrt{\int_{t_0(u,w)}^{t} s^2(u, w, t')\,dt'}}\, du\,dw + c_{A0}\sqrt{\frac{\mathcal{D}_{AB}}{\pi}} \int_{\mathcal{R}}\!\int s^2(u, w, t) \int_{t_0(u,w)}^{t} \frac{k_1''' e^{k_1'''(t_1-t)}}{\sqrt{\int_{t_1}^{t} s^2(u, w, t')\,dt'}}\, dt_1\,du\,dw \qquad (75)$$

For long exposure times these results become simpler, since $e^{k_1'''(t_0(u,w)-t)}$ then goes to zero.

For fast reactions, such that $k_1'''(t - t_0(u, w)) >> 1$ and $k_1''' >> \partial \ln s/\partial t$ everywhere, Equation (75) gives the asymptote

$$\mathcal{W}_{A0} = c_{A0}\sqrt{\mathcal{D}_{AB} k_1'''}\; S(t) \quad \{k_1''' \rightarrow \infty\} \qquad (75a)$$

where $S(t)$ is the instantaneous area of the region $\mathcal{R}(u, w, t)$. This relationship has been used by Onda and co-workers (30) for comparisons of wetted area and interfacial area in packed towers.

This case is more complicated than the preceding one, because the presence of a characteristic time $1/k_1'''$ makes it impossible to combine y and t into a single coordinate. Consequently, the effects of the deformation and chemical reaction do not factor here as they did in Equation (66).

The results found by Danckwerts (26) for absorption into a stationary semi-infinite medium may be recovered from Equations (73) to (75) by setting $s(u, w, t) =$ constant.

Superposition Solutions

The superposition formulas of paper I are paralleled here with appropriate changes. In addition, we give a solution for distributed sources which can be used to describe homogeneous chemical reactions. For simplicity, the net mass transfer velocity v_0 is considered small.

Prescribed Interfacial Composition or Temperature. Consider a nonreacting fluid, initially of uniform composition $\omega_{A\infty}$. The fluid has a constant interfacial composition equal to $\omega_{A\infty}$ until time $t_0(u, w)$ and a variable interfacial composition $\omega_{A0}(u, w, t)$ thereafter. The ensuing composition profile in the fluid may be found by treating $\omega_{A0}(u, w, t)$ as a summation of step functions and by superimposing the resulting composition changes calculated from Equations (32) and (34):

$$\omega_A(u, w, y, t) - \omega_{A\infty} = \int_{t_1<t_0(u,w)}^{t_1=t} (1 - \Pi_\omega)\big|_{u,w,y,t,t_1}\, d\omega_{A0}(u, w, t_1) \qquad (76)$$

The lower limit of integration is taken earlier than $t_0(u, w)$ to insure that all changes in ω_{A0} are included. Here t_1 is the time at which the composition change $d\omega_{A0}(u, w, t_1)$ occurs, and Π_ω is given by Equations (32) and (34) with $C_\omega = 0$ and with $t_0(u, w)$ replaced by the dummy variable t_1. Superposition of Equations (36) and (41) in the same manner gives the interfacial diffusion flux $n_{A0} - \omega_{A\infty}(n_{A0} + n_{B0})$

$$= \rho\sqrt{\frac{\mathcal{D}_{AB}}{\pi}}\, s(u, w, t) \int_{t_1<t_0(u,w)}^{t} \frac{d\omega_{A0}(u, w, t_1)}{\sqrt{\int_{t_1}^{t} s^2(u, w, t')\,dt'}} \qquad (77)$$

and the total diffusion rate from a surface region $\mathcal{R}(u, w, t)$: $w_{A0} - \omega_{A\infty}(w_{A0} + w_{B0})$

$$= \rho\sqrt{\frac{4\mathcal{D}_{AB}}{\pi}} \int_{\mathcal{R}}\!\int \int_{t_1<t_0(u,w)}^{t}$$

$$\frac{\partial}{\partial t}\sqrt{\int_{t_1}^{t} s^2(u,w,t')\,dt'}\,d\omega_{A0}(u,w,t_1)\,du\,dw \quad (78)$$

Finally, the total mass of A that has diffused into the fluid, from the elements currently in $\mathcal{R}$, is given by the right side of (78) with $\partial/\partial t$ removed.

The bulk flow terms on the left of Equations (77) and (78) are evaluated, for convenience, at the initial composition $\omega_{A\infty}$. This is a satisfactory approximation as long as v_0 is small (or, more precisely, as long as $|R_\omega| << 1$ throughout the region considered).

Prescribed Interfacial Flux. Consider a nonreacting fluid, initially of uniform composition $\omega_{A\infty}$. The interfacial diffusion flux is zero until time $t_0(u, w)$ and varies arbitrarily thereafter. The resulting composition profile, which satisfies Equation (17) with $v_0 \doteq 0$, is

$$(\omega_A - \omega_{A\infty}) = \frac{1}{\rho\sqrt{\pi \mathcal{D}_{AB}}}\int_{t_1=t_0(u,w)}^{t_1=t} \frac{\exp(-\eta^{*2})}{\sqrt{\int_{t_1}^{t} s^2(u,w,t')\,dt'}}\, j_{A\infty}(u,w,t_1)\,s(u,w,t_1)\,dt_1 \quad (79)$$

Here $j_{A\infty}$ is the modified diffusion flux used in Equation (77), and η^* is given by Equation (32) with $t_0(u, w)$ replaced by the dummy variable t_1. This solution is obtained by paralleling Equations (28) to (39) of paper I. It should be useful for analyzing interfacial reactions, particularly in dropping mercury electrode measurements.

Prescribed Sources in the Fluid. Consider a system in which species A is confined to one phase, initially at uniform composition $\omega_{A\infty}$. Beginning at time $t_0(u, w)$, species A is produced by homogeneous chemical reaction at a variable rate $r_A(u, w, y, t)$. The resulting composition profile, which satisfies Equation (17) with $v_0 \doteq 0$, is

$$(\omega_A - \omega_{A\infty}) = \frac{1}{\rho\sqrt{4\pi\,\mathcal{D}_{AB}}}\int_{t_1=t_0(u,w)}^{t_1=t}\int_{y_1=0}^{y_1=\infty} \frac{e^{-(\eta-\eta_1)^2}+e^{-(\eta+\eta_1)^2}}{\sqrt{\int_{t_1}^{t} s^2(u,w,t')\,dt'}}\, r_A(u,w,y_1,t_1)\, s(u,w,t_1)\,dy_1\,dt_1 \quad (80)$$

Here η and η_1 are evaluated from Equation (32) at y and y_1, respectively, with $t_0(u, w)$ replaced both times by t_1, and y_1 and t_1 are dummy variables. This solution can be added to Equation (79) to describe systems with simultaneous mass transfer and homogeneous chemical reaction.

These superposition solutions can all be rewritten for heat transfer by the substitutions of Table 2. Equations (76) to (79) can also be rewritten in molar units, and Equation (80) can be so rewritten if $(R_A + R_B)$ vanishes.

EXTERNALLY STEADY SOLUTIONS

Some systems, although time dependent in the u, w, y coordinates, appear steady in some external coordinate frame. Laminar jets, for example, are usually regarded as steady flows in fixed coordinates, and certain wave motions become stationary when viewed from moving axes. When dealing with such externally steady systems, one can simplify the general solutions by the substitutions described below. The external coordinates are treated as nondeforming throughout.

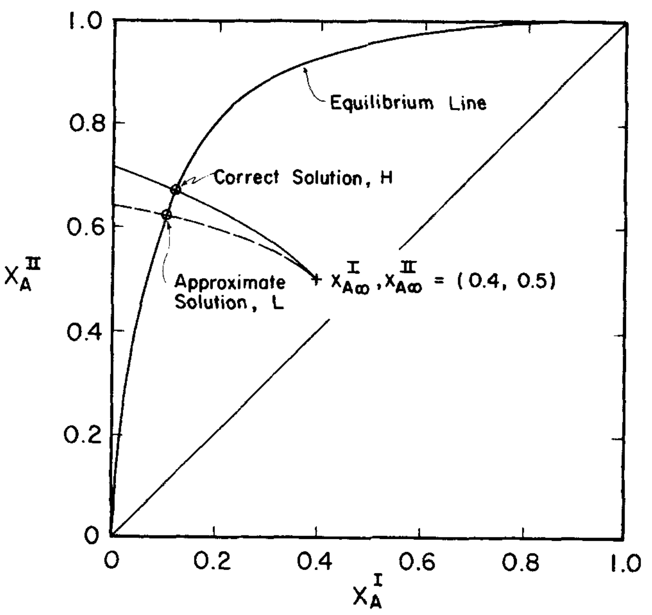

Fig. 4. Calculation of interfacial composition for an extraction problem with $(c^2\mathcal{D}_{AB})^I = (c^2\mathcal{D}_{AC})^{II}$. The approximate solution L is from Equations (45) and (47). The correct solution H is from Equations (45), (49) to (51), and Table 1.

In externally steady motion, the streamlines and particle trajectories coincide, and the positions of these lines relative to the external coordinates are fixed. We may then identify the surface streamlines as lines of constant u. The surface elements on each streamline may be distinguished by their time of arrival at some chosen point. We choose this time, t_a, as the w coordinate.

In these coordinates, the surface element (u, t_a) leads the neighboring element $(u, t_a + \Delta t_a)$ by a constant time interval Δt_a across each fixed point on their common path. The distance between the two elements at any time is given by $(\partial \mathbf{r}_s/\partial t_a)\Delta t_a = -\mathbf{V}_s \Delta t_a$, where $\mathbf{V}_s$ is the local velocity of the surface elements relative to the external coordinates. Thus, Equation (6) gives

$$s = \left|\frac{\partial \mathbf{r}_s}{\partial u} \times \mathbf{V}_s\right| = \frac{V_s}{|\nabla u|} \quad (81)$$

when the coordinates u and w are chosen as above. The second expression for s is the simpler, since $1/|\nabla u|$ is just the infinitesimal distance between two streamlines u and $u + \Delta u$ divided by the infinitesimal increment $|\Delta u|$.

For external coordinates, we choose u, y, and l, where l is the arc length along the streamline from some reference point. Then, for any surface element (u, t_a), the variables t and l are related as

$$dt = dl/V_s(u, l) \quad \left\{\begin{matrix}\text{constant}\\ u \text{ and } t_a\end{matrix}\right\} \quad (82)$$

whereas on a given streamline u, at any time t, the variables w and l are related as

$$dw \equiv dt_a = -\,dl/V_s(u, l) \quad \left\{\begin{matrix}\text{constant}\\ u \text{ and } t\end{matrix}\right\} \quad (83)$$

The variables t and w can thus be eliminated in favor of l, and the surface velocity can be handled as a function of

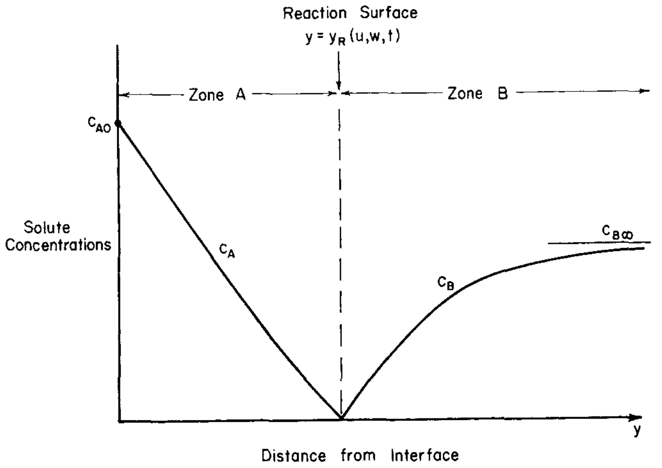

Fig. 5. Typical snapshot of profiles in gas absorption with diffusion controlled reaction.

u and l rather than u, w, and t.

Now consider the application of Equation (41) to an externally steady system, with the transfer surface extending streamwise from $l = 0$ to $l = L(u)$ and laterally from u_I to u_{II}. Insertion of Equations (81) to (83) gives

$$w_{A0} - \omega_{A0}(w_{A0} + w_{B0})$$

$$= (\omega_{A0} - \omega_{A\infty}) \sqrt{\frac{\rho^2 \mathcal{D}_{AB}}{4}}\, \Pi_\omega'(0) \int_{u_I}^{u_{II}} \int_0^{L(u)} \frac{(V_s/\nabla u)^2 (dl/V_s)\, du}{\sqrt{\int_0^l (V_s/\nabla u)^2 (dl'/V_s)}}$$

$$= (\omega_{A0} - \omega_{A\infty}) \sqrt{\rho^2 \mathcal{D}_{AB}}\, \Pi_\omega'(0) \int_{u_I}^{u_{II}} \sqrt{\int_0^{L(u)} \left.\frac{V_s}{(\nabla u)^2}\right|_{u,l'} dl'}\; du \quad (84)$$

when $dudw$ is considered positive as in Equation (4). This result is a generalization of the steady state formulas of Levich (*8*), Baird and Hamielec (*12*), and Beek and Kramers (*13*).

In the presence of a first-order homogeneous reaction of A, the mass transfer rate is given by Equation (75). Reduction to steady state form via Equations (81) to (83) gives

$$\mathcal{W}_{A0} = c_{A0} \sqrt{\frac{\mathcal{D}_{AB}}{\pi}} \int_{u_I}^{u_{II}} \int_0^{L(u)} \left.\frac{V_s}{(\nabla u)^2}\right|_{u,l} \frac{\exp \int_0^l - \frac{k_1''' \, dl'}{V_s(u, l')}}{\sqrt{\int_0^l \left.\frac{V_s}{(\nabla u)^2}\right|_{u,l'} dl'}}\, dl du$$

$$+ c_{A0} \sqrt{\frac{\mathcal{D}_{AB}}{\pi}} \int_{u_I}^{u_{II}} \int_0^{L(u)} \left.\frac{V_s}{(\nabla u)^2}\right|_{u,l} \int_0^l \frac{k_1''' \exp \int_{l_1}^l - \frac{k_1''' \, dl'}{V_s(u, l')}}{\sqrt{\int_{l_1}^l \left.\frac{V_s}{(\nabla u)^2}\right|_{u,l'} dl'}} \frac{dl_1 dl du}{V_s(u, l_1)} \quad (85)$$

Here, as in Equation (75), the first exponential term goes to zero at long times of exposure of the imbedded surface elements. Thus it will vanish in the externally steady state on any streamline that starts from a point of zero velocity (stagnation point) within the mass transfer region. Examples 3 and 4 illustrate this simplification.

The other general solutions can be specialized to externally steady systems by the same substitutions.

EXAMPLES

The foregoing solutions hold for arbitrary hydrodynamics. Here some simple systems are analyzed to show how the hydrodynamics is specified.

Absorption from a Growing Bubble

Consider the absorption of gas A from a growing bubble formed by injection of A into a nonvolatile liquid B. The interfacial mole fraction of A in the liquid is constant. The coordinates u and w may be identified with the spherical coordinates θ and ϕ; the element of area is then given by

$$dS = \left| \frac{\partial \mathbf{r}}{\partial \theta} \times \frac{\partial \mathbf{r}}{\partial \phi} \right| d\theta d\phi$$

$$= R^2 \sin\theta \; d\theta d\phi \quad (86)$$

where R is the instantaneous radius of the bubble. Thus

$$s(\theta, \phi, t) = [R(t)]^2 \sin\theta \quad (87)$$

Substitution in Equations (31) and (41) then gives the instantaneous boundary-layer thickness

$$\delta_\omega = \frac{1}{R^2(t) \sin\theta} \sqrt{4\mathcal{D}_{AB} \int_0^t [R^2(t') \sin\theta]^2 \, dt'}$$

$$= \sqrt{4\mathcal{D}_{AB} \int_0^t \left[\frac{R(t')}{R(t)}\right]^4 dt'} \quad (88)$$

and the instantaneous absorption rate

$$w_{A0} = \frac{\omega_{A0}}{1 - \omega_{A0}} \rho \sqrt{\mathcal{D}_{AB}}\, \Pi'_\omega(0) \int_0^{2\pi} \int_0^\pi \frac{\partial}{\partial t} \sqrt{\int_0^t R^4(t') \sin^2\theta \; dt'} \; d\theta d\phi$$

$$= \frac{\omega_{A0}}{1 - \omega_{A0}} \rho \sqrt{\mathcal{D}_{AB}}\, \Pi'_\omega(0) \frac{2\pi R^4(t)}{\sqrt{\int_0^t R^4(t') \, dt'}} \quad (89)$$

These results hold for any integrable function $R(t)$ as long as $\delta_\omega << R(t)$; see approximation 3.

The interfacial deformation is quite important here. Thus, in the case of constant volumetric growth rate, encountered in dropping mercury polarography, the deformation increases the mass transfer rate at given R and t by more than 50%.

Special cases of this problem have been solved by Ilkovic (*6*) and by Beek and Kramers (*13*). The polarographic case $R(t) \sim t^{1/3}$ has been analyzed further by perturbation methods (*8, 31, 32*) to obtain a correction for the interfacial curvature. The correction increases w_{A0} by a factor $[1 + 0.76(\delta_\omega/R)]$, which may be used tentatively [with $1/R$ replaced by $-\frac{1}{2}(\nabla \bullet \mathbf{n})$] to estimate the effect of curvature on interfacial fluxes in other geometries.

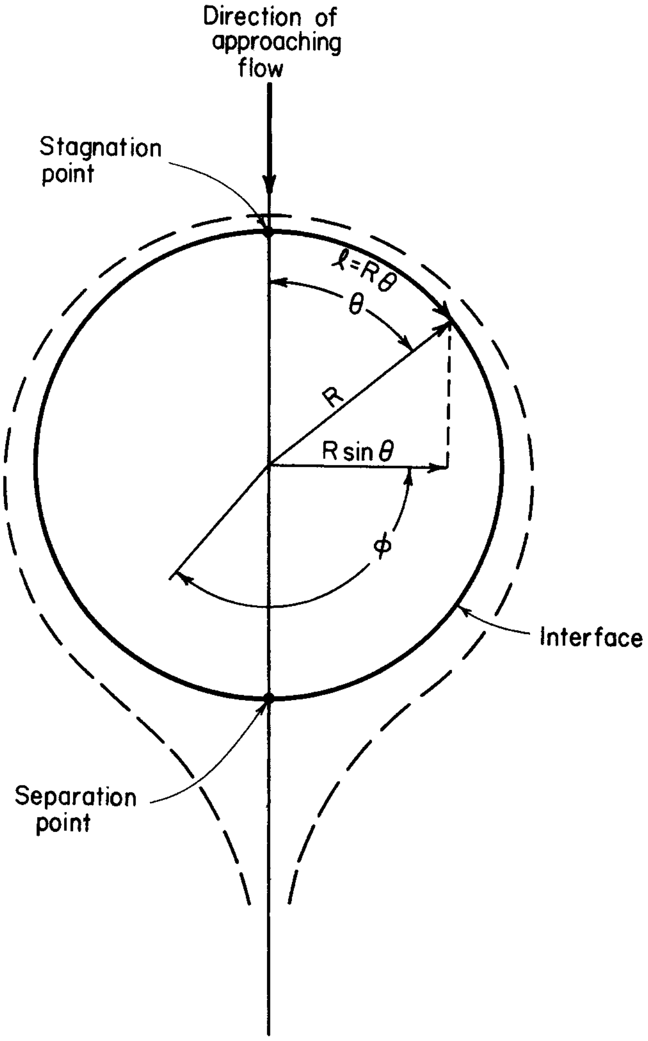

Fig. 6. Absorption from a circulating bubble. The dotted line indicates the shape of the diffusional boundary layer.

Absorption from a Circulating Bubble

Gas A is being absorbed from a freely circulating spherical bubble of gas A rising in creeping flow through a solution of A in nonvolatile liquid B. The absorption rate is to be calculated in the externally pseudo steady state which sets in after a short exposure time.

The external coordinates are measured from the center of the bubble, and the coordinates u and l of Equation (84) are chosen as ϕ and $R\theta$, respectively (see Figure 6). The geometry of the coordinates gives $|\nabla u|^{-1} = R\sin\theta$, and the analyses of Rybczynski (*33*) and Hadamard (*34*) give the surface velocity relative to the bubble:

$$V_s = V_{\max}\sin\theta \qquad (90)$$

Substitution into Equation (84) gives the absorption rate

$$w_{A0} = \frac{(\omega_{A0} - \omega_{A\infty})}{(1 - \omega_{A0})}\,\rho\sqrt{\mathcal{D}_{AB}}\;\Pi'_\omega(0)\int_0^{2\pi}\sqrt{\int_0^{\pi} V_{\max}\,R^2\sin^3\theta(R\,d\theta)}\;d\phi$$

$$= \frac{(\omega_{A0} - \omega_{A\infty})}{(1 - \omega_{A0})}\,\rho\sqrt{\mathcal{D}_{AB}}\;\Pi'_\omega(0)\;4\pi\,R^2\sqrt{\frac{1}{3}\,\frac{V_{\max}}{R}} \qquad (91)$$

When the solubility ω_{A0} is small, so that $R_\omega \to 0$ and $\Pi'_\omega(0) \to 2/\sqrt{\pi}$, this equation reduces to the result given by Levich (*8*). The range of application of Levich's result is discussed by several authors (*13, 16, 35, 36, 37*).

If the absorption occurs from a gas mixture instead of the pure gas A, then Equation (91) can be applied to calculate the diffusion in each phase. However, in that case the result is limited to shorter exposure times, since the resulting internal boundary layer flows inward from the separation point and soon reaches the front of the drop (see Figure 7). An improved analysis of this situation has recently been made by Taunton and Lightfoot (*38*).

The diffusional analyses of Baird and Hamielec (*12*), Redfield and Houghton (*16*), Winnikow (*18*), and Cheh and Tobias (*20*), for circulating bubbles in noncreeping flow, may all be obtained from Equation (84) by inserting the appropriate expressions for $|\nabla u|$ and V_s.

The penetration and surface-renewal theories fail completely for this system, since the exposure time of the surface elements is unlimited. The surface elements are not renewed but are simply stretched out from the front of the sphere and crowded in at the rear. Thus these earlier theories, which ignore the changes in size of the surface

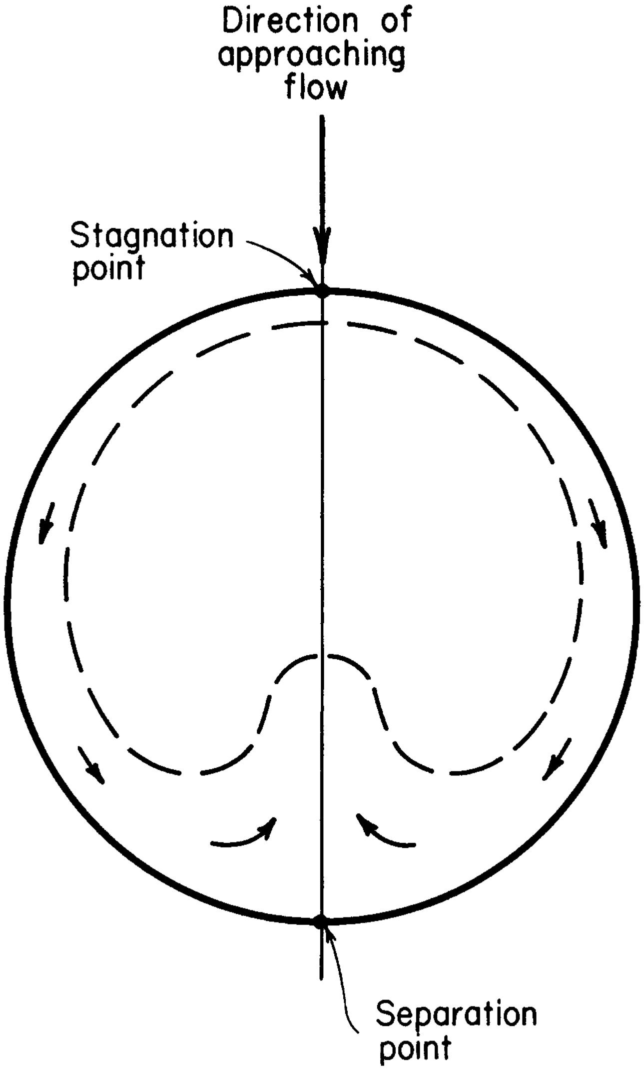

Fig. 7. Internal boundary layer in absorption from a circulating bubble of mixed gases. The boundary layer will start to overlap itself when the bulge in the lower part nears the stagnation point.

elements, fail to predict the pseudo steady behavior exhibited by Equation (91) and by experiments (*16, 35, 37, 39*).

Steady Absorption Near Stagnation Loci

Consider the absorption of gas A in pure liquid B, near an axial stagnation point (such as the front of a bubble or drop) in a steady axially symmetric flow. The rate of absorption is to be calculated for a region of radius R around the stagnation point (see Figure 8), with and without first-order reaction of the solute A.

The surface streamlines are given by $z = 0$, $\theta = u$ in cylindrical polar coordinates. The surface velocity is $V_s = \gamma r$, where γ is a constant for the system. In addition, $|\nabla u| = 1/r$ and $l = r$. Substitution into the molar analogue of Equation (84) gives the rate of absorption without reaction:

$$\mathcal{W}_{A0}{}^{(\text{phys})}$$

$$= \frac{x_{A0}}{1 - x_{A0}} \sqrt{c^2 \mathcal{D}_{AB}}\ \Pi'_x(0) \int_0^{2\pi} \sqrt{\int_0^R (\gamma r)(r)^2 dr}\ d\theta$$

$$= \frac{x_{A0}}{1 - x_{A0}} \sqrt{c^2 \mathcal{D}_{AB}}\ \Pi'_x(0) \sqrt{\gamma}\ (\pi R^2) \qquad (92)$$

The interfacial flux N_{A0} here is uniform and equal to $\mathcal{W}_{A0}/\pi R^2$.

The rate of absorption with reaction is obtained from Equation (85):

$$\mathcal{W}_{A0} = c_{A0} \sqrt{\frac{\mathcal{D}_{AB}}{\pi}} \int_0^{2\pi} \int_0^R \gamma r^3 \int_0^r \frac{k_1''' \exp \int_{r_1}^r - k_1'''\ dr'/\gamma r'}{\sqrt{\int_{r_1}^r \gamma r'^3\ dr'}}\ \frac{dr_1 dr d\theta}{\gamma r_1}$$

$$= c_{A0} \sqrt{\frac{4\gamma\ \mathcal{D}_{AB}}{\pi}}\ (\pi R^2)\ \frac{\Gamma\left(\frac{k_1'''}{4\gamma} + 1\right)\ \Gamma\left(\frac{1}{2}\right)}{\Gamma\left(\frac{k_1'''}{4\gamma} + \frac{1}{2}\right)} \qquad (93)$$

The first integral in Equation (85) vanishes here because the streamlines all come from a stagnation point within the mass transfer region. Here again, N_{A0} is uniform over the region.

For dilute solutions (small x_{A0}), the ratio of the absorption rates with and without reaction is

$$Ha \equiv \frac{\mathcal{W}_{A0}}{\mathcal{W}_{A0}{}^{(\text{phys})}} = \frac{\Gamma\left(\frac{k_1'''}{4\gamma} + 1\right) \Gamma\left(\frac{1}{2}\right)}{\Gamma\left(\frac{k_1'''}{4\gamma} + \frac{1}{2}\right)} \qquad (94)$$

and is plotted in Figure 9. For small values of k_1'''/γ the reaction factor Ha approaches unity, and for large values it approaches $\sqrt{\pi k_1'''/4\gamma}$.

A stagnation line in two-dimensional flow, with $V_s = \gamma l$, can be similarly treated to give

$$N_{A0}{}^{(\text{phys})} = \frac{x_{A0}}{1 - x_{A0}} \sqrt{c^2 \mathcal{D}_{AB}}\ \Pi'_x(0) \sqrt{\frac{\gamma}{2}} \qquad (95)$$

in the absence of reaction and

$$N_{A0} = c_{A0} \sqrt{\frac{2\gamma\ \mathcal{D}_{AB}}{\pi}}\ \frac{\Gamma\left(\frac{k_1'''}{2\gamma} + 1\right) \Gamma\left(\frac{1}{2}\right)}{\Gamma\left(\frac{k_1'''}{2\gamma} + \frac{1}{2}\right)} \qquad (96)$$

for first-order reaction with small x_{A0}. The reaction factor for this case is

$$Ha \equiv \frac{N_{A0}}{N_{A0}{}^{(\text{phys})}} = \frac{\Gamma\left(\frac{k_1'''}{2\gamma} + 1\right) \Gamma\left(\frac{1}{2}\right)}{\Gamma\left(\frac{k_1'''}{2\gamma} + \frac{1}{2}\right)} \qquad (97)$$

and is similar to the axially symmetric solution as indicated in Figure 9.

Chan (*40*) has solved Equation (16) exactly for nonreactive absorption beginning at time t_0 in two-dimensional inviscid stagnation flow. His result agrees with that obtained from Equations (31) and (36) at the small mass transfer rates which he considered. This agreement is to be expected, since approximations 1 to 4 are exact for his flow system. At long exposure times, say $\gamma(t - t_0) > 4$, the absorption attains the steady rate given in Equation (95).

Laminar Jets and Other Axisymmetric Flows

Gas A is being absorbed by an axisymmetric laminar jet of nonvolatile solvent B of total interfacial length L. The interfacial composition x_{A0} is constant, and the system is externally steady. The absorption rate is to be evaluated, with and without first-order liquid-phase reaction.

The coordinate u may be identified with the angle θ around the axis of the jet, and the coordinate l may be measured downstream from the exit of the nozzle. The geometry then gives $|\nabla u|^{-1} = R_s(l)$, where $R_s(l)$ is the local radius of the jet. Both $R_s(l)$ and $V_s(l)$ can be predicted from the calculations of Duda and Vrentas (*41*). Substitution in the molar analogue of Equation (84), and integration from $\theta = 0$ to 2π, gives the absorption rate without chemical reaction:

$$\mathcal{W}_{A0} = \frac{x_{A0}}{1 - x_{A0}} \sqrt{c^2 \mathcal{D}_{AB}}\ \Pi'_x(0)\ 2\pi \sqrt{\int_0^L V_s(l')\ R_s^2(l')\ dl'} \qquad (98)$$

For small values of x_{A0}, this corresponds to Equation (53) of Duda and Vrentas (*21*) (who made the accurate approximation of replacing V_s and dl by their axial projections). The result of Cullen and Davidson (*9*), for the case of flat velocity profiles in each cross section of the jet, is likewise confirmed. The solution given by Scriven and Pigford (*11*) is less accurate, because their Equations (10) to (31) neglect the change of R_s with l.

Substitution in Equation (85) gives the absorption rate in the presence of a first-order reaction:

$$\mathcal{W}_{A0} = c_{A0} \sqrt{\frac{\mathcal{D}_{AB}}{\pi}}\ (2\pi)$$

$$\int_0^L V_s R_s^2\big|_l \int_0^l \frac{k_1''' \exp \int_{l_1}^l - \frac{k_1'''\ dl'}{V_s(l')}}{\sqrt{\int_{l_1}^l V_s R_s^2\big|_{l'}\ dl'}}\ \frac{dl_1 dl}{V_s(l_1)} \qquad (99)$$

The first integral in Equation (85) drops out because the surface streamlines start from zero velocity at the tip of the nozzle. This solution can be used to determine diffusivities and reaction rate constants from laminar jet experiments.

Other steady axisymmetric flows can be handled in the same manner, with l defined as the distance along the streamlines from the start of the transfer region. The function $1/|\nabla u|$ can be taken as the distance R_s from the interface to the axis of symmetry of the flow. Equations (84) and (85) can then be applied for any specified functions $V_s(l)$ and $R_s(l)$.

Absorption in a Large Eddy

Fortescue and Pearson (*19*) have obtained a useful description of turbulent absorption by solving the diffusion equation numerically for a regular array of eddies (see Figure 10). The boundary-layer analysis given here leads to similar results. Pseudo steady conditions will be assumed, and recirculation of solute to the surface will be neglected.

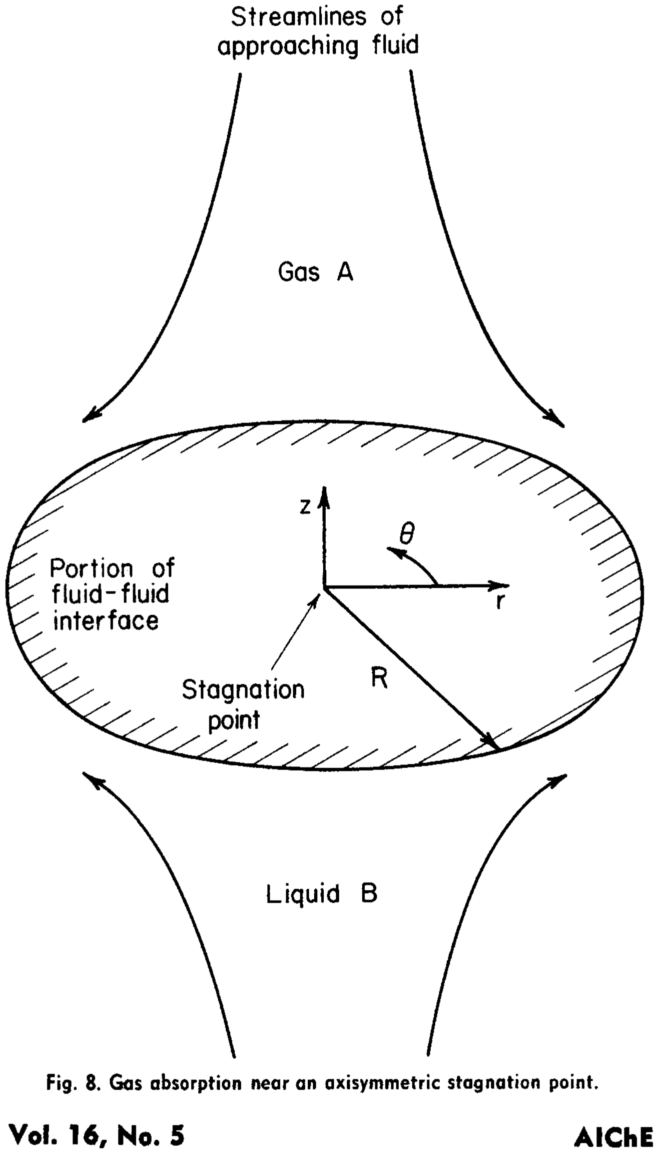

Fig. 8. Gas absorption near an axisymmetric stagnation point.

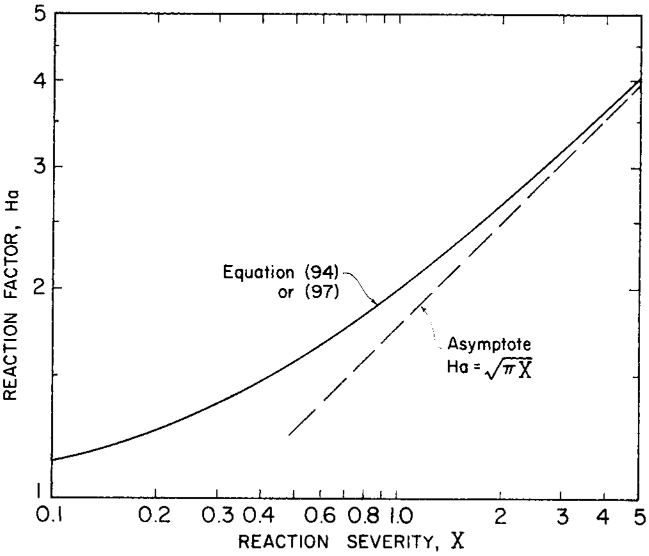

Fig. 9. Effect of first-order reaction on absorption rate. The quantity X is given by $k_1'''/4\gamma$ for axisymmetric stagnation flows and by $k_1'''/2\gamma$ for stagnation flows parallel to a plane. The curve can be approximated within 2% by the simple expression $Ha \doteq \sqrt{1 + \pi X}$.

Consider the interfacial region $0 < z < b$, $0 < x < \Lambda$, which permanently overlies a single eddy. The external coordinates are taken as $u = z$ and $l = x$; hence, $|\nabla u| = 1$. The velocity relative to these coordinates is taken as

$$V_s = V_{\max} \sin \frac{\pi x}{\Lambda} \tag{100}$$

in accordance with Equation (5) of Fortescue and Pearson. With these substitutions, Equation (84) gives (in molar units)

$$\begin{aligned} \mathcal{W}_{A0} - x_{A0}(\mathcal{W}_{A0} + \mathcal{W}_{B0}) &= (x_{A0} - x_{A\infty}) \sqrt{c^2\,\mathcal{D}_{AB}}\;\Pi'_x(0) \int_0^b \sqrt{\int_0^\Lambda V_{\max} \sin \frac{\pi x}{\Lambda}\, dx} \\ &= (x_{A0} - x_{A\infty}) \sqrt{\frac{2}{\pi}\;\frac{c^2\,\mathcal{D}_{AB}\,V_{\max}}{\Lambda}}\;\Pi'_x(0)\;(b\Lambda) \end{aligned} \tag{101}$$

as the rate of diffusion of species A into the eddy. The mass transfer coefficient for small mass transfer rates (at which $\Pi'_x(0) \to 2/\sqrt{\pi}$) thus becomes

$$k_{xm} = \frac{2\sqrt{2}}{\pi} \sqrt{\frac{c^2\,\mathcal{D}_{AB}\,V_{\max}}{\Lambda}} \tag{102}$$

and if we set $V_{\max} = 2\sqrt{\overline{v_x'^2}}$, in accordance with Equation (6) of reference *19*, we get:

$$k_{xm} = \frac{4}{\pi} \sqrt{\frac{c^2\,\mathcal{D}_{AB}\,\sqrt{\overline{v_x'^2}}}{\Lambda}} \tag{103}$$

Fortescue and Pearson obtained a comparable result but with a coefficient of 1.46 in place of $4/\pi$. Equation (103) appears to agree better with their measurements.

Dimensional Analysis of Forced Convection Systems

In most practical flow systems the detailed velocity field is not known. However, one can still make a dimensional analysis and write the velocity profile symbolically as

$$\mathrm{V}/v^\circ = \mathrm{V}^* \left(\frac{r}{L}, \frac{v^\circ t}{L}, N_{Re}, N_{We}, \ldots \right) \tag{104}$$

Here v° is a characteristic velocity, L is a characteristic length, and N_{Re}, N_{We}, etc., are the dimensionless groups needed to specify the flow conditions of the system.

Insertion of Equation (104) into the boundary-layer

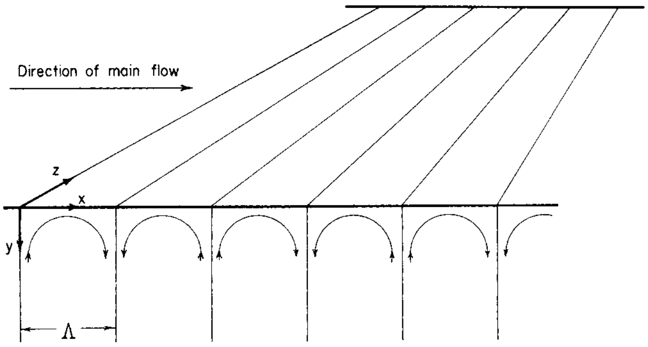

Fig. 10. Flow in an open channel with a regular pattern of eddies. The eddies move downstream with the main flow.

solutions will give the concentration and temperature profiles and the transfer coefficients. Thus, in Equation (41) we make the substitution

$$s^2(u, w, t) = L^4 f\left(u, w, \frac{v^\circ t}{L}, N_{Re}, N_{We}, \ldots \right) \quad (105)$$

Here f is a function derivable from the $\mathbf{V}^*$ function, and u and w are regarded as dimensionless coordinates. The last integral in Equation (41) then becomes

$$\sqrt{v^\circ L^3}\int_{\mathcal{R}}\int \frac{\partial}{\partial t^*}\sqrt{\int_{t_0^*(u,w)}^{t^*} f(u, w, t^{*\prime}, \ldots)dt^{*\prime}}\, dudw$$

$$= \sqrt{v^\circ L^3}\, F(t^*, N_{Re}, N_{We}, \ldots) \quad (106)$$

in which $t^* = v^\circ t/L$. The mass transfer rates for the region $\mathcal{R}$ then must satisfy

$$w_{A0} - \omega_{A0}(w_{A0} + w_{B0})$$

$$= (\omega_{A0} - \omega_{A\infty})\Pi'_\omega(0)\, \sqrt{\rho^2\, \mathcal{D}_{AB} L^3 v^\circ}\; F(t^*, N_{Re}, N_{We}, \ldots) \quad (107)$$

The surface-average Sherwood number may be defined at small mass transfer rates as

$$N_{Sh} = \left\{ \frac{w_{A0} - \omega_{A0}(w_{A0} + w_{B0})}{L^2(\omega_{A0} - \omega_{A\infty})} \right\} \frac{L}{\rho\, \mathcal{D}_{AB}} = \frac{k_{\omega m} L}{\rho\, \mathcal{D}_{AB}} \quad (108)$$

in which $k_{\omega m}$ is based on the characteristic area L^2. Then, Equation (107) can be rewritten as follows for small mass transfer rates:

$$N_{Sh}\sqrt{\frac{\mathcal{D}_{AB}}{v^\circ L}} = \frac{2}{\sqrt{\pi}}\, F(t^*, N_{Re}, N_{We}, \ldots) \quad (109)$$

For high net mass transfer rates, this result should be corrected by use of Table 2.

The function F remains to be found experimentally by measuring $N_{Sh}\sqrt{\mathcal{D}_{AB}/v^\circ L}$ as a function of $(t^*, N_{Re}, N_{We}, \ldots)$. If the system is steady or pseudo steady, then the dependence on t^* can be suppressed. Note that F does not depend on $\mathcal{D}_{AB}$; this prediction comes from the boundary-layer analysis and should be correct as long as $\mathcal{D}_{AB}$ is small enough to justify approximations 1 to 4.

Equation (109) agrees well with liquid-phase measurements in gas absorbers (*27, 30*) and in liquid-liquid extractors (*2, 42, 43*). Its suitability for the gas phase in packed towers is in doubt because of the higher diffusivities and larger velocity gradients that arise there.

Equation (109) can also be used to predict $N_{A0}^{(\mathrm{phys})}$ for the case of absorption with rapid irreversible reaction. Then, multiplication by the reaction factor Ha [see Equations (68) and (68*b*)] gives the absorption rate corrected for the reaction.

For absorption with first-order reaction, the results are not so simple. Insertion of Equation (104) into Equation (75), and reduction to dimensionless form as above, gives

$$N_{Sh}\sqrt{\frac{\mathcal{D}_{AB}}{v^\circ L}} = G\left(\frac{k_1'''L}{v^\circ}, t^*, N_{Re}, N_{We}, \ldots \right) \quad (110)$$

Here G is another integral function, obtainable experimentally by measuring the quantities on the left. The presence of a rate constant here gives rise to an additional dimensionless group, the first Damköhler number, $k_1'''L/v^\circ$. This group must be studied experimentally along with the rest, though an approximate factorization might be achieved by using the Ha function of Equation (4), with γ treated as an adjustable function of the flow conditions.

For enclosed flows, particularly in packed or staged equipment, it should be satisfactory to replace the initial composition $\omega_{A\infty}$ by the bulk composition ω_{Ab} in the given cross section, or at some reference cross section. Then, N_{Sh} can be correspondingly defined for a cross section or for a larger region of the equipment.

DISCUSSION

The results given here, and in paper I, describe two limiting cases of forced convection behavior. Systems which are steady when viewed from the interface (paper I) give $N_{Nu} \sim N_{Pr}^{1/3}$ at high N_{Pr}, whereas systems that are unsteady when so viewed (this paper) give $N_{Nu} \sim N_{Pr}^{1/2}$. Many flow systems can be classified into one or the other category, and the appropriate theory can then be applied as a means of prediction or correlation.

Both theories are formally limited, by the boundary-layer assumptions, to small approaches to equilibrium of the phases. In practice, this limitation can be moderated by the insertion of bulk conditions T_b and ω_{Ab} in place of the initial conditions used here for defining transfer coefficients. This adjustment alone will not suffice, however, for thick boundary layers or large velocity gradients; for these situations, a fuller analysis is needed.

The examples given here illustrate the importance of the surface stretch effect, through which the spreading parts of an interface are kept in proximity with fresh fluid. In systems where no new surface elements enter, as in examples 1, 2, 3, and 4, this effect is particularly important, and the penetration and surface-renewal models cannot be made to fit unless fictitious exposure times are used. The present theory explains these systems reasonably well, as confirmed by experiments (*14, 16, 18, 20, 21, 37, 39*) and is therefore to be preferred.

Better information is needed on the motions of free interfaces. Further applications of the theory will largely depend on the availability of such information. A particularly interesting possibility is the improvement of aeration rates in rivers, for which surface deformation is a decisive factor (*19*).

Applications of the present theory to falling films have been started (*3*), and extensions to variable-property systems are in progress.

ACKNOWLEDGMENT

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NOTATION

a = interfacial area per unit volume of system
a, b = stoichiometric coefficients of species A and B in the diffusion controlled reaction problem
$\mathbf{B}$ = $[\mathbf{n} \bullet \nabla \mathbf{v}]|_{y=0}$, normal component of velocity gradient at interface
B_y = y component of $\mathbf{B}$
B_{tang} = magnitude of tangential projection of $\mathbf{B}$
$\hat{C}_p$ = specific heat at constant pressure
C_ω = dimensionless mass transfer rate defined in Equation (30)
c = molar density of mixture, (moles L^{-3})
c_A, c_B = concentrations of species, (moles L^{-3})
$\mathcal{D}_{AB}$ = binary diffusivity, (L^2t^{-1})
$\sqrt{g}$ = $\sqrt{g}\,(u, w, y, t)$, function defined in Equation (2)
$\overline{H}_i$ = partial molar enthalpy of species i
Ha = Hatta number, defined in Equation (68)
h = heat transfer coefficient evaluated at $\phi_T = 0$
$h^\bullet$ = heat transfer coefficient evaluated at actual ϕ_T
$\mathbf{j}_i$ = diffusion flux of species i relative to mass average velocity, ($ML^{-2}t^{-1}$)
j_{A0} = $n_{A0} - \omega_{A0}(n_{A0} + n_{B0})$, diffusion flux of species A in y direction at the interface
$j_{A\infty}$ = $n_{A0} - \omega_{A\infty}(n_{A0} + n_{B0})$, modified diffusion flux of species A in y direction at the interface
k = thermal conductivity
k_1''' = rate constant for disappearance of species A by homogeneous first-order reaction, (t^{-1})
k_x = mass transfer coefficient evaluated at $\phi_x = 0$, (moles $L^{-2}t^{-1}$)
$k_x^\bullet$ = mass transfer coefficient evaluated at actual ϕ_x, (moles $L^{-2}t^{-1}$)
L = characteristic length in Equation (104)
L = length of laminar liquid jet, measured along a surface streamline
$L(u)$ = total length of streamline u, from its entrance into transfer region
l = distance along streamline u, from its entrance into transfer region
M_i = molecular weight of species i
N_{Re} = Reynolds number
N_{Sh} = Sherwood number at small net mass transfer rates, defined in Equation (108)
N_{We} = Weber number
N_{i0} = $c_{i0}v_{i0}$, molar flux of species i into the given phase at the interface
n_{i0} = $N_{i0}M_i$, mass flux of species i into the given phase at the interface
$\mathbf{n}$ = $\mathbf{n}(u, w, t)$, unit vector normal to interface at (u, w, t), pointing into the given phase
$O(y^2)$ = quantities proportional to the second and higher powers of y
q_0 = conductive heat flux in the y direction at the interface
R = radius of bubble, (examples 1 and 2), mass transfer zone, (example 3)
$R_s(l)$ = local radius of laminar jet or other surface of revolution, (example 4)
R_A, R_B = molar rates of production of species A and B by homogeneous chemical reaction, (moles $L^{-3}t^{-1}$)
r = radial coordinate in cylindrical or spherical coordinates
r_A, r_B = mass rates of production of species A and B by homogeneous chemical reaction, ($ML^{-3}t^{-1}$)
R_T, R_x, R_ω = flux ratios. [see *Equation* (38) and Tables 1 and 2]
$\mathcal{R}$ = $\mathcal{R}(u, w, t)$, interfacial region of interest
$\mathbf{r}$ = position vector, (see Figure 2)
$\mathbf{r}_s$ = position vector of a surface element
S = $S(t)$, instantaneous area of region $\mathcal{R}$
S_D = instantaneous boundary surface of domain D, (Appendix A)
$d\mathbf{S}_D$ = vector of magnitude dS_D, directed normally outward from S_D
s = $s(u, w, t)$, area function given in Equations (4) and (5)
$\mathcal{S}$ = source terms to be added to Equation (8) to obtain the energy equation for mixtures, (Equation F, p. 562, reference *22*)
T = temperature
T_0 = temperature at $y = 0$
$\overline{T}_0$ = mean value of T_0 for the net material being transferred to the given phase at $\mathcal{R}$
T_∞ = temperature at $y >> \delta_T$
t = time
t^* = $v^\circ t/L$, dimensionless time in example 6
t_a = time of arrival of given interfacial element at a reference point in externally steady motion
$t_0(u, w)$ = time when diffusion or heat transfer begins alongside surface element, (u, w)
t_1, t' = dummy variables of integration
u, w = imbedded coordinates of nearest surface element
$\mathbf{V}$ = mass average velocity of fluid relative to external coordinates
$\mathbf{V}_s$ = $\mathbf{V}_s(u, w, t)$, velocity of surface element (u, w) at time t, relative to external coordinates
V_s = magnitude of $\mathbf{V}_s$
$V_{\max}$ = maximum surface velocity in examples 2 and 5
$d\mathcal{V}$ = volume element in Equation (2) and Figure 1
dV = volume element in Equation (53), large compared with boundary-layer dimensions
$\mathbf{v}_i$ = velocity of species i relative to coordinates u, w, y
$\mathbf{v}$ = $\Sigma_i\omega_i\mathbf{v}_i$, mass average velocity of fluid relative to coordinates u, w, y
$\mathbf{v}^*$ = $\Sigma_i x_i\mathbf{v}_i$, molar average velocity of fluid relative to coordinates u, w, y
v_{i0} = y component of $\mathbf{v}_i$ at $y = 0$
v_0 = y component of $\mathbf{v}$ at $y = 0$
$v_0^\star$ = y component of $\mathbf{v}^*$ at $y = 0$
v° = characteristic velocity in Equation (104)
$\sqrt{\overline{v_x'^2}}$ = root-mean-square fluctuation of surface velocity in x direction, measured by a stationary observer
$\mathcal{W}_{i0}$ = molar transfer rate of species i into the given phase
w_{i0} = $\mathcal{W}_{i0}M_i$, mass transfer rate of species i into the given phase
x, z = rectangular coordinates on surface of large eddy
x_i = mole fraction of species i
x_{i0} = mole fraction of species i at $y = 0$
$x_{i\infty}$ = mole fraction of species i at $y >> \delta_x$
y = distance from nearest interfacial element
y_R = local depth of zone occupied by A in absorption with diffusion controlled reaction (see Figure 5)
y_1 = dummy variable of integration

Greek Letters

α = $k/\rho\,\hat{C}_p$, thermal diffusivity
γ = V_s/l in example 3
$\delta_T, \delta_x, \delta_\omega$ = characteristic boundary-layer thicknesses, [see Equation (31) and Table 2]
$\eta_T, \eta_x, \eta_\omega$ = dimensionless boundary-layer coordinates, [see Equation (32) and Table 2]. For definitions in

Equations (79) and (80), see text.

$\theta_T, \theta_x, \theta_\omega$ = correction factors for rapid mass transfer, (see Tables 1 and 2)

θ = angle in cylindrical and spherical coordinates, (examples 1, 2, 3, 4)

Λ = eddy width in example 5

Π_T, Π_x, Π_ω = dimensionless profiles of temperature and composition, [see Equation (24) and Table 2]

$\Pi'(0)$ = $d\Pi/d\eta|_{\eta=0}$, dimensionless gradient of temperature or composition at interface [see Equation (35) and Table 1]

ρ = mass density, (ML^{-3})

$\phi_T, \phi_x, \phi_\omega$ = dimensionless material fluxes, [see Equation (39) and Tables 1 and 2]

ϕ = azimuthal angle in spherical coordinates, (examples 1 and 2)

τ = $\int_{t_0(u,w)}^{t} s^2(u, w, t')dt'$, modified time coordinate

Υ = $ys(u, w, t)$, modified y coordinate

ω_i = mass fraction of species i

ω_{i0} = mass fraction of species i at $y = 0$

$\omega_{i\infty}$ = mass fraction of species i at $y >> \delta_\omega$

Mathematical Operations

$$D/Dt = (\partial/\partial t)_{\mathrm{r}} + (\mathbf{V} \bullet \nabla)$$

$$= (\partial/\partial t)_{u,w,y} + (\mathbf{v} \bullet \nabla)$$

$$\operatorname{erf} x = \frac{2}{\sqrt{\pi}} \int_0^x e^{-z^2}\, dz$$

$$\operatorname{erfc} x = 1 - \operatorname{erf} x$$

$$\exp x = e^x$$

$$\Gamma(x) = \int_0^\infty e^{-z}\, z^{x-1} dz = \text{gamma function of } x$$

LITERATURE CITED

1. Stewart, W. E., *AIChE J.*, **9**, 528 (1963).
2. Angelo, J. B., E. N. Lightfoot, and D. W. Howard, *ibid.*, **12**, 751 (1966).
3. Howard, D. W., and E. N. Lightfoot, *ibid.*, **14**, 458 (1968).
4. Higbie, Ralph, *Trans. Am. Inst. Chem. Engrs.*, **31**, 365 (1935).
5. Danckwerts, P. V., *Ind. Eng. Chem.*, **43**, 1460 (1951).
6. Ilkovic, D., *Coll. Czech. Chem. Commun.*, **6**, 498 (1934).
7. MacGillavry, D., and E. K. Rideal, *Rec. Trav. Chim.*, **56**, 1013 (1937).
8. Levich, V. G., "Physicochemical Hydrodynamics," Chapt. VIII, Prentice-Hall, Englewood Cliffs, N. J. (1962).
9. Cullen, E. J., and J. F. Davidson, *Trans. Faraday Soc.*, **53**, 113 (1957).
10. —————, *Trans. Inst. Chem. Engrs.*, **35**, 51 (1957).
11. Scriven, L. E., and R. L. Pigford, *AIChE J.*, **5**, 397 (1959).
12. Baird, M. H. I., and A. E. Hamielec, *Can. J. Chem. Eng.*, **40**, 119 (1962).
13. Beek, W. J., and R. Kramers, *Chem. Eng. Sci.*, **16**, 909 (1962).
14. Popovich, A. T., R. E. Jervis, and O. Trass, *ibid.*, **19**, 357 (1964).
15. Lochiel, A. C., and P. H. Calderbank, *ibid.*, 471.
16. Redfield, J. A., and G. Houghton, *ibid.*, **20**, 131 (1965).
17. Ruckenstein, Eli, and C. P. Berbente, *Chem. Eng. Sci.*, **20**, 795 (1965); *AIChE J.*, 13, 1205 (1967); Ruckenstein, Eli, *Chem. Eng. Sci.*, **23**, 363 (1968).
18. Winnikow, S., *Chem. Eng. Sci.*, **22**, 477 (1967).
19. Fortescue, G. E., and J. R. A. Pearson, *ibid.*, 1163.
20. Cheh, H. Y., and C. W. Tobias, *Ind. Eng, Chem. Fundamentals*, 7, 48 (1968).
21. Duda, J. L., and J. S. Vrentas, *AIChE J.*, 14, 286 (1968).
22. Bird, R. B., W. E. Stewart, and E. N. Lightfoot, "Transport Phenomena," Wiley, New York (1960).
23. Sternling, C. V., and L. E. Scriven, *AIChE J.*, **5**, 514 (1959).
24. Wills, A. P., "Vector Analysis," p. 175, Dover, New York (1958).
25. Arnold, J. H., *Trans. Am. Inst. Chem. Engrs.*, **40**, 361 (1944).
26. Danckwerts, P. V., *Trans. Faraday Soc.*, **46**, 300 (1950).
27. Sherwood, T. K., and R. L. Pigford, "Absorption and Extraction," 2 ed., Chapt. VIII, IX, McGraw-Hill, New York (1952).
28. Lightfoot, E. N., *Chem. Eng. Sci.*, **17**, 1007 (1962).
29. Hatta, S., *Tech. Repts. Tôhoku Imp. Univ.*, **8**, 1 (1928-1929).
30. Onda, K., E. Sada, and H. Takeuchi, *J. Chem. Eng. Japan*, 1, 62 (1968).
31. Koutecky, J., *Czech. J. Phys.*, **2**, 50 (1953).
32. Kolthoff I. M., and K. Izutsu, *J. Am. Chem. Soc.*, **86**, 1275 (1964).
33. Rybczynski, W., *Bull. Acad. Sci. Cracov.*, **1**, 40 (1911).
34. Hadamard, J., *C. R. Acad. Sci. Paris*, **152**, 1735 (1911).
35. Griffith, R. M., *Chem. Eng. Sci.*, **12**, 198 (1960).
36. Bowman, C. W., D. M. Ward, A. I. Johnson, and O. Trass, *Can. J. Chem. Eng.*, **39**, 9 (1961).
37. Ward, D. M., O. Trass, and A. I. Johnson, *ibid.*, **40**, 164 (1962).
38. Taunton, J. W., and E. N. Lightfoot, *Intern. J. Heat Mass Transfer*, **12**, 1718 (1969).
39. Hammerton, D., and F. H. Garner, *Trans. Inst. Chem. Engrs.*, **32**, 518 (1954).
40. Chan, W. C., Ph.D. thesis, Univ. Minn., Minneapolis (1964); University Microfilms 65-7325, 281 pp. See citation by B. A. Finlayson and L. E. Scriven, *Chem. Eng. Sci.*, **20**, 395 (1965).
41. Duda, J. L., and J. S. Vrentas, *Chem. Eng. Sci.*, **22**, 855 (1967).
42. Rose, P. M., and R. C. Kintner, *AIChE J.*, **12**, 530 (1966).
43. Angelo, J. B., and E. N. Lightfoot, *ibid.*, **14**, 531 (1968).

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APPENDIX A

Equation (7) may be derived as follows. Consider a closed domain $D(u, w, y)$ and integrate Equation (6) over the surface of D:

$$\int_{S_D}\int (\mathbf{V} \cdot d\mathbf{S}_D) = \int_{S_D}\int (\mathbf{v} \cdot d\mathbf{S}_D) + \int_{S_D}\int \left(\left(\frac{\partial \mathbf{r}}{\partial t} \right)_{u,w,y} \cdot d\mathbf{S}_D \right) \quad \text{(A1)}$$

Now, the integrand of the last term is the velocity of the boundary element $d\mathbf{S}_D$; hence, the integral is the rate of change of the volume of D. This term may be rewritten with the aid of Equation (2):

$$\int_{S_D}\int \left(\left(\frac{\partial \mathbf{r}}{\partial t} \right)_{u,w,y} \cdot d\mathbf{S}_D \right) = \frac{d}{dt} \int\int_D\int \sqrt{\mathrm{g}}\, du dw dy = \int_D\int\int \frac{\partial \sqrt{\mathrm{g}}}{\partial t}\, du dw dy \quad \text{(A2)}$$

The second equality is obtained by Leibnitz' rule, noting that the limits of u, w, and y here are constant. Making this substitution in Equation (A1), and using Gauss' theorem, one obtains

$$\int\int_D\int (\nabla \cdot \mathbf{V}) \sqrt{\mathrm{g}}\, du dw dy = \int\int_D\int (\nabla \cdot \mathbf{v}) \sqrt{\mathrm{g}}\, du dw dy + \int\int_D\int \frac{\partial \sqrt{\mathrm{g}}}{\partial t}\, du dw dy \quad \text{(A3)}$$

or

$$\int\int_D\int \left[(\nabla \cdot \mathbf{V}) - (\nabla \cdot \mathbf{v}) - \frac{1}{\sqrt{\mathrm{g}}} \frac{\partial \sqrt{\mathrm{g}}}{\partial t} \right] \sqrt{\mathrm{g}}\, du dw dy = 0 \quad \text{(A4)}$$

Since the choice of the region D is arbitrary, the integrand must be zero everywhere. This gives Equation (7)