planning experiments in order to estimate the parameter values of a nonlinear model.

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NOTATION

A = reactant nitric oxide
B = reactant hydrogen
$\mathbf{G}$ = matrix of partial derivatives defined by Equations (3) and (6)
g_{iu} = partial derivative of a function g with respect to the parameter K_i evaluated at the u^{th} set of experimental conditions and some set of parameter values $\mathbf{K}_o$
K_i = parameter defined by Equation (4), $i = 1, 2,$ or 3
K_j = equilibrium adsorption constant for component j, atm.$^{-1}$
$\hat{K}_j$ = best estimate of parameter K_j
K_{jo} = estimate of parameter K_j
k = forward rate constant, g.-moles/(min.)(g.-catalyst)
N = number of observations
m = total number of independent variables required in a model
p = number of parameters in a model
p_i = partial pressure of component i, atm.
R = product water
r = reaction rate, g.-moles/(min.)(g.-catalyst)
S = product nitrogen
T = absolute temperature, °K.
x_i = independent variable
$\bar{x}_i$ = arithmetic mean of a set of independent variables x_i

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Mechanism of Dispersed-Phase Mass Transfer in Viscous, Single-Drop Extraction Systems

L. E. JOHNS, JR., and R. B. BECKMANN

Carnegie Institute of Technology, Pittsburgh, Pennsylvania

The theory of solute extraction in viscous single-drop systems is extended to show (1) the dependence of the asymptotic Nusselt number on the Peclet number from $N_{Pe} = 0$, the molecular diffusion limit, to $N_{Pe} = \infty$, the Kronig and Brink limit, and (2) the dependence of the diffusion entry region Nusselt number on the Peclet number and the initial concentration profile.

A numerical solution of the diffusion equation, limited to dilute solute concentrations and solute transport by viscous convection and molecular diffusion, is presented from which the nature of the Nusselt number is deduced. The observed oscillatory behavior of the Nusselt number in the diffusion entry region, as $N_{Pe} \to \infty$, is given a simple physical interpretation in terms of the circulation period of the drop liquid.

The model is based upon the Hadamard stream function which theoretically is limited to creeping flow; however some experimental evidence indicates that flow fields similar to the Hadamard stream function exist at continuous phase Reynolds numbers of the order of ten.

It is customary to analyze and correlate the results of single-drop extraction experiments in terms of mathematical models. For example, experiments with viscous drops normally are related to either the stagnant-drop model, at the extreme of vanishing circulation or to the Kronig and Brink (*10*) model at the opposite extreme; whereas experiments with turbulent drops frequently are related to the Handlos and Baron model (*15*).

This paper presents the solution to a viscous flow model which reduces to the stagnant-drop and the Kronig and Brink models in the respective limits, that is, $N_{Pe} = 0$ and $N_{Pe} \to \infty$, and complements these models on the interval $0 < N_{Pe} < \infty$. A mathematical formulation of the model will be given after a brief summary of the problem and a presentation of the major assumptions.

L. E. Johns, Jr., is with Dow Chemical Company, Midland, Michigan. R. B. Beckmann is with the University of Maryland, College Park, Maryland.

Following the convention of Licht and Conway (*12*), three zones of mass transfer are distinguished in the extraction of a solute from a single drop rising through solvent medium: (1) the zone in which the drop forms and accelerates to its terminal velocity, the fluid dynamic entry region; (2) the zone in which the drop travels at its terminal translational velocity; and (3) the zone in which the drop enters the liquid-liquid interface and coalesces.

A force acting at a liquid-drop surface produces the following flow fields within the drop: the tangential component causes a vortexlike flow pattern, referred to as a circulation current, and the normal component causes a deformation from the spherical shape and oscillations about a pseudo ellipsoidal equilibrium shape.

The viscous flow region is characterized by the dominance of the circulatory component of the flow field. In the limit, when the terms quadratic in velocity are negligible, Hadamard (*5*) solved the linearized equations of motion for the dispersed phase and continuous phase stream functions. Recent experimental studies by Heertjes (*7*) and Garner (*3, 4*) indicate that the circulation patterns exhibited by some liquids drops for N'_{Re} (continuous phase Reynolds number) in the neighborhood of 10 are similar to those predicted by Hadamard's analytical stream function. Hadamard's solution assumes a spherical drop shape and neglects the surface force contribution to the stress boundary conditions. Rayleigh (*13*) has shown that the change in drop shape accompanying a translation is of a higher order of smallness than the inertia terms, so that Hadamard's assumption of a spherical shape is consistent with the linearized equations of motion.

In a system of spherical coordinates (r, θ, ϕ), with the origin at the center of the drop, the Hadamard stream function ψ is given by

$$\psi = \frac{1}{2} K \left(1 - \frac{r^2}{a^2} \right) r^2 \sin^2 \theta \quad r \leqq a \tag{1}$$

where

$$K = \frac{1}{2} \left(\frac{\mu'}{\mu + \mu'} \right) U = \frac{1}{3} g \, \Delta\rho \, a^2 \frac{1}{3\mu + 2\mu'} \tag{2}$$

for an incompressible, viscous drop in an infinite continuous phase. The components of the velocity vector derived from ψ for the axially symmetric flow are

$$V_r = -K \left(1 - \frac{r^2}{a^2} \right) \cos \theta \tag{3a}$$

$$V_\theta = K \left(1 - \frac{2r^2}{a^2} \right) \sin \theta \tag{3b}$$

and

$$V_\phi = 0 \tag{3c}$$

To check Equation (1), Spells (*14*) photographed the striae in glycerine–water drops dispersed in castor oil and measured the distance between the vortex ring and the drop center. The values found were *0.69a* and *0.72a*, whereas Equation (1) would predict a value of *0.71a*. Hamielec and Johnson (*6*) presented an approximate series solution to the equations of motion, including both inertia and viscous terms and pointed out that the region of approximate validity of Equation (1) depends upon N'_{Re} and the viscosity ratio $\frac{\mu}{\mu'}$.

In reference *10* a convenient coordinate transformation is introduced as follows:

$$\xi = 4R^2(1 - R^2) \sin^2 \theta = 8\psi / K a^2 \tag{4a}$$

$$\zeta = R^4 \cos^4 \theta / (2R^2 - 1) \tag{4b}$$

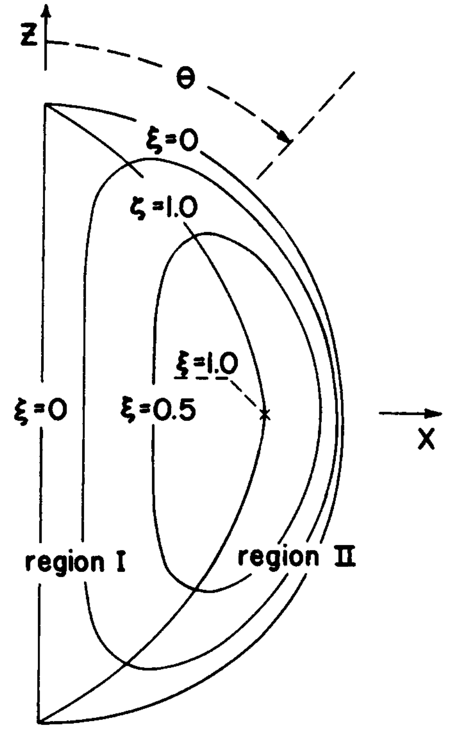

Fig. 1. Hadamard's dispersed phase stream function, Equation (1).

$$\phi = \phi \tag{4d}$$

where

$$R = r/a$$

In particular, the curve $\zeta = 1$, shown in Figure 1, divides the drop into two regions: the drop interior region or region I and the drop surface region, or region II. The functions t_c and t_{cI} are defined as follows and are evaluated in references *10* and *8*:

t_c = the time required to traverse the closed curve, ξ = constant. $t_c = t_{cI} + t_{cII}$

t_{cI} = the time required to traverse the portion of the closed curve, ξ = constant, which lies in region I.

SOLUTE TRANSFER

The solute flux at a point in a drop is the sum of two contributions: the flux of the solute relative to the mass average velocity (the molecular diffusion flux defined by Fick's first law) and the convective flux accompanying the mass average velocity.

For a binary system consisting of a solvent and a single solute, the solute concentration profiles are part of the solution of the equations of motion and continuity which relate ρ_1, ρ, and $\mathbf{V}$. In the limiting case of dilute solution however, the drop properties are independent of ρ_1, and $\mathbf{V}$ and ρ are given approximately by $\mathbf{V}_{20}$ [Equation (3)] and ρ_{20}, that is, the flow and diffusion problems, are uncoupled in the limit of dilute solute concentrations.

The equation of continuity applied to species *i*, in mass units, and referred to the center of the drop is given by

$$\frac{\partial \rho_i}{\partial t} + \nabla \cdot \mathbf{n}_i = 0 \tag{5a}$$

where

$$\mathbf{n}_i = -\rho D_{12} \nabla \frac{\rho_i}{\rho} + \frac{\mathbf{n}}{\rho} \rho_i \tag{5b}$$

or, in the limit of a dilute solute and a fluid dynamic entry region much shorter than the diffusion entry region, Equation $(5b)$ becomes

$$\mathbf{n}_1 = -\rho_{20} D_{120} \nabla \frac{\rho_1}{\rho_{20}} + \frac{\mathbf{n}_1 + \mathbf{n}_2}{\rho_{20}} \rho_1$$

or

$$\mathbf{n}_1 \left(1 - \frac{\rho_1}{\rho_{20}}\right) = -D \nabla \rho_1 + \mathbf{V}_{20} \rho_1$$

or

$$\mathbf{n}_1 = -D \nabla \rho_1 + \mathbf{V}_{20} \rho_1$$

which, when substituted into Equation $(5a)$ gives

$$\frac{\partial \rho_1}{\partial t} = D \nabla^2 \rho_1 - \mathbf{V}_{20} \nabla \rho_1 \tag{6a}$$

The boundary and initial conditions follow from the assumptions of equilibrium at the phase boundary, ρ_1', which is independent of position, time $(D' >> D)$, and axial symmetry and are given by

$$\rho_1(a, \theta, t) = m \rho_1' = \rho_1^* \tag{6b}$$

and

$$\rho_1(r, \theta, 0) = \rho_{10}(r, \theta) \tag{6c}$$

In terms of the dimensionless variables

$$\tau = Dt/a^2 \tag{7a}$$

$$R = r/a \tag{4d}$$

and

$$C(R, \theta, \tau) = \frac{\rho_1(r, \theta, t) - \rho_1^*}{\rho_{10} - \overline{\rho_1}^*} \tag{7b}$$

Equation (6) becomes

$$\frac{\partial C}{\partial \tau} = \frac{1}{R^2} \frac{\partial}{\partial R}\left(R^2 \frac{\partial C}{\partial R}\right) + \frac{1}{R^2 \sin\theta} \frac{\partial}{\partial \theta}\left(\sin\theta \frac{\partial C}{\partial \theta}\right) +$$

$$N_{Pe}\left[(1 - R^2)\cos\theta \frac{\partial C}{\partial R} + \frac{2R^2 - 1}{R} \sin\theta \frac{\partial C}{\partial \theta}\right] \tag{8a}$$

$$\begin{gathered} C(1, \theta, \tau) = 0 \\ C(R, \theta, 0) = C_o(R, \theta) = \frac{\rho_{10}(r, \theta) - \rho_1^*}{\overline{\rho_{10}} - \rho_1^*} \end{gathered} \tag{8b}$$

where

$$\overline{\rho_1}(t) = \frac{1}{V} \int_V \rho_1(r, \theta, t)\, dV$$

and

$$N_{Pe} = \left(\frac{\mu'}{\mu + \mu'}\right) (N'_{Pe}/4) \tag{9}$$

$$N'_{Pe} = d\,U/D$$

THE MASS TRANSFER COEFFICIENT

The mass transfer coefficient k and the surface average flux $\overline{Q}$ are defined by an instantaneous material balance equation:

$$kA(\overline{\rho_1} - \rho_1^*) = -V \frac{d\overline{\rho_1}}{dt} = \overline{Q}A \tag{10a}$$

so that

$$k = -\frac{a}{3} \frac{d\overline{\rho_1}}{dt} / (\overline{\rho_1} - \rho_1^*) \tag{10b}$$

and

$$Q = -\frac{a}{3} \frac{d\overline{\rho_1}}{dt} \tag{10c}$$

The time average mass transfer coefficient $\overline{k}$ is defined over the time interval (o, t) by

$$\overline{k}A(\overline{\Delta\rho})t = -V \int_o^t \frac{d\overline{\rho_1}}{dt}\, dt = -V(\overline{\rho_1} - \overline{\rho_{10}}) \tag{11a}$$

or

$$\overline{k} = k_{LM} = \frac{-V(\overline{\rho_1} - \rho_{10})}{A(\Delta\rho)_{LM} t} = \frac{1}{t} \int_o^t k dt$$

$$= -\frac{a}{3t} LN \frac{\overline{\rho_1} - \rho_1^*}{\overline{\rho_{10}} - \rho_1^*} \tag{11b}$$

In terms of dimensionless parameters τ, $\overline{c}$, $N_{Nu} = \dfrac{kd}{D}$ and $\overline{N} = \dfrac{d\overline{Q}}{D(\overline{\rho_{10}} - \rho_1^*)}$, the preceding equations are given by

$$N_{Nu} = -(2/3\overline{C})\ (d\overline{C}/d\tau) \tag{12a}$$

$$\overline{N}_{Nu} = -(2/3\tau) \ln \overline{C} \tag{12b}$$

$$\overline{N}_{Nu\infty} = \lim_{\tau \to \infty} \overline{N}_{Nu}(\tau) \tag{12c}$$

and

$$\overline{N} = (2/3)\, d\overline{C}/d\tau \tag{12d}$$

so that N_{Nu}, $\overline{N}_{Nu}$, and $\overline{N}$ follow directly from the solution of Equation (8).

A common feature of penetration types of problems, for example, the analogous Graetz problem, is a time-dependent Nusselt number during the period of profile development. If at time $t = 0$ an arbitrary solute concentration profile is imposed on a drop, then during the period $0 < t < \infty$ the normalized concentration profile adjusts from the given initial state to a final state, the asymptotic profile, which depends upon the nature of the condition imposed at the drop boundary during the transition period, for example, $\rho_1(a, \theta, t) = \rho_1^*$, $0 < t < \infty$ in the absence of continuous phase resistance. The point Nusselt number is proportional to the normalized rate of extraction per unit of driving force at time t; thus is quite sensitive, particularly at time slightly greater than zero, to the relation between the initial profile and the boundary condition. In fact a negative Nusselt number easily could be arranged over a short time interval near $t = 0$. Nonetheless, the Nusselt number approaches a limiting value, denoted by $N_{Nu\infty}$, dependent on the boundary condition but independent of the initial condition, in conjunction with the approach of the normalized concentration profile to a limiting shape.

A summary of the principal assumptions is presented in Table 1 as a guide in the application of the model to specific cases. The assumptions listed are similar to those underlying the Kronig and Brink model *(10)*, except that the limitation $N_{Pe} \to \infty$ is relaxed.

TABLE 1. LIST OF ASSUMPTIONS

1. The drop is a dilute binary mixture; that is

$$\rho = \rho_1 + \rho_2 = \rho_{02}$$
$$\mathbf{V} = \mathbf{V}_{20}$$

so that the flow and diffusion equations are uncoupled.

2. The drop is a viscous sphere in linear or creeping motion; that is, the Hadamard stream function gives the solution of the equations of motion independent of time.
3. The continuous phase resistance to solute diffusion is negligible and the system is in equilibrium at the phase boundary; that is

$$\rho_1^{(a,\theta,t)} = \rho_1^*$$

where ρ_1^* and ρ_1' are corresponding phase equilibrium compositions.

The solutions of the limiting model equations, the stagnant drop equation, $N_{Pe} = 0$, and the Kronig and Brink equation, $N_{Pe} \to \infty$, are found by the use of the classical method of separation of variables (see reference *10* for specific details relating to the latter model). Therefore the form of solution of Equation (8) given by the separation of variables method is shown, although a numerical method of solution must be introduced at some later stage. The substitution of $C(R, \theta, \tau) = c(R, \theta)T(\tau)$ into Equation (8) gives the following eigenvalue problem.

$$\frac{1}{R^2}\frac{\partial}{\partial R}\left(R^2\frac{\partial c}{\partial R}\right) + \frac{1}{R^2 \sin\theta}\frac{\partial}{\partial \theta}\left(\sin\theta\frac{\partial c}{\partial \theta}\right) + N_{Pe}\left[(1 - R^2)\cos\theta\frac{\partial c}{\partial R} + \frac{2R^2 - 1}{R}\sin\theta\frac{\partial c}{\partial \theta}\right] + \gamma c = 0 \tag{13a}$$

$$c(1, \theta) = 0 \tag{13b}$$

$$T = e^{-\gamma\tau} \tag{14}$$

The general solution of Equation (8) is then given by

$$C(R, \theta, \tau) = \sum_{n=1}^{\infty} a_n\, c_n(R, \theta) e^{-\gamma_n\tau} \tag{15}$$

where $c_i(R, \theta)$ and γ_i satisfy Equations (13*a*) and (13*b*). As a result

$$\overline{C}(\tau) = \sum_{n=1}^{\infty} a_n\, \overline{c}_n\, e^{-\gamma_n\tau} \tag{16}$$

and from Equations (12) and (17)

$$N_{Nu} = \frac{2}{3}\gamma_1\frac{1 + (a_2/a_1)(\gamma_2/\gamma_1)e^{-(\gamma_2-\gamma_1)\tau} + \ldots}{1 + (a_2/a_1)e^{-(\gamma_2-\gamma_1)\tau} + \ldots} \tag{17}$$

and $N_{Nu\infty} = \frac{2}{3}\gamma_1$. The values of γ_1 in the limiting cases are $N_{Pe} = 0$: $\gamma_1 = 9.870$, $N_{Pe} \to \infty$: $\gamma_1 = 26.848$.

From Equation (17) $N_{Nu}(\tau)$ depends upon the set of constants a_i defined by the expansion

$$C_o(R, \theta) = \sum_{n=1}^{\infty} a_n\, c_n(R, \theta) \tag{18}$$

in particular if $C_o(R, \theta)$ is proportional to $c_1(R, \theta)$ then $a_1 \neq 0$, $a_2 = \ldots = 0$ and

$$\overline{C}(\tau) = a_1\, \overline{c}_1\, e^{-\gamma_1\tau} = e^{-\gamma_1\tau} \tag{19a}$$

and

$$N_{Nu}(\tau) = \frac{2}{3}\gamma_1 \tag{19b}$$

The first half-life, $t_{1/2} = \frac{a^2\tau_{1/2}}{D}$, of the solute is the time required for the average solute concentration to fall half the difference between the initial average value and the equilibrium value and depends on the initial solute concentration profile. In particular if $C_o(R, \theta) = a_1c_1(R, \theta)$ then $\overline{C}(\tau_{1/2}) = \frac{1}{2} = e^{-\gamma_1\tau_{1/2}}$ so that

$$\tau_{1/2} = \ln(2)/\gamma_1 \tag{20}$$

THE METHOD OF SOLUTION

A transformation from polar (R, θ) coordinates to rectangular (x, y) coordinates is introduced prior to the numerical solution of Equation (8), even though the curved boundary is awkward to deal with in rectangular coordinates. The transformation is given by

$$x = R\sin\theta$$

$$y = R\cos\theta$$

and thus Equation (8) becomes

$$\frac{\partial C}{\partial \tau} = \frac{\partial^2 C}{\partial x^2} + \frac{1}{x}\frac{\partial C}{\partial x} + \frac{\partial^2 C}{\partial y^2} + N_{Pe}\left(xy\frac{\partial C}{\partial x} + (1 - 2x^2 - y^2)\frac{\partial C}{\partial y}\right) \tag{21}$$

$$C(x, \pm\sqrt{1 - x^2}, \tau) = 0$$

$$C(x, y, 0) = C_o(x, y)$$

The explicit difference analog of Equation (21) for $0 < x < 1$, and $x^2 + y^2 < 1$ is given by

$$U_{ij}^{K+1} = \left[R + \left(\frac{1}{x_i} + N_{Pe}\, x_i y_j\right)\frac{1}{2}R\,\Delta X\right]U^K{}_{i+1,\,j} + \left[R - \left(\frac{1}{x_i} + N_{Pe}\, x_i y_i\right)\frac{1}{2}R\Delta X\right]U^K{}_{i-1,\,j} + \left[R + N_{Pe}\,(1 - 2x_i{}^2 - y_j{}^2)\frac{1}{2}R\Delta X\right]U^K{}_{i,\,j+1} + \left[R - N_{Pe}\,(1 - 2x_i{}^2 - y_j{}^2)\frac{1}{2}R\Delta X\right] U^K{}_{i,\,j-1} + (1 - 4R)\, U^K{}_{i,\,j} \tag{22}$$

where

$$R = \Delta\tau/\Delta x^2; \quad M\Delta x = 1$$

$$x_i = i\Delta x; \quad i = 1, \ldots, M$$

$$y_j = j\Delta x; \quad j = -(\sqrt{M^2 - i^2}, \ldots, +(\sqrt{M^2 - i^2}$$

$$\tau_K = K\Delta\tau; \quad K = 0, \ldots\ldots$$

and

$$U^K{}_{i,\,j} = U(x_i, y_j, \tau_K)$$

It is convenient to consider the ordered set of quantities

$$U^K{}_{ij},\ i = 0, \ldots, M;\ j = -(\sqrt{M_i{}^2 - i^2}), \ldots, +(\sqrt{M_i{}^2 - i^2})$$

as the components of a vector denoted by $\mathbf{U}^K = (U_1{}^K, \ldots\ldots U_Q{}^K)$ so that Equation (22) and the counterpart equations at the points along the axis $x = 0$, $-1 < y < 1$ and in the neighborhood of the boundary $x^2 + y^2 = 1$ can be written in the form

$$\mathbf{U}^{K+1} = A\mathbf{U}^K \qquad K = 0, \ldots\ldots\ldots \tag{23}$$

where A is the matrix of coefficients. For example, the q^{th} row of A, A_{qn}, $n = 1, \ldots\ldots, Q$ is given by

$$A_{qn} = 0 \quad n = 1, \ldots, Q \quad n \neq p, q - 1, q, q + 1, s$$

$$A_{qp} = R - N_{Pe}\,(1 - 2x_i{}^2 - y_j{}^2)\frac{1}{2}R\Delta X$$

$$A_{qq-1} = R - \left(\frac{1}{x_i} + N_{Pe}\, x_i y_j\right)\frac{1}{2}R\Delta X$$

$$A_{qq} = 1 - 4R$$

$$A_{qq+1} = R + \left(\frac{1}{x_i} + N_{Pe}\, x_i y_j\right)\frac{1}{2}R\Delta X$$

and

$$A_{qs} = R + N_{Pe}\,(1 - 2x_i{}^2 - y_j{}^2)\frac{1}{2}R\Delta X$$

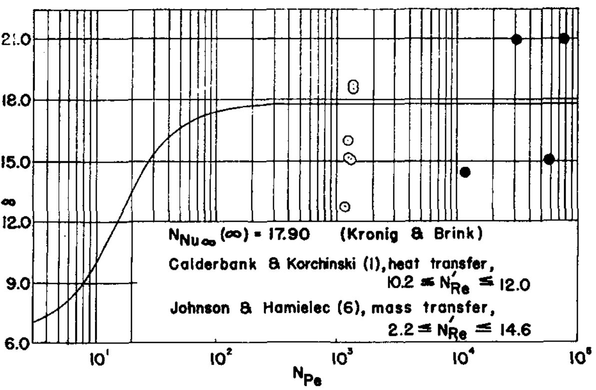

Fig. 2. Asymptotic Nusselt number.

when

$$i > 0,\ |j| < |\sqrt{M_i^2 - i^2}|$$

and when the points $(i, j-1)$, $(i-1, j)$, (i, j) $(i+1, j)$, and $(i, j+1)$ are numbered p, $q-1$, q, $q+1$, and s.

The question of the stability of Equation (23) and the related question of the convergence of $\mathbf{U}^K$ to $\mathbf{C}(\tau_K)$ as Δx approaches zero at constant values of τ_K, R, and N_{Pe}, together with other relevant issues such as the round-off error in the numerical calculation of $\mathbf{U}$, are answered theoretically and numerically in reference *8*.

RESULTS

The asymptotic Nusselt number and selected asymptotic concentration profiles are shown in Figures 2 and 3. The dilute region in the neighborhood of the axis $\theta = 0$ results from the counterclockwise flow about the point $R = \frac{\sqrt{2}}{2}$, $\theta = \frac{\pi}{2}$ and the boundary condition $C(1, \theta, \tau) = 0$. The profile shown in Figure 3g represents the Kronig and Brink assumption, $C \rightarrow C(\xi, \tau)$ as $\tau \rightarrow \infty$ and $N_{Pe} \rightarrow \infty$, and provides a logical limit to the sequence of profiles shown in Figure 3. Qualitatively, the asymptotic Nusselt number satisfies two independent conditions:

(1) $N_{Nu} \rightarrow 17.90$ (Kronig and Brink limit) as $N_{Pe} \rightarrow \infty$

(2) $N_{Nu} = 6.56$ (Stagnant drop limit) at $N_{Pe} = 0$

The asymptotic Nusselt number also satisfies the form of Peclet number dependence prescribed by the perturbation analysis of Kronig, Van Der Veen, and Ijzerman (*11*) for small Peclet numbers. Selected values of the solute half-life are given in Table 2 for $C_o = a_1c_1$ and $C_o = 1$.

The Nusselt number, the surface average flux, and the volumetric average concentration are shown in Figures 4 to 7 for $C_o = 1$ at parametric values of the Peclet number. The nature of these functions in the diffusion entry region is sensitive to C_o; for example, if $C_o = a_1c_1$, then

$$N_{Nu} = \overline{N}/\overline{C} = \frac{2}{3}\gamma_1,\ \overline{N} = \frac{2}{3}\,\frac{d\overline{C}}{d\tau} = \frac{2}{3}\gamma_1 \exp(-\gamma_1\tau) \text{ and } \overline{C} = \exp(-\gamma_1\tau)$$

Carslaw and Jaeger (*2*) give the analytical solution to Equation (8) for $C_o = 1$, $C(1, \theta, \tau) = 0$, and $N_{Pe} = 0$.

TABLE 2. SOLUTE HALF-LIFE

$C_o = a_1/c_1$		$C_o = 1.0$
N_{Pe}	$\tau_{1/2}$	$\tau_{1/2}$
0	0.0704	0.0307
5	0.0603	0.0306
10	0.0462	0.0304
20	0.0339	0.0296
40	0.0284	0.0274
80	0.0266	0.0231
800	0.0258	

DISCUSSION

The problem of viscous single-drop extraction is similar to the classical Graetz-Nusselt problem in that both are examples of transient, forced convection, transport problems limited to constant fluid properties and a laminar flow dependent on mechanical forces but independent of the transport process. The principal difference is geometrical. The single curve, $\frac{k_{LM}d}{K}$ vs. $N_{Pe}\frac{d}{L}$ (Figure 27, p. 463, *31*), is analogous to the set of curves shown in Figure 5 and illustrates the variation of the Nusselt number in diffusion entry region of a cylindrical tube accompanying the development of the temperature profile.

Solutions to heat and mass transport problems are interchangeable in the limit when the flow and transport aspects of the problems are uncoupled. The substitution of α for D and T for C converts the solution of a given mass transfer problem into that for the corresponding heat transfer problem.

A sample of experimental data at low Reynolds numbers available in the literature—a heat transfer study by Calderbank and Korchinski (*1*) and a mass transfer study by Johnson and Hamielec (*9*)—is presented in Figure 2 for comparison with the asymptotic Nusselt number. The Reynolds numbers for these systems are in the range $2.2 \leq N_{Re}' \leq 14.6$ and the drops are reported to be spherical and nonoscillating. The conversion from the effective diffusivity representation of the data to the asymptotic Nusselt number is summarized in reference *8*.

To illustrate a particularly simple application, consider a single-drop system with the following properties:

$$\mu' = 1 \text{ poise},\quad \mu = 1 \text{ poise},\quad d = 0.10 \text{ cm.}$$

$$\Delta\rho = 0.1 \text{ g./cc.},\quad \rho' = 1 \text{ g./cc. and}$$

$$D = 1 \times 10^{-5} \text{ sq. cm./sec.}$$

so that for this example, $N_{Pe} = 80$ and $N_{Re}' = 0.0064$, a highly conservative value with respect to the justification of Hadamard's stream function.

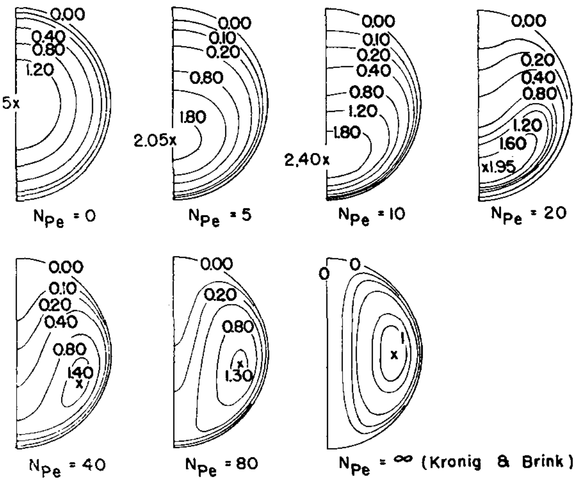

Fig. 3. Normalized asymptotic concentration profiles.

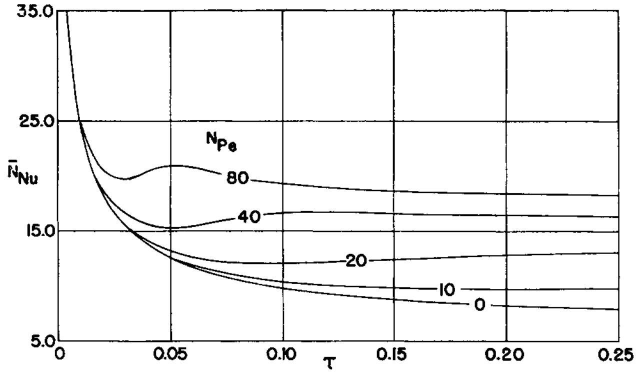

Fig. 4. Diffusion entry region of zone II.

If $C_o = 1$, then from Figure 7*a* zone II contact time of 26.0 sec. ($\tau = 0.104$) yields $C = 0.05$ (95% approach to equilibrium); whereas if $C_o = a_1 c_1 (\overline{C_o} = 1)$, then from Equations (19*a*) and (19*b*), that is, $\overline{C} = \exp(-\gamma_1 \tau)$ and $N_{Nu\infty} = 2/3\, \gamma_1$, and Figure 2, a zone II contact time of 28.7 sec. ($\tau = 0.115$) also yields $C = 0.05$.

As expected, the time for a 95% approach to equilibrium is relatively independent of the initial concentration profile.

A simple explanation is available for the surface average flux on the interval $0 < \tau < \tau_o$ (see Figure 6) when $C_o = 1$, $C^* = 0$, and $N_{Pe} \to \infty$. Consider a thought experiment which is similar to a real drop in every respect except that for $0 < \tau$ the fluid which crosses the surface $\zeta = 1$ from region I to region II is replaced continuously by fresh fluid with a solute concentration $C = 1$. This problem possesses a nontrivial asymptotic steady state solution for parametric Peclet number. In the limit as $N_{Pe} \to \infty$, the significant portion of the solute concentration gradient is restricted to a thin region near the drop surface and the time constant for the approach to steady state approaches τ_{cI}, the region I residence time. In the limit as $N_{Pe} \to \infty$, a real drop behaves as follows: the initial contents of region I at $C = C_o = 1$ cross the surface $\zeta = 1$ into region II during the time interval $0 < \tau < \tau_{cI}$; moreover the partially contacted initial contents of region II require a minimum time τ_{cI} to traverse region I and reappear once again in region II. Therefore in the limit as $N_{Pe} \to \infty$ the surface average flux of the thought experiment and of the drop are identical on the interval $0 < \tau < \tau_{cI}$, whereas the flux from the drop falls below that of the thought experiment for $\tau_{cI} < \tau$, as the solute concentration of the unreplenished drop approaches zero rather than an asymptotic steady state.

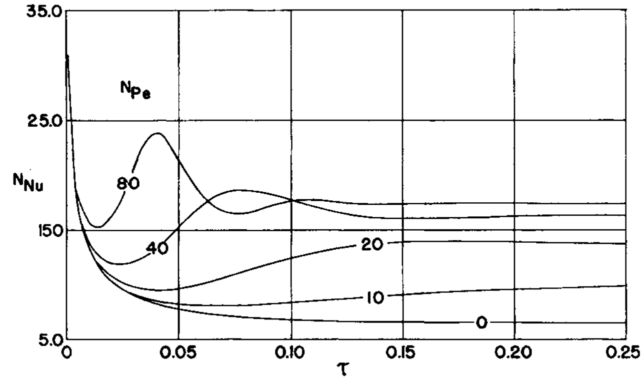

Fig. 5. Diffusion entry region of zone II.

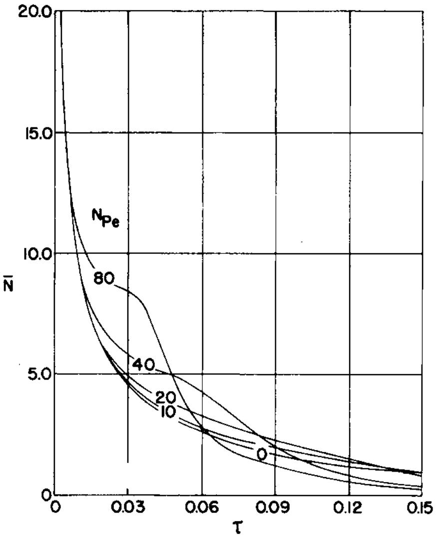

Fig. 6. Dimensionless surface average flux.

Conversely, as $N_{Pe} \to 0$ the diffusion flux increases relative to the convection flux so that, in general

$$\tau_o < \tau_{cI}$$

and $\tau_o \to \tau_{cI}$ as $N_{Pe} \to \infty$ where τ_o is the first inflection point along a surface average flux curve as indicated in Figure 6. Therefore, in the limit as $N_{Pe} \to \infty$, the characteristic features of the surface flux are directly related to τ_{cI} and thus to the circulation period of the drop. A comparison of τ_o and τ_{cI} (evaluated at $\xi = 0.1$, characteristic of the penetration region) is shown in Table 3.

An extension of the above analysis leads to a short time approximation to $\overline{C}(\tau)$. For τ close to zero the curvature, velocity gradient, and finite size of the drop may be neglected and $\overline{Q}(\tau)$ approximated by the transient flux for a one-dimensional, semi-infinite, stagnant region. Thus

$$\overline{Q}(\tau) = \frac{D}{a\pi^{1/2}} (\rho_o - \rho^*) \frac{1}{\tau^{1/2}} \tag{24}$$

so that from Equation (10*c*)

$$\frac{d\overline{C}}{d\tau} = -3 \frac{a}{D} \frac{\overline{Q}}{\rho_o - \rho^*} = -\frac{3}{\pi^{1/2}} \frac{1}{\tau^{1/2}}$$

or

$$1 - \overline{C} = \frac{6}{\pi^{1/2}} \tau^{1/2} = 3.38\tau^{0.50} \tag{25}$$

The average concentration $\overline{C}$ is plotted in Figure 7, as suggested by Equation (25), for parametric Peclet numbers. The curves extrapolate to $\tau = 0$ as $1 - \overline{C} = 3.22\tau^{0.497}$ independent of N_{Pe}.

CONCLUSION

The mechanism of viscous single-drop extraction is analyzed in terms of transport by viscous convection and

TABLE 3. A COMPARISON OF τ_o AND τ_{cI}, $C_o = 1$

N_{Pe}	τ_o	τ_{cI}
20	0.0700	0.120
40	0.0470	0.060
80	0.0275	0.030

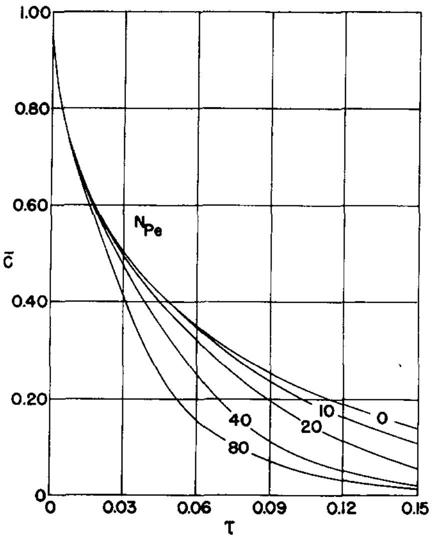

Fig. 7. Dimensionless volume average concentration.

molecular diffusion. The solution of the model equations spans the transition between the convection limited or stagnant-drop model and the diffusion-limited or Kronig and Brink model and thereby extends and places in perspective the models which commonly are applied in the analysis of experimental data.

The asymptotic Nusselt number is within 95% of the Kronig and Brink limit when $N_{Pe} > 60$, a condition more common in mass transfer than in heat transfer experiments. However the Kronig and Brink model is strictly valid only following a diffusion entrance period in which the influence of the initial profile vanishes. For short contact times recourse must be had to the exact solution presented in Figures 4, 5, 6, and 7 for $C_o = 1$. The oscillation period of the surface average flux is related to the circulation period of the drop in the diffusion limited case.

The factor preventing the wide application of viscous drop models is the validity of the Hadamard stream function which theoretically is limited to systems for which $N_{Re}' < 1$.

There are some indications, however, that for practical purposes the validity of the Hadamard stream function may be extended to systems for which $N_{Re}' < 10$.

NOTATION

A (Agn) = matrix (matrix element)
A = drop surface area, $= 4\pi a^2$
a = drop radius
a_n $(n = 1, \ldots$ = constants in expansion of $C(R, \theta)$
$C(R, \theta, \tau)$ = dimensionless solute concentration
$c_n(R, \theta)$ = eigenfunction
D = diffusivity
d = drop diameter
e (exp) = base of natural logarithms
$K = \frac{1}{2}\frac{\mu'}{\mu + \mu'}U = N_{Pe}\frac{D}{a}$
k = thermal conductivity
k = mass transfer coefficient
m = equilibrium distribution ratio
M = number of equal increments on the interval $0 \leq x \leq 1$, $M\Delta X = 1$
N = dimensionless surface average flux
N_{Nu} = Nusselt number, Kd/D
N'_{Pe} = Peclet number, dU/D
N_{Pe} = Peclet number, $\frac{1}{4}\frac{\mu'}{\mu + \mu'}N'_{Pe}$
N'_{Re} = Reynolds number, du/ν'
$\mathbf{n}$ = mass flux vector
Q = number of points in a mesh
$\bar{Q}$ = surface average flux
r = radial variable, spherical coordinate system
$\mathcal{R}$ = r/a
R = $\Delta\tau/\Delta X^2$
t = time
U = translational velocity
$\mathbf{U}^K$ = numerical approximation to $\mathbf{C}(\tau_K)$
V = drop volume $= 4/3\ \pi a^3$
V_R, V_θ, V_ϕ = velocity components
X, Y = dimensionless cylindrical coordinate (radial, axial)

Greek Letters

ΔX = dimensionless spatial increment
α = thermal diffusivity
γ = eigenvalue
ζ = dimensionless coordinate orthogonal to ξ, $\zeta = R^4 \cos^4\theta/(2R^2 - 1)$
θ = polar angle, spherical coordinate system
μ = viscosity
ξ = dimensionless coordinate, $\frac{8}{Ka^2}\psi$
ρ = concentration or density
τ = dimensionless time $= Dt/a^2$
$\Delta\tau$ = dimensionless time increment
ϕ = azimuthal angle, spherical coordinate system
ψ = stream function

Subscripts

i, j = mesh point coordinates
0 = initial condition; zero solute concentration
1 = solute
2 = solvent
LM = natural log mean
∞ = asymptotic value

Superscripts

K = time increment $= \tau_K/\Delta\tau$
$'$ = continuous phase
$-$ = average value
$*$ = phase equilibrium

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