the above-mentioned components is possible. Provided these conditions are satisfied, the main advantage of the technique is that of reducing the dimensionality of the original set. This approach was, for example, utilized in the reduction of our model for the smog formation problem.

If, however, the quasi steady variables cannot be eliminated, the set of differential-algebraic equations must be integrated. This is possible by using a modification of the present method (Michelsen, 1976), but no computational advantage is obtained, and in our opinion it is better in this case to retain the full original set.

NOTATION

$\mathbf{A}$ = Jaoobian matrix of ODE
a, b_i, b_{ij} = Runge-Kutta coefficients, Equations (4) to (6)
$\mathbf{e}$ = deviation vector, Equation (11)
$\mathbf{f}$ = vector function
h = step length
k = rate constant
$\mathbf{k}_i$ = Runge-Kutta vectors
n = step index
q = tolerance parameter
R_i = Runge-Kutta weights, Equation (7)
t = independent variable
$\mathbf{y}$ = vector of dependent variables
$\mathbf{y}^*$ = predictor vectors

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Manuscript received November 14, 1975; revision received January 9 and accepted January 16, 1976.

Effectiveness Factors in Gas-Liquid Reactions: The General n$^{\text{th}}$ Order Case

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The concept of the effectiveness factor, commonly used in gas-solid catalytic and noncatalytic reactions to account for the effect of diffusion, was extended in an earlier paper (Kulkarni and Doraiswamy, 1975*a*) to include gas-liquid reactions with first-order kinetics. In the present analysis, a general n^{th} order reaction is considered by using the same parameter β defined in our earlier communication to represent the relative contributions to the reaction from the bulk and the film. The effectiveness factor expression for an n^{th} order isothermal gas-solid catalytic reaction obtained by Mehta and Aris (1971) is shown to be a special case of this more general analysis by letting β tend to zero, which represents the condition where the bulk may be regarded as nonexistent. This case is analogous to gas-solid catalytic reactions where the reaction is essentially complete within the catalyst (regarded as film in gas-liquid reactions).

EQUATIONS FOR THE REACTANT CONCENTRATION PROFILE

Let us consider a system in which gas A is absorbed in a liquid and is consumed according to a general n^{th} order reaction. The mass balance equation for A can then be written as

$$D_A \frac{d^2C_A}{dx^2} = k_1 C^n{}_A \tag{1}$$

with the boundary conditions

$$C_A = C_A{}^* \quad \text{at} \quad x = 0 \tag{2a}$$

$$-D_A \frac{dC_A}{dx} = \frac{k_1 C^n{}_{Ao}}{a} \quad \text{at} \quad x = \delta \tag{2b}$$

Equation (2*b*) represents the kinetic boundary condition explained earlier (1975*a*).

Equations (1) and (2) can be rendered dimensionless to give

$$\frac{d^2w_A}{dy^2} = m^2 w^n{}_A \tag{3}$$

$$w_A = 1, \quad y = 0 \tag{4a}$$

$$-\frac{dw_A}{dy} = m^2\,\beta\, w^n{}_{Ao}, \quad y = 1 \tag{4b}$$

where m is the usual Thiele modulus $\delta\sqrt{k_1/D_A\; C_A{}^{*n-1}}$, and β is the ratio of the area per unit volume in the film to that in the liquid bulk and is given by

$$\beta = \frac{1}{a\delta} \tag{5}$$

This parameter provides the bridge between gas-solid catalytic and gas-liquid reactions as explained in our earlier communication (1975*a*). It may be noted that the definition of β is based on unit volume of the bulk exclusive of the film volume. This has been done primarily in the interest of mathematical simplicity, but it is also possible to base the definition of β on the total volume of the bulk and the film. As has been subsequently pointed out (Kulkarni and Doraiswamy, 1975*b*), the two definitions are related by

$$\beta' = \frac{1}{1+\beta} \tag{6}$$

where β' is now based on the total volume.

Since a pure gas A is considered for analysis, the gas phase resistance to the transfer of the species has been assumed to be negligible in writing the conservation equation.

Equation (3) can be integrated once with the boundary conditions (4) to give

$$\frac{dw_A}{dy} = \left(\frac{2}{n+1}\right)^{1/2} m \left[w_A{}^{n+1} - w_{Ao}{}^{n+1} + \frac{n+1}{2} (m\,\beta\, w^n{}_{Ao})^2 \right]^{1/2} \tag{7}$$

Further integration of Equation (7) leads to

$$m = \left(\frac{2}{n+1}\right)^{-1/2} \int_{w_{Ao}}^{1} \left[w_A{}^{n+1} - w_{Ao}{}^{n+1} + \frac{n+1}{2} (m\,\beta\, w_{Ao}{}^n)^2 \right]^{-1/2} dw_A \tag{8}$$

Defining a new concentration variable, ψ:

$$\psi = \left[1 - \left(\frac{w_{Ao}}{w_A}\right)^{n+1} + \frac{n+1}{2}\left(\frac{m^2\beta^2 w_{Ao}{}^{2n}}{w_A{}^{n+1}}\right) \right] \tag{9}$$

Equation (8) may be transformed to

$$m = \left(\frac{2}{n+1}\right)^{-1/2} \frac{1}{n+1} \left(w_{Ao}{}^{n+1} - \frac{n+1}{2} m^2\beta^2 w_{Ao}{}^{2n} \right)^{\frac{1-n}{2(n+1)}} \left[\int_0^{\psi_1} \psi^{-1/2}(1-\psi)^{-\frac{n+3}{2(n+1)}} d\psi - \int_0^{\psi_o} \psi^{-1/2}(1-\psi)^{-\frac{n+3}{2(n+1)}} d\psi \right] \tag{10}$$

The integrals on the right-hand side of Equation (10) are incomplete β functions which can be expanded in terms of the hypergeometric series and rearranged to give

$$W_A = \left\{ \frac{\left(\frac{2}{n+1}\right)^{-1/2} m(1-\psi)^{-\frac{1-n}{2(n+1)}}}{\left[\psi_1{}^{1/2} F_1\left(\frac{1}{2}, \frac{1}{2} + \frac{1}{n+1}; \frac{3}{2}, \psi_1\right) - \psi_o{}^{1/2} F_1\left(\frac{1}{2}, \frac{1}{2} + \frac{1}{n+1}; \frac{3}{2}, \psi_o\right) \right]} \right\}^{\frac{2}{1-n}} \tag{11}$$

Equation (11) represents the concentration in terms of the defined variable ψ.

For the specific case when β is equal to zero, ψ_o also becomes zero, and Equation (11) reduces to

$$w_A = \left\{ \frac{\left(\frac{2}{n+1}\right)^{-1/2} m\psi_1{}^{-1/2}(1-\psi)^{-\frac{1-n}{2(n+1)}}}{F_1\left(\frac{1}{2}, \frac{1}{2} + \frac{1}{n+1}; \frac{3}{2}, \psi_1\right)} \right\}^{\frac{2}{1-n}} \tag{12}$$

This expression has been obtained by Mehta and Aris (1971) for the case of an n^{th} order gas-solid catalytic reaction and is clearly a special case of the more general equation for gas-liquid systems considered in the present communication.

GENERALIZED EFFECTIVENESS FACTORS

The effectiveness factor η can now be defined as

$$\eta = \frac{-D_A \left.\frac{dC_A}{dx}\right|_{x=o}}{k_1 C_A{}^* \left(\frac{1}{a} + \delta\right)} = \left.\frac{1}{m^2(\beta+1)} \frac{dw_A}{dy}\right|_{y=o} \tag{13}$$

where the reaction flux in the absence of diffusion is hypothetically divided into contributions from the film and the bulk. When combined with Equation (7) this becomes

$$w_{Ao}{}^{n+1} - \frac{n+1}{2}(m\beta w_{Ao}{}^n)^2 = 1 - \eta^2 m^2 (1+\beta)^2 \left(\frac{n+1}{2}\right) \tag{14}$$

An expression for η can now be derived by comparing the above equation with Equation (11) written for the surface concentration $[w_A = 1]$; that is

$$w_{Ao}{}^{n+1} - \frac{n+1}{2}(m\beta w_{Ao}{}^n)^2 = \left[\psi_1{}^{1/2} F_1\left(\frac{1}{2}, \frac{1}{2} + \frac{1}{n+1}; \frac{3}{2}, \psi_1\right) - \psi_o{}^{1/2} F_1\left(\frac{1}{2}, \frac{1}{2} + \frac{1}{n+1}; \frac{3}{2}, \psi_o\right) \right]^{\frac{1-n}{2(n+1)}} m^{\frac{2(n+1)}{1-n}} \left(\frac{2}{n+1}\right)^{-\frac{n+1}{1-n}} = C_1 \tag{15}$$

Thus

$$C_1 = 1 - \eta^2 m^2 (1+\beta)^2 \left(\frac{n+1}{2}\right) \tag{16}$$

The term C_1 in this equation [defined by Equation (15)] contains the quantities ψ_1 and ψ_o. These can be expressed in terms of the modulus m by using Equation (9):

$$\left.\begin{aligned} 1 - \psi_1 &= w_{Ao}{}^{n+1} - \frac{n+1}{2} m^2\beta^2 w_{Ao}{}^{2n} \\ \psi_o &= \frac{n+1}{2} m^2\beta^2 w_{Ao}{}^{n-1} \end{aligned}\right\} \tag{17}$$

where w_{Ao} can be obtained from Equation (11) at $y = 1$.

For known values of ψ_1 and ψ_o, Equation (16) can be written as

$$\eta = \left[\frac{2(1-C_1)}{m^2(\beta+1)^2(n+1)} \right]^{1/2} \tag{18}$$

This equation represents a complete generalization of the case considered in our earlier paper (Kulkarni and Doraiswamy, 1975*a*). The value of the effectiveness factor can be obtained for a reaction of any order n from Equation (18) for a given value of the gas-liquid parameter β by first estimating the concentration variables ψ_1 and ψ_o from Equation (17) and by calculating C_1 from Equation (15).

Figure 1 shows a graphical representation of Equation (18) as plots of η vs. m for four specific values of β, namely, 0, 2, 5 and 10, and for three reaction orders, zero, first, and second. It will be noticed that the curves for all three orders tend to be displaced towards the right with decreasing β. For $\beta = 0$, the curves for the three orders coincide completely with those for reaction in a catalyst slab. Thus, as already pointed out by us, at $\beta = 0$ there is no bulk, and the reaction is confined to the film, which in the case of a catalytic reaction is the catalyst slab.

The importance of Equation (18) lies in the fact that it further generalizes the rigorous equation of Mehta and Aris (1971) for reaction in a slab, which is

$$\eta = \left[\frac{2(1 - w_{Ao}{}^{n+1})}{m^2(n+1)}\right]^{1/2} \tag{19}$$

where

$$w_{Ao}{}^{n+1} = \left[\psi_1{}^{1/2}F_1\left(\frac{1}{2}, \frac{1}{2} + \frac{1}{n+1}; \frac{3}{2}, \psi_1\right)\right]^{\frac{1-n}{2(n+1)}} m^{\frac{2(n+1)}{1-n}} \left(\frac{2}{n+1}\right)^{-\frac{n+1}{1-n}} \tag{20}$$

and is applicable to gas-solid catalytic as well as gas-liquid systems. Conclusions regarding the occurrence of a reaction exclusively in the bulk or film or in both can be drawn by a procedure similar to that described earlier.

ASYMPTOTIC SOLUTION

In the asymptotic region, the term C_1 of Equation (18) can usually be neglected, resulting in the following simplified equation for the effectiveness factor:

$$\eta = \frac{1}{m(1+\beta)\left(\dfrac{n+1}{2}\right)^{1/2}} \tag{21}$$

This may be compared with Petersen's solution (1965) for a reaction of general order in a slab:

$$\eta = \frac{\sqrt{A}}{m} \tag{22}$$

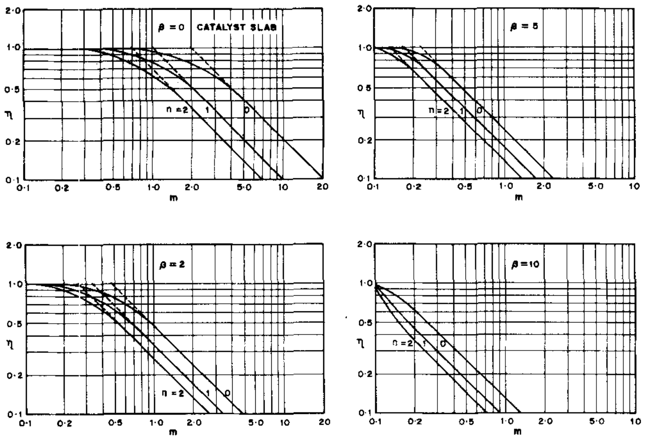

Fig. 1. Effectiveness factors for various orders of reaction (n) and gas-liquid parameter β.

where $A = 2$, 1, and 2/3 for a zero-, first-, and second-order reaction. It may be noticed that the effectiveness factor equation for the gas-liquid reaction reduces to that for the slab when $\beta = 0$.

For first-order kinetics, the equation for the gas-liquid reaction is $\eta = 1/m[\beta + 1]$. This was derived earlier by Kulkarni and Doraiswamy (1975*a*) specifically for a simplified gas-liquid system involving first-order kinetics, which reduces to the well-known equation $\eta = 1/m$ for a catalyst slab.

EXTENSION TO PACKED OR BUBBLE COLUMNS

In many industrial packed or bubble column reactors, the residence time of the liquid phase in the reactor is finite, so that the boundary condition (2*b*) should be corrected for the material leaving in the effluent stream. If Q represents the liquid holdup, then Equation (2*b*) becomes

$$-D_A \frac{dC_A}{dx}\bigg|_{x=\delta} = \frac{k_1 C_{Ao}{}^n}{a} + \frac{QC_{Ao}}{\left(a + \dfrac{1}{\delta}\right)T} \tag{23}$$

A similar boundary condition has been employed by Hoffman et al. (1975). Boundary condition (23) can be recast in dimensionless form as

$$\frac{dw_A}{dy}\bigg|_{y=1} = m^2\beta w_{Ao}{}^n + \frac{\beta}{1+\beta}\theta w_{Ao} \tag{24}$$

By using boundary condition (24) in place of (2*b*) to calculate the effectiveness factor, the following expression results:[*]

$$\eta = \frac{1}{m(\beta+1)\left(\dfrac{n+1}{2}\right)^{1/2}} \left\{1 - w_{Ao}{}^{n+1} + \frac{n+1}{2}\left(m\beta w_{Ao}{}^n + \frac{\beta}{1+\beta}\theta\frac{w_{Ao}}{m}\right)^2\right\}^{1/2} \tag{25}$$

This can be rearranged to the form of Equation (18) with the following modified expressions for the concentration variables:

$$1 - \psi_1 = w_{Ao}{}^{n+1} - \frac{n+1}{2}\left(m\beta w_{Ao}{}^n + \frac{\beta}{1+\beta}\theta\frac{w_{Ao}}{m}\right)^2 \tag{26}$$

$$\psi_o = \frac{n+1}{2}\left(m\beta w_{Ao}{}^n + \frac{\beta}{1+\beta}\theta\frac{w_{Ao}}{m}\right)^2 \frac{1}{w_{Ao}{}^{n+1}} \tag{27}$$

Equation (25) represents the general solution for the effectiveness factor in a packed or bubble column reactor involving a gas-liquid reacting system. Since the very nature of these columns demands a finite residence time, C_1 cannot be zero, and asymptotic solution is not possible. Thus, the effectiveness factor will now be a function not only of the gas-liquid parameter β but also of the time θ and the concentration in the bulk. In view of the large number of parameters involved, graphical representation of this equation is not justified. Values of the effectiveness factor can be readily computed for specific values of a system. Equation (25) assumes the asymptotic form of Equation (21) for large residence times of the liquid.

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[*] Convective terms have not been included here for the sake of simplicity and also because our object is primarily to show the effect of finite residence time.

NOTATION

a = interfacial area, cm^2/cm^3
C_A = concentration of species A, g mole/cm^3
C_1 = as defined by Equation (15)
D_A = diffusion coefficient, cm^2/s
F = hypergeometric series
k_1 = rate constant, 1/s [cm^3/g mole]$^{n-1}$
m = Thiele modulus, $\delta\sqrt{k/D_A\, C_A^{*n-1}}$
n = order of reaction
Q = liquid holdup, cm^3/cm^3
T = residence time, s
w_A = dimensionless concentration, C_A/C_A^*
x = distance parameter, cm
y = dimensionless distance, x/δ

Greek Letters

β = dimensionless gas-liquid parameter defined by Equation (5)
δ = film thickness, cm
θ = dimensionless residence time, $Q\delta^2/D_AT$
ψ_o, ψ_1 = concentration parameters defined by Equation (17)

Superscript

$*$ = condition at the interface

Subscript

o = condition in the bulk

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Manuscript received September 15, 1975; revision received December 31, 1975, and accepted January 17, 1976.

On the Importance of the Inertial Terms in the Modeling of Flow Maldistribution in Packed Beds

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In recent years there has been a growing interest in the development of modeling equations for representing flow maldistribution in packed beds. The main motivation for this work is provided by its relevance to a broad range of problems in chemical reaction engineering (namely, hot spot formation) and in metals processing (namely, the iron blast furnace). There appears to be general agreement that the mathematical models of such systems have made use of the differential, vectorial form of the Ergun equation, that is, Radestock and Jeschar (1970), Stanek and Szekely (1972, 1973, 1974). Moreover, in recent papers, Szekely et al. (1975) presented direct experimental proof for the validity of this approach.

In a recent paper, addressed to nonuniform flow in the iron blast furnace, Kitaev et al. (1975) suggested that even the differential vectorial form of the Ergun equation is an oversimplification, because in this form no allowance is made for inertial effects which could be significant in nonuniform flows. Unfortunately, they did not present a (numerical) solution of the full set of equations, containing these inertial terms, but rather assumed irrotational flow, the appropriateness of which is questionable, so that it is impossible to make a direct comparison between the results obtained from these two different formulations.

The purpose of this note is to present numerical solutions to some selected flow maldistribution problems by using both these approaches so that the practical importance of retaining the inertial terms may be critically assessed.

FORMULATION

The vectorial form of the Ergun equation (Ergun, 1952) may be written as

$$\underline{\nabla} P + \underline{V}(f_1 + f_2 V) = 0 \tag{1}$$

where f_1 and f_2 are defined as

$$f_1 = \frac{150\mu\,(1-\epsilon)^2}{(\phi dp)^2\epsilon^3} \tag{2}$$

$$f_2 = \frac{1.75\,\rho\,(1-\epsilon)}{(\phi dp)\epsilon^3} \tag{3}$$

In recent papers Shvydkii et al. (1974) and Kitaev (1975) suggested that in the proper representation of nonuniform flow through packed beds, allowance should be made for the inertial terms.

Written in terms of the superficial velocity and with two-dimensional Cartesian coordinates used, the equations proposed by Shvydkii and Kitaev take the following form:

$$V_x\frac{\partial V_x}{\partial x} + V_y\frac{\partial V_x}{\partial y} = -\frac{1}{\rho}\frac{\partial P}{\partial x} - \frac{f_1}{\rho}V_x - \frac{f_2}{\rho}V_xV \tag{4}$$

$$V_x\frac{\partial V_y}{\partial x} + V_y\frac{\partial V_y}{\partial y} = -\frac{1}{\rho}\frac{\partial P}{\partial y} - \frac{f_1}{\rho}V_y - \frac{f_2}{\rho}V_yV \tag{5}$$

where

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