parameter estimation problems. Since the quasilinearization technique has recently been proposed as an efficient and useful estimation procedure, this technique has been used as the basis of comparison for the results obtained with the linearization procedure. These comparisons show that the linearization procedure is particularly suited for the solution of large dimensioned linear problems because at most only the integration of $2n$ ordinary differential equations, where n is the dimension of the state vector, will be required per iteration. This differs from the quasilinearization algorithm for which the number of integrations involved is dependent on both the dimension of the differential system and the number of unknown parameters. The increased region of convergence obtained with the linearization procedure is characteristic of a Gauss-Newton procedure. Analysis of the difference between the quasilinearization and Gauss-Newton algorithms shows that the quasilinearization algorithm uses all the second-order variations of the performance criteria to generate a new estimate of the parameter, while the Gauss-Newton procedure uses only part of the second-order variation terms. This causes the linearization technique to converge at a slower rate but to be less sensitive to errors in the initial guesses of the unknown parameters.

NOTATION

$\mathbf{A}(\mathbf{x}_s, \mathbf{c}_s)$ = matrix of dimension $n \times n$
$\mathbf{B}(\mathbf{x}_s, \mathbf{c}_s)$ = matrix of dimension $n \times m$
$\mathbf{c}$ = m dimensional vector of unknown parameters
$\mathbf{c}_s$ = nominal value of the vector c
$\mathbf{f}(\mathbf{x}, \mathbf{c})$ = arbitrary vector function of $\mathbf{x}$ and $\mathbf{c}$
j = iteration parameter
k = time step parameter
m = number of unknown parameters
n = dimension of the state vector
N = total number of time steps for the discretized system
$\mathbf{Q}$ = weighting matrix of dimension $n \times n$
$T(k)$ = length of the kth time interval
$\mathbf{u}$ = control vector of dimension m
$\mathbf{v}$ = normalized control vector: $\mathbf{v} = \mathbf{c} - \mathbf{c}_s$
$\mathbf{w}(k)$ = vector of observations of dimension n
$\mathbf{w}_s(k)$ = normalized value of the observation vector: $\mathbf{w}_s(k) = \mathbf{w}(k) - \mathbf{x}_s(k)$
$\mathbf{x}$ = state vector of dimension n
$\mathbf{x}(0)$ = initial value of the state vector
$\mathbf{x}_s$ = nominal value of the state
$\mathbf{y}$ = normalized state vector: $\mathbf{y} = \mathbf{x} - \mathbf{x}_s$
$'$ = denotes transpose of a vector or matrix
^{0} = denotes the optimal value of some quantity

Greek Letters

$\boldsymbol{\varphi}(k)$ = transition matrix: $\boldsymbol{\varphi}(k) = \exp\,(\mathbf{A}(\mathbf{x}_A, \mathbf{c}_s)^* T(k))$
$\boldsymbol{\varphi}(-1) = \mathbf{I}n \times n$
$\boldsymbol{\Delta}(k)$ = forcing function weighting matrix:
$$\boldsymbol{\Delta}(k) = [\int \exp\,(\mathbf{A}(\mathbf{x}_A, \mathbf{c}_s)^* t)dt]\ \mathbf{B}(\mathbf{x}_A, \mathbf{c}_s)$$

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Simultaneous Mass Transfer and Equilibrium Chemical Reaction From Moving Bubbles: Film Theory

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Convective gas-liquid mass transfer in the presence of an equilibrium reaction was first analyzed by Olander (1960) for a quiescent gas-liquid system. Because of its practical significance, in this note we extend the analysis to cover mass transfer between a liquid and an ensemble of moving bubbles in the presence of a generalized liquid phase equilibrium chemical reaction involving one reactant and one product.

The analytical results for the mass transfer rate (or Sherwood number) from an ensemble of uniform bubbles are obtained. The analysis assumes the well-known cell model (Gal-Or, 1970), that is, the dispersed phase is distributed uniformly throughout the system so that everywhere in the system its volume fraction is Φ. A representative cell contains the same amount of liquid as the relative volume of liquid to particle volume in the entire assemblage. Hence, a mass transfer analysis of a spherical cell represents a similar analysis of the entire assemblage. The analysis considers various degree of internal circulation of bubbles.

THEORY

The reaction considered is

$$Y_A\, A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} Y_E\, E \qquad (1)$$

wherein at equilibrium

$$K = \frac{E^n}{A^m} = \frac{k_1}{k_2} \qquad (2)$$

K is the equilibrium constant; m and n are the orders of the reaction with respect to species A and E respectively. Y_A and Y_E are the stoichiometric coefficients and k_1 and

k_2 are the rate constants for the forward and the backward reaction rates.

We assume that the fluids are Newtonian and that isothermal condition prevails; diffusivities, viscosities, and the equilibrium constant are constant. The mass transfer resistances inside bubbles are negligible. The bubbles contain only one chemical component. The flow is assumed to be axisymmetric. Under these conditions, for a thin boundary layer ($Pe = 2aU/D_A >> 1$), the total A component material balance in the boundary layer is governed by

$$\frac{V_r}{Y_A}\frac{\partial A}{\partial y} + \frac{V_\theta}{aY_A}\frac{\partial A}{\partial \theta} + \frac{V_r}{Y_E}\frac{\partial E}{\partial y} + \frac{V_\theta}{aY_E}\frac{\partial E}{\partial \theta} = \frac{D_A}{Y_A}\frac{\partial^2 A}{\partial y^2} + \frac{D_E}{Y_E}\frac{\partial^2 E}{\partial y^2} \quad (3)$$

$$y = r - a; \quad y << a$$

where A and E are the concentrations of species A and E in the diffusional boundary layer around bubbles. D_A and D_E are the diffusivities of species A and E in the liquid phase. Equation (3) is subjected to the boundary conditions

$$\begin{aligned} A = A_i; \quad E = E_i \quad &\text{for} \quad y = 0 \\ A = A_\delta; \quad E = E_\delta \quad &\text{for} \quad y = \delta\ (\theta) \end{aligned} \quad (4)$$

with A and E subjected to the equilibrium restriction given by Equation (2). $\delta\ (\theta)$ is the thickness of diffusional boundary layer.

With the help of continuity equation, Equation (3) can be integrated with respect to y between the limits 0 and $\delta\ (\theta)$. Combining the resulting expression * with an approximate concentration field in the boundary layer, namely (Ruckenstein, 1964),

$$\frac{A - A_\delta}{A_i - A_\delta} = 1 - \frac{2y}{\delta} + 2\left(\frac{y}{\delta}\right)^3 - \left(\frac{y}{\delta}\right)^4 \quad (5)$$

and θ-component velocity V_θ proposed by Waslo and Gal-Or (1971), namely,

$$V_\theta = \left[U_0 + \frac{y}{a}\left(\frac{3}{2}U_s - 2U_0\right) + \frac{15}{2}\frac{y}{a}\Phi^{5/3}\left(U_0 - \frac{1}{2}U_s\right)\right]\sin\theta \quad (6)$$

one can obtain the differential equation *

$$\frac{d(\delta/a)}{d\theta} = \frac{4(a/\delta)(1 + y_A)}{Pe \quad \sin\theta} - 2\cot\theta\,\frac{\left\{\beta_1\frac{U_0}{U_s}\left(\frac{\delta}{a}\right) + \left(\frac{\delta}{a}\right)^2\beta_2\left[\left(\frac{3}{2} - 2\frac{U_0}{U_s}\right) + \frac{15}{2}\Phi^{5/3}\left(\frac{U_0}{U_s} - \frac{1}{2}\right)\right]\right\}}{\left\{\beta_1\frac{U_0}{U_s} + \left(\frac{\delta}{a}\right)\left[\left(\frac{3}{2} - 2\frac{U_0}{U_s}\right) + \frac{15}{2}\Phi^{5/3}\left(\frac{U_0}{U_s} - \frac{1}{2}\right)\right]2\beta_2\right\}} \quad (7)$$

where

$$\beta_1 = \frac{3}{10} + \left[\frac{Y_A}{Y_E}K^{1/n}\frac{A_\delta{}^{m/n}}{(A_i - A_\delta)}\right]\alpha_1\ (m/n) \quad (8)$$

$$\beta_2 = \frac{1}{15} + \left[\frac{Y_A}{Y_E}K^{1/n}\frac{A_\delta{}^{m/n}}{(A_i - A_\delta)}\right]\alpha_2\ (m/n) \quad (9)$$

$$\bar{y} = \frac{1}{2}\,\frac{\Lambda}{(A_i - A_\delta)}\,\frac{D_E\,Y_A}{D_A\,Y_E} \quad (10)$$

$$\Lambda = 2\Gamma\,K^{1/2}\,A_\delta{}^{m/n}\,\frac{m}{n}\,[1 + \Gamma]^{m/n-1} \quad (11)$$

$$\alpha_1(m/n) = \frac{1}{\delta}\int_0^\delta \left\{\left[1 + \Gamma\left(1 - \frac{2y}{\delta} + \frac{2y^3}{\delta^3} - \frac{y^4}{\delta^4}\right)\right]^{m/n} - 1\right\}dy \quad (12)$$

$$\alpha_2(m/n) = \frac{1}{\delta^2}\int_0^\delta y\left\{\left[1 + \Gamma\left(1 - \frac{2y}{\delta} + \frac{2y^3}{\delta^3} - \frac{y^4}{\delta^4}\right)\right]^{m/n} - 1\right\}dy \quad (13)$$

In the absence of a chemical reaction, Equation (5) has been shown (Ruckenstein, 1964; Yaron and Gal-Or, 1971) to represent well the concentration profile within the boundary layer. Also, in the case of a first-order irreversible reaction, Equation (5) allows predictions of Sherwood numbers well in agreement with the ones obtained from well-known penetration theory (Shah, 1972). Because of these results, Equation (5) is assumed to be applicable to the present situation. The quantities $\alpha_1(m/n)$ and $\alpha_2(m/n)$ as function of m/n and Γ were evaluated by Simpson's rule of integration on a computer. These results are described in Figure 1.

Defining the average value of convective mass transfer coefficient k_A over the whole surface of a particle by

$$k_A = \frac{\int_0^\pi \left[-\frac{D_A}{Y_A}\frac{\partial A}{\partial y}\bigg|_{y=0} - \frac{D_E}{Y_E}\frac{\partial E}{\partial y}\bigg|_{y=0}\right]2\pi\,a^2\sin\theta\,d\theta}{4\pi\,a^2\,(A_i - A_\delta)} \quad (14)$$

and using Equation (14) together with the definition $Sh = 2ak_A/D_A$, one obtains

$$Sh = \frac{2(1 + \bar{y})}{Y_A}\int_0^\pi \frac{\sin\theta}{(\delta/a)}\,d\theta \quad (15)$$

When $A_\delta \rightarrow 0$, the above results will require some changes. For example, Equation (7) is now valid if $\dfrac{A_\delta{}^{m/n}}{(A_i - A_\delta)}$ in Equations (8) to (11) is replaced by $A_i{}^{m/n-1}$ and $\Gamma\,(1 + \Gamma)^{m/n-1}$ in Equation (11) is replaced by 1. The quantities $\alpha_1(m/n)$ and $\alpha_2(m/n)$ in this case would be defined as

$$\alpha_1(m/n) = \frac{1}{\delta}\int_0^\delta\left(1 - \frac{2y}{\delta} + \frac{2y^3}{\delta^3} - \frac{y^4}{\delta^4}\right)^{m/n}dy \quad (16)$$

$$\alpha_2(m/n) = \frac{1}{\delta^2}\int_0^\delta\left(1 - \frac{2y}{\delta} + \frac{2y^3}{\delta^3} - \frac{y^4}{\delta^4}\right)^{m/n}y\,dy \quad (17)$$

Now we present the solution to Equations (7) to (15) separately for three main domains of internal circulation,

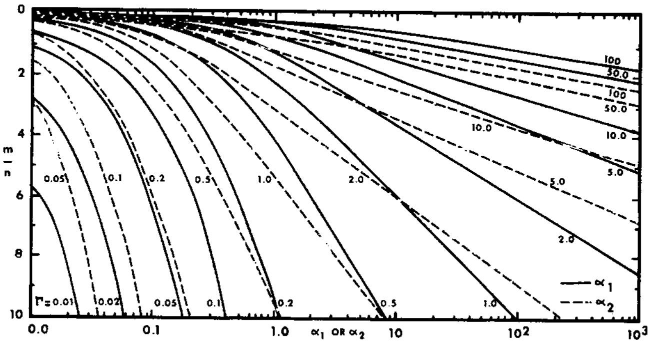

Fig. 1. α_1 and α_2 as functions of m/n and Γ.

namely, rapid circulation, zero circulation, and the intermediate circulation.

RAPIDLY CIRCULATING BUBBLES

For rapidly circulating bubbles, Equation (14) can be approximated as*

$$(\delta/a)\,\frac{d(\delta/a)}{d\theta}=\frac{4}{\beta_1}\,\frac{(1+\bar{y})}{Pe\sin\theta}\left(\frac{U_s}{U_0}\right)-2\cot\theta\,(\delta/a)^2 \qquad (18)$$

The above equation is subjected to the boundary conditions $\delta\,(\theta)\rightarrow$ finite when $\theta\rightarrow 0$. Upon integration, and substituting the result in Equation (15) one obtains after integration

$$Sh=\frac{\sqrt{\beta_1(1+\bar{y})}}{Y_A}\,1.633\,\left(\frac{U_0}{U_s}\right)^{1/2}\,Pe^{1/2} \qquad (19)$$

As shown by Yaron and Gal-Or (1971) the above equation can be rewritten as

$$Sh=1.633\,\frac{\sqrt{\beta_1(1+\bar{y})}}{Y_A}\left[\beta\,\frac{(1-\Phi^{5/3})}{Y}\right]^{1/2}\,Pe^{1/2} \qquad (20)$$

where $Y=2+2\beta+\Phi^{5/3}\,(3-2\beta)$ and

$$\beta=\frac{\mu_c}{\mu_d+\gamma}$$

γ is the interfacial viscosity due to surfactant impurities and is related to surface tension gradient (Gal-Or, 1970).

NONCIRCULATING BUBBLES

For negligible values of U_0/U_s, Equation (14) can be approximated as*

$$\frac{d(\delta/a)}{d\theta}=\frac{4}{3\beta_2}\,\frac{(a/\delta)^2}{Pe\,\sin\theta}\left(1-\frac{5}{2}\,\Phi^{5/3}\right)^{-1}-\cot\theta\,(\delta/a) \qquad (21)$$

The results of integration of above equation with boundary condition $(\delta/a)\rightarrow$ finite when $\theta\rightarrow 0$ combined with Equation (15) would give

$$Sh=\frac{(1+\bar{y})}{Y_A}\,\beta_2^{1/3}\,2.555\,\left(1-\frac{5}{2}\,\Phi^{5/3}\right)^{1/3}\,Pe^{1/3} \qquad (22)$$

INTERMEDIATE RATES OF INTERNAL CIRCULATION

For intermediate values of β or U_0/U_s one can use an approximate interpolation method described by Ruckenstein (1964) and Yaron and Gal-Or (1971). Using this method, one obtains

$$2.83\,\beta_1\left(\frac{(1+\bar{y})}{Y_A{}^2}\right)\left(\beta\,\frac{(1-\Phi^{5/3})}{Y}\right)Sh^{-2}+9.92\,\beta_2\,\frac{(1+\bar{y})^3}{Y_A{}^3}\left[\left(\frac{3}{2}-2\beta\,\frac{(1-\Phi^{5/3})}{Y}+\frac{15}{2}\,\Phi^{5/3}\left(\beta\,\frac{(1-\Phi^{5/3})}{Y}-\frac{1}{2}\right)\right]Sh^{-3}=Pe^{-1} \qquad (23)$$

The results of Sherwood number obtained here applies to the case of a single bubble when $\Phi\rightarrow 0$. These results would be useful in analyzing the mass transfer rates in systems such as extraction of acetic acid from carbon tetrachloride into a water phase (Farmer, 1949). The mass transfer rates in many other systems outlined by Farmer (1949) can also be analyzed with the help of present theory. Experimental data for mass transfer rates under controlled and wide variety of reaction conditions for these systems are, however, needed to verify the accuracy of predictions of Sherwood number by Equations (20), (22), and (23).

NOTATION

a = radius of a typical bubble in the population
r = radial distance
U = relative velocity between continuous and dispersed phase
U_0 = interfacial velocity at equator of particle
U_s = Stoke's velocity of single particle
V_r, V_θ = radial and tangential components of velocity vector in continuous phase
y = normal distance to particle surface; $r-a$
Y = function defined by Equation (20)

Greek Letters

γ = interfacial viscosity due to adsorbed surfactant impurities
θ = cone angle between the radius vector and the vertical directed in the sense of the drop motion
μ = viscosity
Φ = volume fraction occupied by dispersed phase

Subscripts

c = refers to continuous phase
d = refers to dispersed phase

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