Part III. Effect of Pressure Gradients on the Effectiveness of Porous Catalysts

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The effect of a change in moles, due to reaction, on the effectiveness of a catalytic reaction is analyzed by calculating the concentration profile along a capillary whose wall surface acts as a catalyst and within a spherical, porous, catalyst pellet. The effectiveness factor *E* is influenced most when the diffusion is predominately of the bulk type and none at all for Knudsen diffusion. For an increase in moles, the diffusion of reactant into the pellet is suppressed because of the opposing pressure gradient. The result is a decrease in *E*.

Application to a typical bidisperse catalyst pellet such as alumina indicates that the reduction in *E* due to an increase in moles is not likely to be large. The effect can be important only if the change in moles exceeds 1 or 2, and the pellet is of the low-density type with large macropores.

In contrast the pressure gradient is large only when mass transfer is by the Knudsen process.

If a gaseous reaction on a solid catalyst is accompanied by a change in moles, an intrapellet pressure gradient is established. Suppose the reaction is of the form

$$A \rightarrow n\ B;\ n > 1 \tag{1}$$

The pressure drop from the center of the catalyst pellet toward the exterior surface will enhance the mass transfer of B outwards. However, the diffusion of reactant A into the pellet will be suppressed by the pressure gradient. This results in a decreased concentration of A and a lower average rate of reaction for the pellet. The purpose of this paper is to determine the magnitude of this decrease in the effectiveness of the catalyst in terms of the pertinent variables. A single cylindrical capillary is analyzed first, and then these results are applied to a bidisperse, porous pellet such as alumina. The treatment is restricted to isothermal conditions and a first-order irreversible reaction but includes the whole range of mass transfer from Knudsen diffusion to Poiseuille flow. In an earlier study (*1*) it was shown that for the special case of Knudsen diffusion, the effectiveness of the catalyst is not influenced by pressure gradients. Hence significant reduction in the effectiveness factor is only possible when the diffusion process is in the intermediate or bulk regimes.

CONCENTRATION AND PRESSURE GRADIENTS IN A CAPILLARY

A capillary of the total length $2L$ and radius a is exposed to the gas mixture. The first-order rate of reaction, per unit surface, in accordance with Equation (1) is

$$r = k_s\ C_A \tag{2}$$

It has been shown (*1*) that the mass balance of A, and the flow due to a pressure gradient, along the capillary may be written as

$$\frac{d\,N_A}{dx} + \frac{2k_s\,C_A}{a} = 0 \tag{3}$$

and

$$N_A\ (n - n^{1/2}) = \frac{C}{RT}\ \frac{dP}{dx} \tag{4}$$

Here N_A is the mass flux of A in the direction x along the capillary, and C is a flow parameter, which for a capillary is given by

$$C = \frac{n^{1/2} D_{KA}}{1 + [1 - (1 - n^{1/2}) y_A] \dfrac{D_{KA}}{D_{AB}}} + \left[\frac{a^2 P}{8\mu} + \frac{\pi D_{KA}}{4[y_A + n^{-1/2}(1 - y_A)]} \right] \left\{ \frac{n^{1/2} y_A}{1 + \dfrac{D_{AB}}{D_{KA}}} + \frac{1 - y_A}{1 + \dfrac{D_{AB}}{D_{KB}}} \right\} \tag{5}$$

In general, C is a function of pressure and mole fraction y_A. However, along a pore, or in a catalyst pellet, the pressure gradient is not large enough to cause significant variations in C. Furthermore, the expression is rather insensitive to changes in composition. This was demonstrated in Part II by diffusion and flow measurements across catalyst pellets subjected to a pressure gradient. Hence, in the integration of Equation (4), C will be taken as a constant. When the pore geometry or pressure level is changed, C varies considerably, for example from about 0.03 (for Vycor) to 20 sq.cm./sec. (for low-density alumina pellets). Equation (5) shows that C is equal to

$n^{1/2} D_{KA}$ if the transport of A is solely by Knudsen diffusion.

The mass flux of A can be related (*1*) to the concentration gradient by the equation

$$N_A = -\frac{D_{AB}}{1-(1-n)y_A + \frac{D_{AB}}{D_{KA}}} \frac{dC_A}{dx} \tag{6}$$

The bulk diffusivity D_{AB} in this equation is a function of pressure and may be written

$$D_{AB} = \frac{D_{AB_0} P_o}{P} \tag{7}$$

where P_o is the pressure at one end ($x = 0$) of the capillary.

Equation (6) can be used to eliminate N_A from Equations (3) and (4), so that the result is two equations expressing C_A and P as a function of x. The boundary conditions are $C_A = C_{A_0}$ at $x = 0$ and $dC_A/dx = 0$ at $x = L$ (midpoint in capillary). In dimensionless form the resulting equations are

$$\frac{d^2P^*}{dx^{*2}} + y_{A_0} (n - n^{1/2}) G h_{AB}^2 C_A^* = 0 \tag{8}$$

and

$$\frac{d}{dx^*}\left[\frac{-1}{P^* - (1-n) y_{A_0} C_A^* + H} \frac{dC_A^*}{dx^*}\right] + h^2_{AB} C_A^* = 0 \tag{9}$$

The Thiele modulus h_{AB} is expressed in terms of the bulk diffusivity D_{AB_0}. The parameter $G = D_{AB_0}/C$ is a measure of the relative importance of bulk diffusion and Poiseuille flow; as Poiseuille flow becomes more important, C increases and G decreases. Similarly, $H = D_{AB_0}/D_{KA}$ defines the importance of bulk diffusion with respect to the Knudsen process; as H increases, Knudsen diffusion predominates.

The boundary conditions can be expressed as

$$C_A^* = P^* = 1 \quad \text{at} \quad x^* = 0 \tag{10}$$

$$\frac{dC_A^*}{dx^*} = \frac{dP^*}{dx^*} = 0 \quad \text{at} \quad x^* = 1 \tag{11}$$

The effectiveness factor is the average rate of reaction for the capillary divided by the rate at $x = 0$:

$$E = \frac{\int_0^L k_s C_A \pi a dx}{k_s C_{A_0} \pi a L} = \int_0^1 C_A^* dx^* \tag{12}$$

EFFECTIVENESS FACTORS FOR CAPILLARY

For $n = 1$, no pressure gradient exists, and the solution of Equations (8) to (12) is

$$E = \frac{\tanh h_{AB}\sqrt{1+H}}{h_{AB}\sqrt{1+H}} \tag{13}$$

This is the same as Scott's result (*4*). When Knudsen diffusion predominates, $H >> 1$ and $h_{AB}\sqrt{1+H} \doteq h_{KA}$. When bulk diffusion controls the process, H approaches zero.

When $n \neq 1$, but Knudsen diffusion predominates, H is large and Equation (9) reduces to

$$\frac{1}{H} \frac{d^2C_A^*}{dx^{*2}} = h_{AB}^2 C_A^*$$

or

$$\frac{d^2C_A^*}{dx^{*2}} = h_{KA}^2 C_A^* \tag{14}$$

This equation leads to the Thiele expression

$$E = \frac{\tanh h_{KA}}{h_{KA}} \tag{15}$$

There is a pressure gradient along the pore, as developed in (*1*), but this has no effect on E.

When the diffusion of A is not predominately Knudsen and $n \neq 1$, Equations (8) to (12) require numerical solution. This was done with an analogue computer for the following ranges of parameters:

y_{A_0}: 0.1 to 0.9

n: 0.01 to 9

$G = \frac{D_{AB_0}}{C}$: 0.01 to 1

$H = \frac{D_{AB_0}}{D_{KA}}$: 0.01 to 100

h_{AB}: 0.1 to 10

Since $C \geqq n^{1/2} D_{KA}$, the ratio G/H must be less than $n^{-1/2}$. This restriction limited the values of H and G.

For most conditions neither the pressure gradient nor the effect of n upon the effectiveness factor was large. Illustrative results where the effects were significant are presented in Figures 1 to 3. In Figure 1 pressure and concentration profiles are shown for two sets of conditions. The solid lines, for $G = 1$ and $H = 10$, represent a condition approaching Knudsen diffusion with little Poiseuille flow, that is a capillary of small diameter. The pressure and concentration gradients are both significant for this extreme case of $n = 9$. The dotted lines represent a case of intermediate diffusion and considerable Poiseuille flow. The pressure gradient is negligible, but the effectiveness factor would be expected to be reduced below that for $n = 1$.

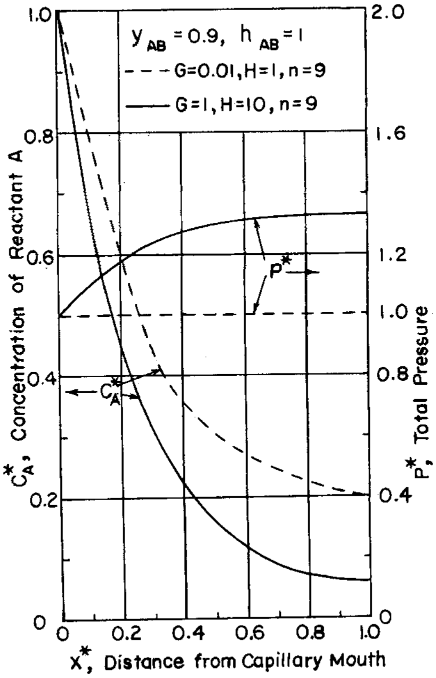

Fig. 1. Concentration and pressure profiles in a single capillary.

This effect on E is shown directly in Figure 2, where the same H and G values apply as for the dotted lines in Figure 1. It is evident that for these conditions of intermediate diffusion there is a significant decrease in effectiveness factor as n increases. The curve shown for $n = 1$ is essentially the same as the analytical solution [Equation (13)], thus verifying the computer technique. The spread in curves for different n values depends upon the diffusion and flow conditions.

This conclusion is illustrated in Figure 3. Here, for the same values of G and y_{A_0} as for Figure 2, the change in E with H is shown. The line for a specific n terminates at a minimum value of H corresponding to the limitation that $G/H \leqq n^{-1/2}$. The influence of the diffusion regime is clearly evident.

Increasing the mole fraction of A at the capillary mouth reduces the effectiveness factor when n is greater than unity. The decrease is not great and increases with the value of n. Parameter G by itself has little effect on E.

From this single capillary analysis an approximate criterion can be given regarding the importance of a change in moles on the effectiveness factor. If $H > 5$ and $n \leqq 2$, an important (more than 10%) reduction in E is unlikely. In general the effect of n upon E will not be significant for small pores or low pressures but could be for large pores at high pressures.

APPLICATION TO A BIDISPERSE

Catalyst Pellet

The effectiveness factor of a bidisperse catalyst pellet at constant pressure ($n = 1$) has been evaluated (5) in terms of the macro- and micropore sizes and void fractions. The essential feature of the method is that the mass transfer rate through the pellet is the sum of three contributions: a flux through the macropores, micropores, and a series mechanism involving both types of pores. The model is described in detail in reference 5 and has been shown to agree well with experimental rate data (2, 3). The same concepts can be used to develop equations analogous to Equations (3), (4), and (6) for a single capillary. This will be done for a spherical pellet.

The mass flux equation becomes

$$N_A = -\left[\frac{\epsilon_a^2 D_{AB}}{1-(1-n)y_A + \dfrac{D_{AB}}{\overline{D}_{KA_a}}} + \frac{\epsilon_i^2(1+3\epsilon_a)}{1-\epsilon_a} E_i \overline{D}_{KA_i} \right] \frac{dC_A}{dx} \qquad (16)$$

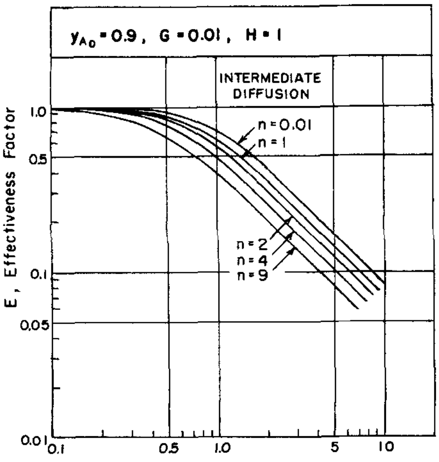

Fig. 2. Reduction in effectiveness factor vs. n for single capillary.

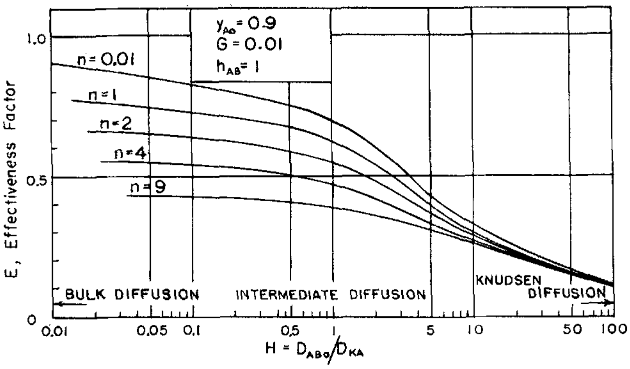

Fig. 3. Influence of diffusion regime on effectiveness factor.

where $\overline{D}_{KA_a}$ and $\overline{D}_{KA_i}$ are Knudsen diffusivities for A, evaluated for the mean macropore radius $\overline{a}_a$ and mean micropore radius $\overline{a}_i$, respectively. E_i is the effectiveness factor for the microporous particles from which the bidisperse pellet is made. Normally the particle size is so small that E_i is unity (5).

A mass balance of A in the pellet, analogous to Equation (3) for a capillary, is

$$\frac{1}{x^2}\frac{d}{dx}(x^2 N_A) + \rho\, k_m C_A = 0 \qquad (17)$$

Here the rate of reaction is expressed per unit mass of catalyst as

$$r_m = k_m\, C_A \qquad (18)$$

The flow equation, analogous to Equation (4), is

$$N_A\,(n - n^{1/2}) = \frac{C_e}{RT}\frac{dP}{dx} \qquad (19)$$

where C_e is the effective flow parameter for the pellet. By applying the bidisperse pore model, C_e was shown in Part II to be given by the expression

$$C_e = \epsilon_a^2\, C_a + \frac{\epsilon_i^2(1+3\epsilon_a)}{1-\epsilon_a} C_i \qquad (20)$$

where C_a and C_i are obtained from Equation (5). Thus taking $D_{KA} = \overline{D}_{KA_a}$ and $D_{KB} = \overline{D}_{KB_a}$ one gets C_a for the macropores, and $D_{KA} = \overline{D}_{KA_i}$ and $D_{KB} = \overline{D}_{KB_i}$ gives C_i for the micropores. Just as C for a single capillary did not change significantly along the capillary length, C_e can be regarded as constant within a given catalyst pellet.

Equations (16), (17), and (19) with boundary conditions establish the concentration and pressure profiles within the pellet. Combining these equations to eliminate N_A, and writing the results in dimensionless form, one obtains

$$\frac{1}{x^{*2}}\frac{d}{dx^*}\left[x^{*2}\left\{\frac{\epsilon_a^2}{P^* - (1-n)y_{A_0}C_A^* + H_a} + \frac{\epsilon_i^2(1+3\epsilon_a)}{(1-\epsilon_a)H_i}\right\}\frac{dC_A^*}{dx^*}\right] - h_e^2 C_A^* = 0 \qquad (21)$$

and

$$\frac{1}{x^{*2}}\frac{d}{dx^*}\left[x^{*2}\left(\frac{dP^*}{dx^*}\right)\right] + y_{A_0}\,(n - n^{1/2})G_e h_e^2 C_A^* = 0 \qquad (22)$$

with boundary conditions

$$C_A^* = P^* = 1 \text{ at } x^* = 1 \quad \text{(surface of pellet)} \tag{23}$$

$$\frac{dC_A^*}{dx^*} = \frac{dP^*}{dx^*} \text{ at } x^* = 0 \quad \text{(center of pellet)} \tag{24}$$

The effectiveness factor expression is

$$E = \frac{\int_0^L 4\pi x^2 C_A \rho k_m dX}{(4/3)\pi L^3 C_{A_o} \rho k_m} = 3 \int_0^1 C_A^* x^{*2} dx^* \tag{25}$$

The dimensionless parameters for the pellet, in addition to n and y_{A_o}, are

$$G_e = \frac{D_{AB_o}}{C_e} \tag{26}$$

$$H_a = D_{AB_o}/\overline{D}_{KA_a} \quad \text{(macropore } H\text{)} \tag{27}$$

$$H_i = D_{AB_o}/\overline{D}_{KA_i} \quad \text{(micropore } H\text{)} \tag{28}$$

$$h_e = L\sqrt{\frac{\rho k_m}{D_{AB_o}}} \tag{29}$$

Equations (21) to (25) can be solved by numerical techniques to obtain concentration and pressure profiles within the catalyst pellet and also the effectiveness factor. This was done with the aid of an analogue computer for various values of the parameters. Figure 4 illustrates the results for a case where the influence of n is important. The parameters were evaluated so as to correspond to a low-density, alumina, catalyst pellet operating at 1-atm. pressure and 25°C. For a reaction system of properties similar to the nitrogen-hydrogen system, C_e, D_{AB_o}, and D_{KN_2} would be such that the parameters would have the following approximate values: $G_e = 0.01$, $H_a = 0.1$, and $H_i = 10$. These conditions are such that the diffusion in the macropores is predominantly of the bulk type. Hence the pressure gradient within the pellet is not important as shown in the upper part of Figure 4. In contrast, these conditions should lead to the largest effect of n on the effectiveness factor. Figure 4 shows the results for $y_A = 0.5$. When $n = 2$, E is reduced less than 10% below the value for $n = 1$.

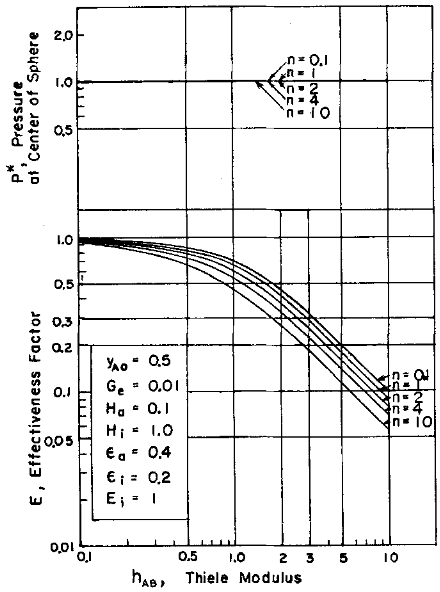

Fig. 4. Influence of *n* on effectiveness factor in a porous catalyst.

This illustration indicates that the influence of a change in moles on the effectiveness factor would be less than 10% for most conditions. Only when n is large and the pore diffusion is of the bulk type will significant effects occur.

ACKNOWLEDGMENT

This work in part was supported by a grant from the National Science Foundation. The assistance of Mr. Kouichiro Ando and Mr. Takeya Yamamoto, Toyo Rayon Company, Ltd., in the computer calculations is acknowledged.

NOTATION

A, B = reactant and product components
C_A^* = C_A/C_{A_o}
E = effectiveness factor for capillary or pellet; E_i = effectiveness factor for microporous particle
G = Poiseuille flow parameter for capillary, D_{AB_o}/C
G_e = effective Poiseuille flow parameter for porous catalyst, D_{AB_o}/C_e
H = relative diffusion parameter, D_{AB_o}/D_{KA}
H_a = relative diffusion parameter in macropores of catalyst, $D_{AB_o}/\overline{D}_{KA_a}$
H_i = relative diffusion parameter in micropores of catalyst, $D_{AB_o}/\overline{D}_{KA_i}$
h_{AB} = Thiele modulus for capillary, $L\left(\frac{2k_s}{aD_{AB_o}}\right)^{1/2}$
h_{KA} = Thiele modulus for capillary, based upon Knudsen diffusivity, $L\left(\frac{2k_s}{aD_{KA}}\right)^{1/2}$
h_e = Thiele modulus for catalyst pellet, defined by Equation (29)
k_s = first-order, rate constant for capillary, cm./sec.
k_m = first-order, rate constant for porous catalyst, cc./(g.)(sec.)
L = half-length of capillary, or radius of spherical catalyst pellet, cm.
n = moles of product per mole of reactant
P = total pressure, atm.
P^* = P/P_o
r = rate of reaction per unit surface in capillary, g. moles/(sec.)(sq.cm.)
r_m = rate of reaction per unit mass in catalyst pellet, g. moles/(sec.)(g.)
x = distance measured from mouth of capillary, or radial distance from center of spherical catalyst pellet, cm.
x^* = x/L
y = mole fraction; y_{A_o} = mole fraction of A at mouth of capillary, or surface of spherical catalyst pellet
ρ = density of catalyst pellet, g./cc.
o = mouth of pore, or surface of catalyst pellet

LITERATURE CITED

1. Otani, S., N. Wakao, and J. M. Smith, *A.I.Ch.E. Journal*, **10**, 130 (1964).
2. Rao, M. R., and J. M. Smith, *ibid.*, **9**, 485 (1963).
3. ———, N. Wakao, and J. M. Smith, *Ind. Eng. Chem. (Fundamentals)*, **3**, 127 (1964).
4. Scott, D. S., *Can. J. Chem. Eng.*, **40**, 173 (1962).
5. Wakao, N., and J. M. Smith, *Ind. Eng. Chem. (Fundamentals)*, **3**, 123 (1964).

Manuscript received June 24, 1964; revision received October 12, 1964; paper accepted October 15, 1964.