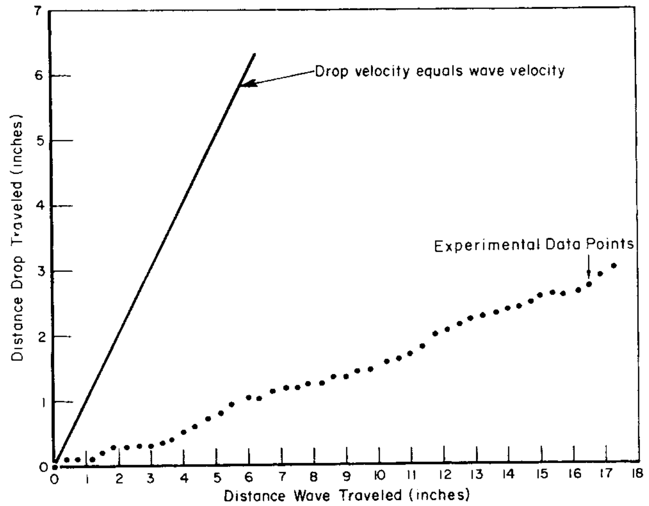

Fig. 3. Distance a drop of mercury with approximately 0.5-in. diam. has travelled as a function of the distance the potential wave has travelled. (The wave velocity is 6 in./sec.).

particle travelled at only about one-fourth the wave velocity. The apparent scatter in the experimental data is believed to be a real reflection of the particle motion. When viewed as a motion picture, the drop indeed appeared to stutter in its climb up the plane.

SUMMARY

It has been demonstrated that drops of a conducting liquid can be pumped by a travelling electrical potential wave. For drop below some critical size the drops travel at approximately the potential wave velocity. As the size of the drop is increased the drops no longer travel at the potential wave velocity but are pumped along by the wave at a slower velocity. It is anticipated that for a particular gravitational field opposing the motion and for a given strength potential wave, drops above a certain size would not be pumped but would roll down the inclined plane.

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Boundary Layer Effects on Catalytic Reactions with Volume Change

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The asymptotic solution proposed by Petersen (*1*, *9*) for catalytic effectiveness under conditions of large diffusional limitation has proved very useful. Aris (*10*) and Bischoff (*11*, *12*) have developed the technique to include fairly complex reaction rate forms. Recently, the method has been used (*2* to *4*) to explore the importance of uniform boundary layers in systems of relatively simple kinetics. The purpose here is to detail a class of solutions which may be obtained for reactions with volume change in the presence of uniform boundary layers.

We consider the reaction $A \rightarrow (m+1)B$. In general the rate will be a function of y, the mole fraction of A and the temperature T. It is assumed that the reaction is carried out in a porous catalyst in the presence of uniform thermal and concentration boundary layers. To a first approximation of the flux of A in such a system may be written as

$$N_A = -\frac{DP}{RT}\frac{\nabla y}{(1+my)} = -\frac{DP}{RT}\nabla\left[\frac{\ln(1+my)}{m}\right] \qquad (1)$$

so that the mass and energy conservation equations in dimensionless form are

$$\frac{d^2}{dz^2}\left[\frac{\ln(1+my_0c)}{my_0}\right] = \phi^2 r^*(c,\theta) \qquad (2)$$

$$\frac{d^2\theta}{dz^2} = -\beta\phi^2 r^*(c,\theta) \qquad (3)$$

with the normal symmetry conditions

$$\frac{dc}{dz} = 0,\ \frac{d\theta}{dz} = 0 \text{ at } z = 0$$

and with surface conditions specified by external transport rates

$$\left(\frac{1}{my_0}\right)\frac{d}{dz}\left[\ln(1+my_0c)\right] = N_{Sh}(1-c_s)$$

$$\frac{d\theta}{dz} = N_{Nu}(1-\theta_s) \qquad (5)$$

Weekman (*5*) has shown how temperature may be eliminated in terms of concentration for the solution of the pair of Equations (2) and (3), using the procedure of Prater (*6*) in equating the generation terms of the two equations. The result is

$$\theta = \left[\theta_s^{2-a} + \left(\frac{2-a}{my_0}\right)\beta\ln\left(\frac{1+my_0c_s}{1+my_0c}\right)\right]^{1/(2-a)} \qquad (6)$$

in which it is assumed that the temperature dependence of transport coefficients is given by

$$\frac{D}{K} = \left(\frac{D_0}{K_0}\right)\left(\frac{T}{T_0}\right)^a \qquad (7)$$

For $a = 1$ and $m = 0$, Equation (6) collapses to the form previously reported by Damköhler (*7*) and Prater (*6*).

Assuming a linear dependence of the transport coefficients on temperature ($a = 1$), we have by differentiation of Equation (6)

$$-\left(\frac{\beta}{my_0}\right)\frac{d}{dz}\left[\ln(1 + my_0c)\right] = \frac{d\theta}{dz} \tag{8}$$

so, from the boundary conditions of Equation (5)

$$\theta_s = 1 + \beta_T(1 - c_s) \tag{9}$$

Substituting directly into Equation (6) for $a = 1$

$$\theta = 1 + \beta_T(1 - c_s) + \left(\frac{\beta}{my_0}\right)\ln\left(\frac{1 + my_0c_s}{1 + my_0c}\right) \tag{10}$$

By the variable transformations

$$w = \frac{1}{my_0}\ln(1 + my_0c)$$

$$p = \frac{dw}{dz}$$

Equation (2) can be written in the form

$$pdp = \frac{\phi^2 r^*(c, \theta)}{1 + my_0c}dc \tag{11}$$

At large ϕ it can be assumed that $c = 0$ at $z = 0$ and p is zero also at that point. The limits for integration of Equation (11) are thus set and we have

$$\left.\frac{p^2}{2}\right|_{z=1} = \phi^2\int_0^{c_s}\frac{r^*(c, \theta)}{1 + my_0c}dc \tag{12}$$

where θ is given by Equation (10). At $z = 1$, $p = N_{Sh}(1 - c_s)$, from Equation (5), so

$$\left(\frac{N_{Sh}}{\phi}\right)^2 = \frac{2}{(1 - c_s)^2}\int_0^{c_s}\frac{r^*(c, \theta)}{1 + my_0c}dc = f(c_s) \tag{13}$$

In general the integral of Equation (13) will require numerical evaluation. From a plot of $f(c_s)$ vs c_s, we find the value of c_s corresponding to the desired N_{Sh} and ϕ (*4*). For nth order kinetics $r^*(c, \theta) = c^n \exp[\gamma(1 - 1/\theta)]$. The effectiveness factor is then given by

$$\eta = j\frac{N_{Sh}}{\Phi^2}(1 - c_s) \tag{14}$$

Solutions of Equations (13) and (14) for the case of $m = 0$ and integral n have been given elsewhere (*4*). When $m \neq 0$, analytical integration or reduction to standard form is possible in a number of cases detailed below.

1. Isothermal nth order (integral n) reaction with volume change; uniform thermal and concentration boundary layers:

$$\left(\frac{N_{Sh}}{\phi}\right)^2 = \frac{2e^{\gamma(1-1/\theta_s)}}{(my_0)^{1+n}(1 - c_s)^2}\left\{\sum_{r=0}^{n-1}(-1)^r\binom{n}{r}\left[\frac{(1 + my_0c_s)^{n-r} - 1}{n - r}\right] + (-1)^n\ln(1 + my_0c_s)\right\} \tag{15}$$

2. Nonisothermal zero order reaction with volume change; uniform thermal and concentration boundary layers.

A modification of the stated boundary conditions is required in this case, since the reactant is consumed at the extinction radius z_e:

$$\theta = \theta_e;\ \frac{dc}{dz} = \frac{d\theta}{dz} = c = p = 0\ \ @\ z = z_e \tag{16}$$

and, from Equation (11)

$$\left(\frac{N_{Sh}}{\phi}\right)^2 = \frac{2e^\gamma}{(1 - c_s)^2}\left[\theta_e{}^{-\gamma/\theta_e} - \theta_s e^{-\gamma/\theta_s} - \gamma\int_{\gamma/\theta_e}^{\gamma/\theta_s}\frac{e^{-t}}{t}dt\right] \tag{17}$$

The integral of Equation (17) is tabulated in a number of sources (*8*). The limiting values, θ_s at the surface and θ_e at the extinction radius, are determined from Equations (9) and (10) with $c = 0$, respectively.

3. Isothermal nth order reaction with volume change, $N_{Sh} = N_{Nu} = \infty$ (no boundary layer present):

$$c_s = \theta_s = 1\quad @\ z = 1$$

$$\eta = \frac{j\sqrt{2}}{\phi(my_0)^{\frac{n+1}{2}}}\left\{\sum_{r=0}^{n-1}(-1)^r\binom{n}{r}\left[\frac{(1 + my_0)^{n-r} - 1}{n - r}\right] + (-1)^n\ln(1 + my_0)\right\}^{1/2} \tag{18}$$

4. Nonisothermal zero order reaction with volume change, $N_{Sh} = N_{Nu} = \infty$

$$\eta = \frac{j}{\phi}\sqrt{\frac{2e^\gamma}{\beta}}\left[\theta_e e^{-\gamma/\theta_e} - e^{-\gamma} - \gamma\int_{\gamma/\theta_e}^{\gamma}\frac{e^{-t}}{t}dt\right]^{1/2}$$

$$\theta = 1 + \left(\frac{\beta}{m}\right)\ln\left(\frac{1 + my_0}{1 + my_0c}\right) \tag{19}$$

Equation (18) has been reported previously (*14*) for some specific values of n. If the concept of the effective diffusivity is extended to the multicomponent reaction

$$\mu_1A_1 + \mu_2A_2 + \cdots\cdots\cdots\cdots \rightarrow \mu_pA_p$$

where A_1 is the limiting component and the stoichiometric numbers are arranged such that $\mu_1 = 1$ then

$$m = -\Sigma\,\mu_i$$

Uniqueness Criterion

It has been established (*2* to *4*) that the presence of boundary layers can be a critical factor in determining the uniqueness of the steady state in a catalyst pellet. Creswell (*13*) has used the asymptotic solution to find a limiting criterion for uniqueness with a first order reaction, without volume change. The method is readily extended to cover any order $n > -1$ as outlined here.

For nth order reaction (n not necessarily integral) with no volume change we have:

$$\left(\frac{N_{Sh}}{\phi}\right)^2 = \frac{2}{(1 - c_s)^2}\int_0^{c_s}\exp\left[\gamma(1 - 1/\theta)\right]c^n dc \tag{20}$$

If β is small, most of the temperature rise occurs in the boundary layer and we can make the assumption that the pellet is isothermal at its surface value. Equation (20) reduces to

$$\frac{N_{Sh}{}^2(1 - c_s)^2}{\phi^2} = \frac{2}{n + 1}\exp\left[\frac{\gamma\beta_T(1 - c_s)}{1 + \beta_T(1 - c_s)}\right]c_s{}^{n+1} \tag{21}$$

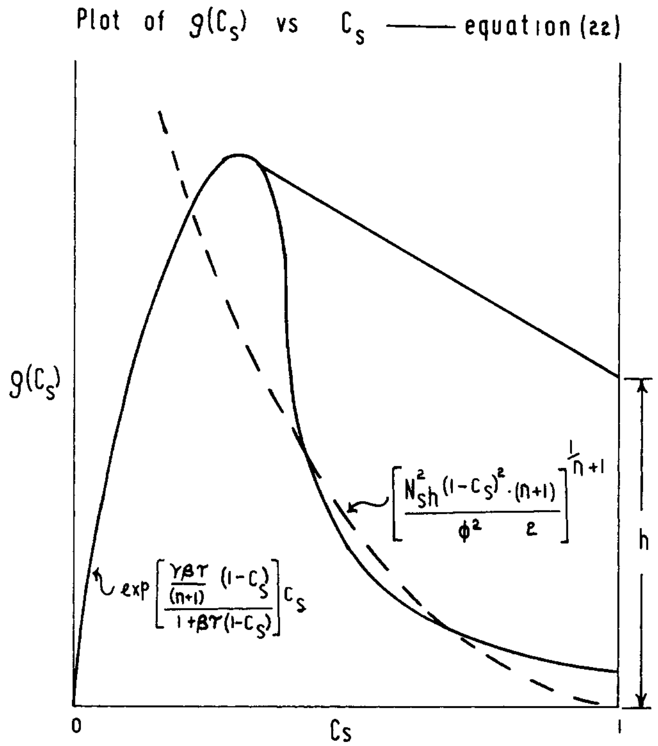

Fig. 1. Typical solution to Equation (22) for n>1.

or

$$\left[\frac{N_{Sh}^2(1-c_s)^2}{\phi^2}\cdot\frac{n+1}{2}\right]^{1/(n+1)} = \exp\left[\frac{\dfrac{\gamma\beta\tau}{(n+1)}(1-c_s)}{1+\beta\tau(1-c_s)}\right] c_s = g(c_s) \qquad (22)$$

Graphs of the left- and right-hand sides are shown in Figure 1. Three intersections are possible under certain circumstances. It is apparent that if multiple steady states are to exist, the $g(c_s)$ curve must have a point of inflection $\frac{d^2g}{dc_s^2} = 0$ at $c_s = c_{\text{inf}}$. A sufficient condition for uniqueness (*13*) is that the tangent at the point of inflection should have a positive intercept, that is, $h\ (c_{\text{inf}}) > 0$ where

$$h(c_s) = g(c_s) + (1 - c_s)\frac{dg}{dc_s} \qquad (23)$$

by setting $\frac{d^2g}{dc_s^2} = 0$ we find

$$c_{\text{inf}} = \frac{2(n+1)(1+\beta\tau)^2}{\beta\tau[\gamma + 2(n+1)(1+\beta\tau)]} \qquad (24)$$

and by substitution the criterion for uniqueness becomes

$$\gamma\beta\tau < 4(n+1)(1+\beta\tau) \qquad (25)$$

If $\beta\tau >> 1$ the criterion reduces to

$$\gamma < 4(n+1) \qquad (26)$$

NOTATION

a = parameter defined in Equation (7)
A, B = chemical species
C = dimensionless mole fraction $\frac{y}{y_0}$
D = effective diffusivity
E = activation energy
h = film heat transfer coefficient
$-\Delta H$ = heat of reaction
j = shape factor = 1, 2, 3 for plate, cylinder, sphere
k = rate constant $A_0 \exp(-E/RT)$
k_c = film mass transfer coefficient
K = effective thermal conductivity
L = pellet dimension
m = volume change factor in reaction
n = reaction order
N_A = flux of species A
N_{Nu} = Nusselt number $\frac{hL}{K}$
N_{Sh} = Sherwood number $\frac{k_cL}{D}$
P = pressure
r^* = dimensionless rate of reaction
R = gas constant
t = dummy variable in Equations (17) and (19)
T = temperature
X = distance
y = mole fraction
Z = dimensionless distance $\frac{X}{L}$
$\binom{n}{r}$ = binomial coefficient = $\frac{n!}{r!(n-r)!}$

Subscripts

0 = bulk values
S = surface values
e = extinction radius values

Greek Symbols

β = $\frac{Py_0D_0(-\Delta H)}{RT_0^2K_0}$
η = effectiveness factor
θ = dimensionless temperature $\frac{T}{T_0}$
τ = $\frac{N_{Sh}}{N_{Nu}}$
ϕ = Thiele modulus = $L\left[\frac{k_0P^{n-1}y_0^{n-1}RT_0}{D_0}\right]^{1/2}$
γ = $\frac{E}{RT_0}$

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