The Effectiveness of Diluted Porous Catalysts

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Beginning with Thiele's classical paper (*1*) a large number of works have been devoted to the calculation of the effectiveness of porous catalysts. Only a few of them will be quoted here (*2* through *12*). The effectiveness depends on the diffusion coefficient of the reactants through the pores and on the surface reaction rate constants. If the diffusion coefficient through the porous structure is very small, the effectiveness is small. It is possible, at least in principle, to increase the value of this quantity by introducing small particles of active catalyst into an inert porous solid which (though inactive from a chemical point of view) has a much larger value of the diffusion coefficient. It is the aim of this communication to show that such situations are possible.

Let us consider a nonhomogeneous spherical particle, consisting of small spherical particles of active porous catalyst included into a porous inactive solid. The problem is similar from a formal point of view to that of the effectiveness of a pellet having a distribution of pores (*3*). Two scales will be considered in the description of the diffusion processes taking place in this nonhomogeneous system: a large scale for the diffusion process taking place in the inert solid medium, and a small scale for the diffusion accompanied by a chemical reaction which takes place in each small active porous medium. The large scale will be considered sufficiently great compared to the dimension of the small particles, but also sufficiently small compared to the radius of the nonhomogeneous sphere.

For the process taking place at the large scale it is therefore possible to write:

$$\frac{d\left(D_0 4\pi r^2 \dfrac{dc}{dr}\right)}{dr} = 4\pi r^2 m\, D_1 \left(\frac{dn}{dr_1}\right)_{r1=a} 4\pi a^2 \qquad (1)$$

Equation (1) is valid only if mv is smaller than the value corresponding to the most compact structure of the small spheres.

Considering a first-order reaction and assuming for the time being isothermic conditions, one may write for the diffusion process accompanied by a chemical reaction which takes place in the small particles:

$$D_1 \frac{d}{dr_1}\left(4\pi r_1^2 \frac{dn}{dr_1}\right) = 4\pi r_1^2\, k\, n \qquad (2)$$

Equation (2) must be solved for the boundary condition

$$n = n_0 \quad \text{for} \quad r_1 = a \qquad (3)$$

The usual change of variable $N = nr_1$ permit the transformation of Equation (2) into

$$D_1 \frac{d^2N}{dr_1^2} = kN \qquad (4)$$

the solution of which leads to

$$n = \frac{an_0}{r_1} \; \frac{sh\; r_1 \sqrt{\dfrac{k}{D_1}}}{sh\; a \sqrt{\dfrac{k}{D_1}}} \qquad (5)$$

It will be assumed that the concentration c in the inert medium is proportional to the concentration n_0.

$$n_0 = H\, c \qquad (6)$$

H being a proportionality constant.

Equation (5) becomes

$$n = \frac{a\, H\, c}{r_1} \; \frac{sh\; r_1 \sqrt{\dfrac{k}{D_1}}}{sh\; a \sqrt{\dfrac{k}{D_1}}} \qquad (7)$$

Consequently,

$$\left(\frac{dn}{dr_1}\right)_{r1=a} = \frac{Hc}{a}\left[a\sqrt{\frac{k}{D_1}}\left(cth\; a\sqrt{\frac{k}{D_1}}\right) - 1\right] \equiv \frac{H\, E\, c}{a} \qquad (8)$$

Eliminating $\left(\dfrac{dn}{dr_1}\right)_{r1=a}$ between Equations (1) and (8),

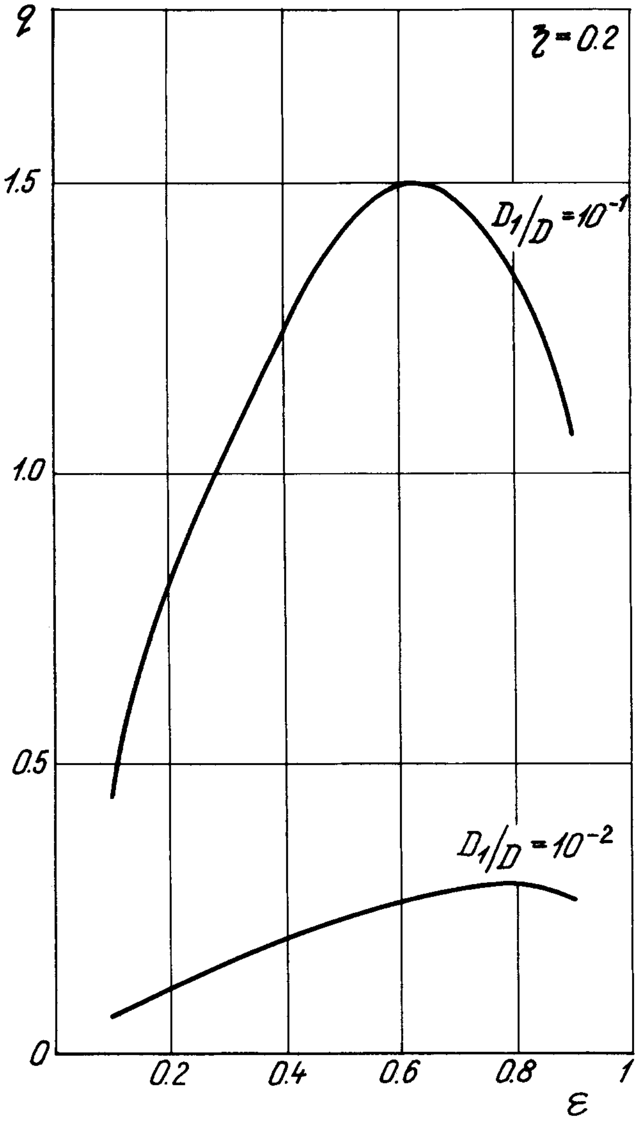

Fig. 1. Dimensionless total reaction rate (q) vs. the fraction of the volume occupied by active particles (ε). R = 0.5 cm., $a = 10^{-2}$ cm., $H = 1$.

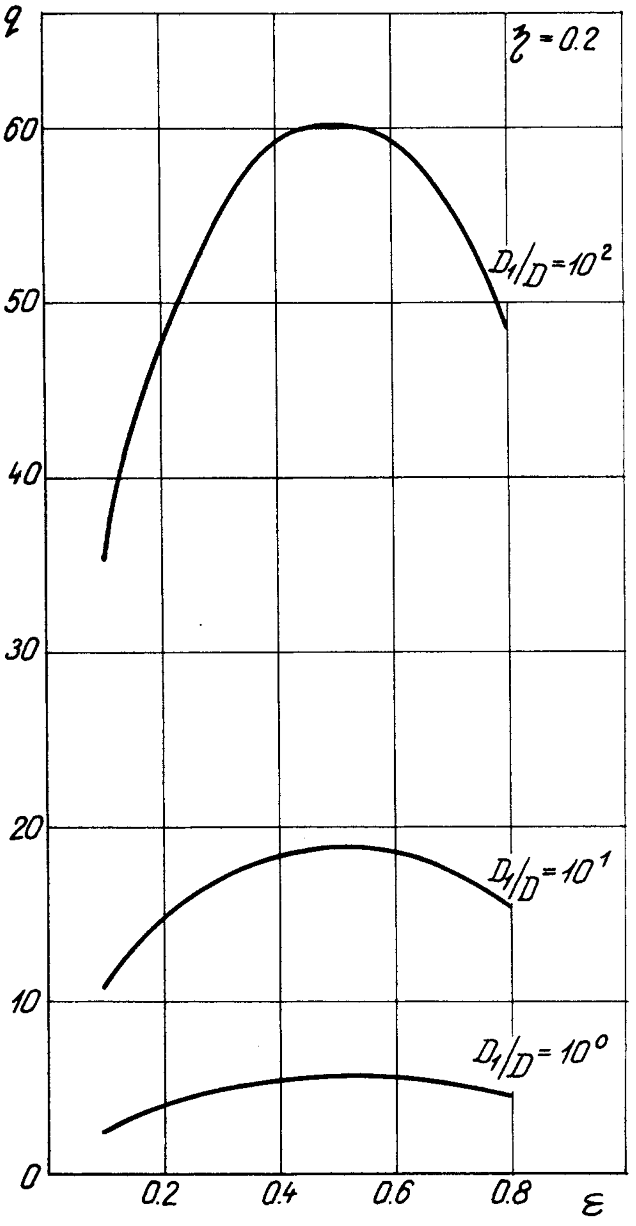

Fig. 2. Dimensionless total reaction rate ***(q)*** **vs. the fraction of the volume occupied by active particles (ε).** $R = 0.5$ **cm.,** $a = 10^{-2}$ **cm.,** $H = 1$.

one obtains

$$\frac{d\left(D_0 r^2 \dfrac{dc}{dr}\right)}{dr} = 4\pi r^2 m a D_1 H E c \tag{9}$$

Equation (9) must be solved for the boundary condition

$$c = c_0 \quad \text{for} \quad r = R \tag{10}$$

The solution is:

$$\frac{c}{c_0} = \frac{R}{r}\;\frac{sh\; r\sqrt{4\pi a m H E\dfrac{D_1}{D_0}}}{sh\; R\sqrt{4\pi a m H E\dfrac{D_1}{D_0}}} \tag{11}$$

The total reaction rate in the nonhomogeneous particle results from

$$Q = 4\pi R^2\, D_0\left(\frac{dc}{dr}\right)_{r=R} = 4\pi R c_0 D_0 \left\{R\sqrt{4\pi a m H E\frac{D_1}{D_0}}\left(cthR\sqrt{4\pi a m H E\frac{D_1}{D_0}}\right) - 1\right\} \tag{12}$$

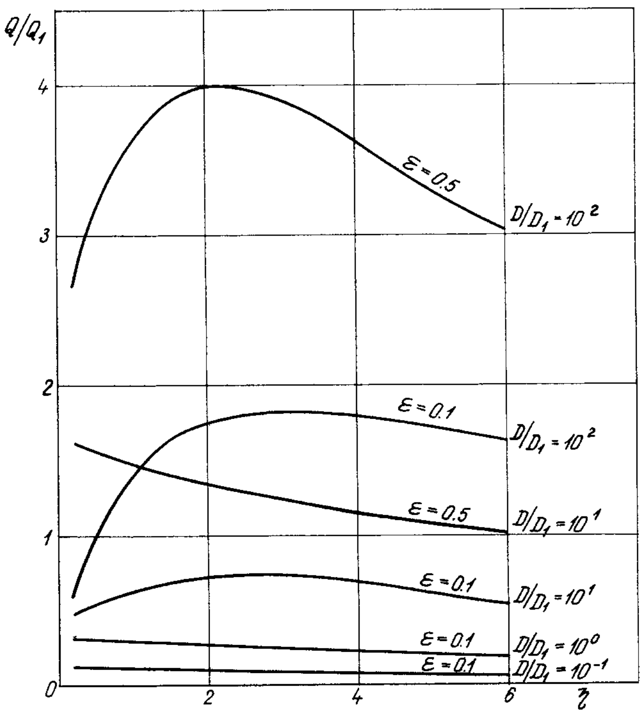

Fig. 3. Ratio between total reaction rate in the diluted particle and total reaction rate in a particle having the same radius but formed only of active material vs. Thiele's modulus (η). $R = 0.5$ **cm.,** $a = 10^{-2}$ **cm.,** $H = 1$.

For the analysis of the effect of the fraction of active volume ε on the total reaction rate, it is necessary to take into account the dependence of the physical quantities on ε. Because only a fraction of the surface $4\pi r^2$ is available for diffusion, we shall write for the mass flux the expression

$$D(1-\epsilon)\, 4\pi r^2 \frac{dc}{dr} \tag{13}$$

where D is the diffusion coefficient in the inert material free of active catalyst. Equation (13) is an approximate one, since along the radius r only some regions are available for diffusion in the inert medium, and the gradient of concentration dc/dr does not take this fact into account.

For obtaining the dependence of Q on ε it is sufficient to replace D_0 by $D(1-\epsilon)$. One obtains

$$Q = 4\pi R c_0 D(1-\epsilon)\left\{R\sqrt{\frac{4\pi\, a\, \epsilon\, HED_1}{v(1-\epsilon)D}}\; cth\left(R\sqrt{\frac{4\pi\, a\, \epsilon\, HED_1}{v(1-\epsilon)D}}\right) - 1\right\} \tag{14}$$

In Equation (14) it was taken into account the fact that $mv = \epsilon$.

To illustrate let us consider $R = 0.5$ cm., $a = 10^{-2}$ cm., $a\sqrt{\dfrac{k}{D_1}} = 0.2$ and $H = 1$. For $q \equiv Q/4\pi R c_0 D$ one obtains in this case the curves from Figures 1 and 2.

It is however more important to compare the values of Q given by Equation (14) with the total reaction rate Q_1 taking place in a particle having the same radius as the first, but formed only of active material.

For Q_1 the following is valid

$$Q_1 = 4\pi R\, D_1\, c_0 \left[R\sqrt{\frac{k}{D_1}}\left(cth\; R\sqrt{\frac{k}{D_1}}\right) - 1 \right] \qquad (15)$$

The ratio Q/Q_1 is given therefore by

$$\varphi \equiv \frac{Q}{Q_1} = \frac{D}{D_1}\; \frac{(1-\epsilon)\left[R\sqrt{\dfrac{4\pi\, a\, \epsilon\, HED_1}{v(1-\epsilon)D}}\; cth\left(R\sqrt{\dfrac{4\pi\, a\, \epsilon\, HED_1}{v(1-\epsilon)D}}\right) - 1\right]}{R\sqrt{\dfrac{k}{D_1}}\; cth\left(R\sqrt{\dfrac{k}{D_1}}\right) - 1} \qquad (16)$$

For illustration purposes we shall take $R = 0.5$ cm., $a = 10^{-2}$ cm., $H = 1$. In Figure 3, Q/Q_1 is plotted as a function of $a\sqrt{k/D_1}$ for various values of D/D_1 and for two values of ϵ.

From this figure one may conclude that in some conditions the diluted catalyst particle may be more active than a catalyst particle having the same radius and formed only from active material.

It is also possible to show that there exists an optimum value for ϵ.

We notice that a similar idea has been extended to the nonisothermic case and has been used in connection with adsorption and with ion exchange (*13*).

ACKNOWLEDGMENT

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NOTATION

a = the radius of a small active particle
c = concentration in the inert medium; c_0—value of c for $r = R$
D = diffusion coefficient in the particle formed only of inert material
D_0 = diffusion coefficient in the inert medium of the heterogeneous particle
D_1 = diffusion coefficient in the small active particle
E = quantity defined by Equation (8)
H = equilibrium constant defined by Equation (6)
k = surface reaction rate constant
m = number of particles per volume unit
n = concentration in the small particles; n_0—value of n for $r_1 = a$
q = $Q/4\pi R\, c_0 D$
Q = total reaction rate in the diluted particle [defined by Equation (14)]
Q_1 = total reaction rate in a particle formed only of active material and having the same radius as the diluted particle
r = distance at the center of the large sphere
r_1 = distance at the center of the small sphere
R = the radius of the nonhomogeneous particle
v = the volume of the small sphere
ϵ = the fraction of volume occupied by active particles
η = $a\sqrt{k/D_1}$
φ $\equiv Q/Q_1$

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On Transient Heat Transfer in a Porous Medium

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In a recent communication, Kohlmayr (*1*) derived infinite series solutions to a transient heat transfer problem which are computationally more useful than Schumann's (*2*) solution. Kohlmayr used a double Laplace transform method to obtain a transform which was expanded into infinite series using a binomial expansion, and he used a term-by-term inversion to obtain infinite series solutions. He then demonstrated convergence of the series by giving two sequences of upper and lower bounds with some numerical demonstrations and concluded that it was no longer necessary to resort to finite-difference methods when computing theoretical response functions.

The purposes of this communication are twofold: to show that the infinite series solutions and two sequences of bounds given by Kohlmayr follow naturally from the two forms of integral (analytical) solutions which are obtained directly from the inversion of the transform and hence avoids the laborious analysis given by Kohlmayr, and to bring attention to a large number of pertinent literature which was not cited by Kohlmayr. Some of these give, by various methods, either one or the other form of the integral solution given here and also the infinite series solutions of Kohlmayr. Hence, it had not been necessary to resort to finite-difference methods since the appearance of these references.

In addition to those references given by Kohlmayr (*1*),