*n*th - Order Reaction with Mole Changes in Porous Catalysts in the Molecular, Transition, and Knudsen Regimes

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If a reaction with mole changes takes place isothermally in a porous catalyst, intrapellet concentration and pressure gradients can develop and mass transfer will occur by simultaneous diffusion and flow. A very useful equation for describing simultaneous diffusion and flow in porous media is the one representing the extended dusty-gas model. It was derived by Mason et al. (1967) and independently by Gunn and King (1969). The equation contains three constants C_0, C_1, and C_2 which characterize the porous medium and must be determined experimentally. Abed and Rinker (1973) have derived and solved numerically the equations for intrapellet pressure and composition profiles for a zero-order reaction in a porous catalyst. Since their derivation was based on the extended dusty-gas model, it is valid for all transport regimes, namely, the Knudsen, transition, and the molecular regimes.

Otani et al. (1965) have also derived and solved equations for the intrapellet pressure and composition profiles in all transport regimes for a first-order reaction with mole changes. They did this by extending the validity of the simple capillary model to include porous catalysts by applying it in conjunction with the random-pore model.

The main purpose of the present paper is to extend the work reported by Abed and Rinker (1973) to a consideration of first- and higher-order reactions. By following their same procedure in deriving the equations for a zero-order reaction, a set of general equations for an *n*th-order reaction can be obtained. To avoid redundancy, only the final results of the derivation are presented in this paper.

THEORY

The case under consideration in this work is an irreversible reaction of *n*th-order and is given stoichiometrically by

$$A \rightarrow \theta B \tag{1}$$

The mole-fraction derivative for species A in dimensionless form is given by

$$\frac{dY}{dX} = \frac{\gamma_K{}^2 \delta}{j\left[\dfrac{\xi}{V} + QY\left(\dfrac{1+\sqrt{\theta}\,\alpha\xi}{V} + \sqrt{\theta}\,\beta_0\alpha\xi\right)\right]} \tag{2}$$

where γ_K, θ, α, β_0 are dimensionless parameters; δ is the dimensionless flux; ξ is the dimensionless pressure; and Q is given by Equation (3):

$$Q = (1 - \sqrt{\theta})\, y_{AL}\xi / W \tag{3}$$

where W is given by

$$W = (1 - Yy_{AL})(1 + \alpha\xi) + \sqrt{\theta}\,(1 + \sqrt{\theta}\,\alpha\xi) Yy_{AL} + V[\theta\beta_0\alpha\xi Yy_{AL} + \beta_0\alpha\xi(1 - Yy_{AL})] \tag{4}$$

and V is given by

$$V = 1 + (1 - Yy_{AL})\,\alpha\xi + \sqrt{\theta}\,\alpha Yy_{AL}\xi \tag{5}$$

The derivative of the pressure in dimensionless form is given by

$$\frac{d\xi}{dX} = Q\frac{dY}{dX} \tag{6}$$

Finally, the continuity equation for species A in dimensionless form is as follows:

$$\frac{d\delta}{dX} = j\xi^n Y^n - (j-1)\frac{\delta}{X} \tag{7}$$

The boundary conditions for Equations (2), (6), and (7) are given by Equations (8) and (9)

at

$$X = 0,\ \frac{dY}{dX} = 0,\ \frac{d\xi}{dX} = 0,\ \delta = 0 \tag{8}$$

at

$$X = 1,\ Y = 1,\ \xi = 1,\ \delta = E \tag{9}$$

where E is the effectiveness factor.

RESULTS AND DISCUSSION

The numerical integration of Equations (2), (6), and (7) with the boundary conditions (8) and (9) was accomplished with a fourth-order, Runge-Kutta integration formula. The correctness of the results was checked for two different cases: first, by choosing $\theta = 1$, the results from the numerical integration were found to be in good agreement with the results obtained analytically; secondly, a comparison was made with the results that were reported by Otani, et al. (1965) for a first-order reaction, wherein $j = 1$, $\alpha = 1$, $\beta_0 = 1$, $\theta = 4$, $y_{AL} = 0.9$, and $\gamma_K = 1$. Our computed effectiveness factor of $E = 0.464$ compares well with their value of 0.47.

By keeping the parameters j, α, θ, y_{AL}, and γ_K at the values stated above, the calculated effectiveness factor was $E = 0.453$ at $\beta_0 = 100$, and $E = 0.483$ at $\beta_0 = 0.001$. This shows that the effect of the flow parameter β_0 on the effectiveness factor is insignificant and is in agreement with Otani et al. (1965) wherein their flow parameter G had no significant effect on the effectiveness factor.

Figure 1 shows a plot of the effectiveness factor E versus the pressure parameter α, giving the effect of the Knudsen Thiele modulus γ_K. In Figure 1, the computed effectiveness factor is for slab geometry and for a first-order reaction. The value of the parameters, β_0, θ, and y_{AL}, was set at 1.0, 4.0 and 1.0, respectively. It is important to note that γ_K in a first-order reaction is independent of operating pressure just as the molecular Thiele parameter γ_M is independent of operating pressure for a zero-order reaction. For $n > 1$, neither γ_K nor γ_M is independent of pressure; so that plots similar to Figure 1 or to those shown for $n = 0$, (*1*), cannot be obtained. In

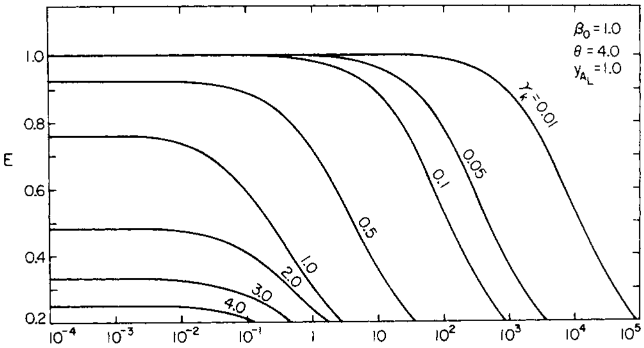

Fig. 1. Effectiveness factor in the Knudsen, transition, and molecular regimes for slab geometry and first-order reaction, showing the effects of the Knudsen Thiele modulus.

fact for $n > 1$, there is no main parameter that can be held constant while showing the variation of E with α as can be done with γ_M for $n = 0$ and γ_K for $n = 1$.

Figure 1 also shows that when α is small the effectiveness factor is independent of α; and it reaches an asymptotic value that can be calculated by

$$E = \frac{\tanh \gamma_K}{\gamma_K} \tag{10}$$

The merging of curves in Figure 1 to the limit of $E = 1$ for $\gamma_K \leq 0.1$ is simply a limitation of accuracy in plotting. In the molecular region in which α is large, the effectiveness factor decreases with increasing α for constant γ_K. For zero-order reactions, E increases with increasing α for constant γ_M(1). Direct comparison of the opposing variations of E with α for $n = 0$ and 1 is not meaningful since the parameter which remains constant is different for each order.

An additional observation was made by computing the dimensionless pressure at the center plane ξ_0 in the Knudsen region at different values of γ_K. All other parameters were kept constant at $\alpha = 10^{-4}$, $\beta_0 = 1$, $\theta = 4$, $y_{A_L} = 1$, $j = 1$, and $n = 1$. It was found that at $\gamma_K = 0.01$, $\xi_0 = 1.00$; at $\gamma_K = 0.5$, $\xi_0 = 1.11$; at $\gamma_K = 2.0$, $\xi_0 = 1.73$; and at $\gamma_K = 9.0$, $\xi_0 = 1.999$. These calculations show that for a first-order reaction in the Knudsen regime of transport, the dimensionless pressure at the center plane ξ_0 will not always reach a value of $\sqrt{\theta}$ unless $\gamma_K \geqq 9$.

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NOTATION

A = component A
B = component B
C_0 = constant dependent only upon structure of porous medium and giving relative D'Arcy flow permeability, cm^2
C_1 = constant dependent only upon structure of porous medium and giving relative Knudsen flow permeability, cm
C_2 = constant dependent only upon structure of porous medium and giving ratio of molecular diffusivity within the porous medium to the free gas diffusivity, dimensionless
D_{AB} = free gas mutual diffusivity in a binary mixtu of components A and B, cm^2/s
D^0_{AB} = $D_{AB}P$, dynes/s
E = effectiveness factor, dimensionless
j = geometric constant having values of 1, 2, and for an infinite slab, cylinder, and sphere, respec tively
k = rate constant based on unit volume of catalys 1/s, for first-order reaction
K_A = Knudsen effective diffusivity = $C_1\sqrt{R_gT/M}$ cm^2/s
L = radial distance from the center for spheres, fro the center line for cylinders and from the cente plane for slabs to the exterior surface of th catalyst pellet, cm
M = molecular weight, g/g-mole
n = order of reaction
$\vec{N}$ = molar flux, g-mole/cm^2-s
P = total pressure, dynes/cm^2
P_L = total pressure at the same position as taken fo y_{AL}; that is, the exterior of the pellet, dynes/cm^2
Q = lumped dependent variable defined by Equatio (3), dimensionless
R_g = gas constant, 8.31×10^7 ergs/g-mole-°K
T = absolute temperature, °K
V = grouping of terms defined by Equation (5), dimensionless
W = grouping of terms defined by Equation (4), dimensionless
X = dimensionless distance in the pellet = Z/L
y = mole fraction
y_{AL} = mole fraction of component A at the external face of the pellet
Y = mole fraction ratio = y_A/y_{AL}
Z = distance in direction of mass transfer, cm

Greek Letters

α = dimensionless pressure parameter = $K_AP_L/C_2D^0_{AB}$
β_0 = dimensionless flow parameter = $C_0C_2D^0_{AB}/\mu_m\sqrt{\theta}K^2_A$
γ_K = Knudsen Thiele modulus

$$= L\left[\frac{k}{K_A}\left(\frac{P_Ly_{AL}}{R_gT}\right)^{n-1}\right]^{1/2}$$

γ_M = molecular Thiele modulus

$$= L\left[\frac{k}{C_2D_{AB}}\left(\frac{P_Ly_{AL}}{R_gT}\right)^{n-1}\right]^{1/2}$$

δ = dimensionless flux

$$= \frac{\vec{N}_Aj}{Lk\left(\frac{P_Ly_{AL}}{R_gT}\right)^n}$$

θ = dimensionless parameter = M_A/M_B
μ = viscosity, g/cm-s
ξ = dimensionless pressure = P/P_L.

Subscripts

A = component A
B = component B
K = Knudsen
L = at exterior pellet face
M = molecular
m = mixture
0 = at the centerplane

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Dilute Polymer Solution Pressure Hole Errors in Turbulent Boundary Layers

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The errors in the use of a pressure tap to measure the static pressure or normal stress on the wall of a flow channel are well known for Newtonian fluids when the ratio of the length l to diameter d of the hole is greater than 2.5. Summaries of previous work can be found in the experimental investigation of Franklin and Wallace (1970). For smaller l/d ratios the results are not so clear and small imperfections at the hole become important. Ray (1956) reports that the error, which is normally positive (the hole pressure is larger than the true static pressure), can be negative for l/d of 0.1.

In viscoelastic solutions, measurements have only been made in laminar flow. Errors can be large when the first normal stress difference N_1 is large, but in very dilute polymer solutions N_1 is small. When the streamlines bend into the hole and there is no flow into the hole, the error for viscoelastic fluids has been theoretically shown to be negative and equal to $-0.25\,N_1$ (Tanner and Pipkin, 1969). This effect has been verified by Broadbent and Lodge (1971) and Novotny and Eckert (1973). At very high flow rates Novotny and Eckert find a positive error using l/d of 0.144. They erroneously compare their results to Newtonian fluids for high l/d and conclude that viscoelastic fluids give large errors. Novotny and Eckert attribute the error to the diverging of the streamlines out of the hole when an eddy is present in the hole. Ray (1956) has shown that this occurs in Newtonian fluids also.

It is clear that this problem merits careful experimental evaluation to determine the static pressure tap errors for both Newtonian and viscoelastic fluids under turbulent flow conditions. A preliminary study is presented in this note. The results show little difference in the errors for water or 100 ppm of Polyox WSR 301, and large errors are present in both cases for small l/d.

EXPERIMENTAL PROCEDURE

Six pressure tap holes and a one-quarter-in. flush mount type pressure transducer (Sensotec Model TAH-6H(W), 0.1-0.2 MN/m^2 (0-15 psig), G Type flange mounted, with welded diaphragm) were mounted in the center of the rectangular test section of a 0.305 m water tunnel at the Garfield Thomas Water Tunnel Facility. The holes were patterned after those of Franklin and Wallace with d, the hole diameter l the hole depth and d_t, the diameter of the tube from the hole to the pressure transducer, held at fixed ratios. Hole sizes used in this work were 6.35, 3.175, and 1.5875 mm, l/d was approximately 15.5, and d_t/d was 2. A Statham ± 35 kN/m^2 (±5 lb./sq.in.abs.) pressure transducer was used to measure the pressure hole static pressure with reference to a column of water whose surface was at the tunnel centerline. Since the flush mounted transducer was at this same location, all measurements were referenced to the atmospheric pressure at the tunnel centerline.

The holes were drilled in brass cylinders which were pressed in a brass plate. After plugs were placed in the holes, the surface was milled and then hand finished. The plugs were removed before installation of the plate in the tunnel. The holes under 20 power magnification appeared sharp.

The flush mounted transducer was mounted in the middle 3.175-mm hole and held in place by screws on an outside flange. The location of the flush mount could be changed with respect to the tunnel wall by using shims between the outside flange and the outside of the brass plate. The reference for this transducer was atmospheric pressure on the outside of the tunnel.

To make a measurement the zero of the flush mounted transducer was found with no flow in the tunnel. One major source of error found by Franklin and Wallace was zero drift and we encountered it also. Only by recalibrating the zero for each measurement was it possible to obtain reasonable results. After the 1.5875-mm hole and the flush mounted transducer were compared with no flow, the tunnel was brought up to