Concentration Distribution, Effectiveness Factor, and Reactant Exhaustion for Catalytic Reaction with Volume Change

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Analytic expressions for the concentration distribution of reactant and for effectiveness factor have been obtained for zero-order catalytic reactions of the type $A \longrightarrow bB$. They can be summarized for various physical forms of catalyst to be

$$\ln \frac{1 + mC}{1 + m} = -M_j \left\{ f(\xi) - \frac{g(\xi)}{g(\xi_e)} \cdot h\left(\xi_e, \frac{K_e}{K}\right) \right\}$$

and

$$\eta' = 1 + h\left(\xi_e, \frac{K_e}{K}\right) \Big/ 2g(\xi_e) = 1 - \xi_e^j$$

where $f(\xi)$, $g(\xi)$, $h\left(\xi_e, \frac{K_e}{K}\right)$, and M_j are differently defined for thin-disk ($j = 1$), infinite-cylinder ($j = 2$), and spherical ($j = 3$) geometries. The results are also presented graphically for rapid calculation of these quantities. The phenomenon of reactant exhaustion associated with a zero-order reaction and the criteria for its occurrence are also discussed.

Ever since the concept of effectiveness factor was first introduced by Sir James Jeans (*15*) and further developed by Thiele (*23*), Wheeler (*30*), and Aris (*1*), this subject has been studied by a number of investigators, both theoretically and experimentally (*2*, *3*, *6* to *13*, *16* to *22*, *24* to *29*). With the advent of the electronic digital computer, virtually no problem remains unsolved. However, due to the ease and the increasing use of numerical methods, we have often neglected or abandoned our attempt to obtain analytical solutions which generally offer better insight into the problem and solution.

This paper describes the analytical solutions of cases heretofore thought to be impossible. By the proper use of transformation of variables, the effectiveness factors for the zero-order reaction

$$A \longrightarrow bB \tag{1}$$

occurring in the pores of cylindrical and spherical catalyst particles, as well as thin disks, can be obtained. The reactant exhaustion phenomenon associated with this zero-order reaction will also be discussed.

It should be noted that in an important piece of previous work (*26*), the case of a spherical particle has been solved both numerically and asymptotically. In the latter method an approximation was made such that the starting equation became identical to that for thin-disk geometry. In that case, solutions for effectiveness factors for zero-, first-, and second-order reactions were obtained. Even so, the mathematical procedure employed was such that the difficult task of obtaining concentration distribution itself was bypassed. In our present work the difficulty has been overcome and a complete set of expressions for pertinent quantities is tabulated and similarities compared.

PROBLEM FORMULATION

In solving any problem in the physical sciences, two types of equations are usually required. One, the conservation equation, or the equation of change, describes the system, while the other, the constitutive equation, or the equation of state, describes the properties of the material involved.

In our present case, the equation of change is the steady state equation of continuity (*4*)

$$(\nabla \cdot \mathbf{N}_A) = R_A \tag{2}$$

where $\mathbf{N}_A$ is the total molar flux (diffusional plus bulk flow) of species A, and R_A the molar rate of production of A. For the general case of an n^{th}-order reaction

$$R_A = -kac_A^n \tag{3}$$

The negative sign exists since A is being consumed rather than produced.

The equation of state for this case is Fick's law of diffusion, which, in terms of the total molar fluxes $\mathbf{N}_A$ and $\mathbf{N}_B$, mole fraction x_A, and total molar concentration c of the mixture, is (5)

$$\mathbf{N}_A - x_A(\mathbf{N}_A + \mathbf{N}_B) = -c\mathcal{D}_{\text{eff}} \nabla x_A \tag{4}$$

Taking note of the stoichiometric equation [Equation (1)], we have $\mathbf{N}_B = -b\mathbf{N}_A$, which, when substituted into Equation (4), gives

$$\mathbf{N}_A = -\frac{c\mathcal{D}_{\text{eff}}}{1 + (b-1)x_A} \nabla x_A \tag{5}$$

Now, combining Equations (2), (3), and (5) and defining

$$C = \frac{c_A}{c_{A_s}} = \frac{x_A}{x_{A_s}}$$

and

$$m = (b-1)x_{A_s}$$

where subscript s denotes properties at the exterior surface, we have, after further mathematical expansion and manipulation

$$\nabla^{*2} C - \frac{m}{1+mC}(\nabla^* C \cdot \nabla^* C) = K^2(1+mC)C^n \tag{6}$$

In the equation

$$K = R\sqrt{\frac{kac_{A_s}^{n-1}}{\mathcal{D}_{\text{eff}}}}$$

and is the "generalized Thiele modulus," while $\nabla^* = R\nabla$, is the dimensionless differential operator.

SPHERICAL CATALYST PELLETS

For the spherical case, Equation (6) is reduced to

$$\frac{1}{\xi^2}\frac{d}{d\xi}\left(\xi^2 \frac{dC}{d\xi}\right) - \frac{m}{1+mC}\left(\frac{dC}{d\xi}\right)^2 = K^2(1+mC)C^n \tag{7}$$

If we let $u = 1 + mC$ we have (8)

$$\frac{1}{\xi^2}\frac{d}{d\xi}\left(\xi^2 \frac{du}{d\xi}\right) - \frac{1}{u}\left(\frac{du}{d\xi}\right)^2 = K^2 m^{1-n} u(u-1)^n \tag{9}$$

If we further make the transformation of variables

$$v = \frac{1}{u}\frac{du}{d\xi} \tag{10}$$

a much simplified equation results:

$$\frac{dv}{d\xi} + \frac{2v}{\xi} = A(u-1)^n \tag{11}$$

If we now confine ourselves to solving this equation for a zero-order reaction ($n = 0$), Equation (11) becomes

$$\frac{dv}{d\xi} + \frac{2v}{\xi} = A \tag{12}$$

with

$$A = K^2 m \tag{13}$$

The solution to Equation (12) can be easily obtained as

$$v = \frac{A\xi}{3} + \frac{S_1}{\xi^2}$$

which, upon substituting Equation (10), solving for u, and substituting Equation (8), gives

$$\ln(1+mC) = \frac{A\xi^2}{6} - \frac{S_1}{\xi} + S_2 \tag{14}$$

where S_1 and S_2, the integration constants, are to be determined from the boundary conditions.

At this point, two different cases can be considered, as represented by two different sets of boundary conditions. In the first case, the reactant is exhausted before reaching the center of the sphere. This reactant exhaustion phenomenon is unique among zero-order reactions. For higher-order reactions the reaction rate will decrease with decreasing reactant concentration in such a way that the rate will approach zero *before* the reactant runs out. For the zero-order reaction, the rate remains constant *until* the reactant is exhausted. In the critical case, the reactant will be exhausted *just as* it reaches the center of the sphere. This is the borderline between reactant exhaustion and nonexhaustion, which is the second case we will consider.

REACTANT EXHAUSTED

The boundary conditions for this case are

B.C.1. at $\xi = 1$, $C = 1$
B.C.2. at $\xi = \xi_e$, $C = 0$

where ξ_e is the dimensionless radial distance from the center within which there is no reactant because reactant has been exhausted before reaching that point. The application of these boundary conditions yields the following expression:

$$\ln\frac{1+mC}{1+m} = -m\left\{\frac{K^2}{6}(1-\xi^2) - \frac{1-\frac{1}{\xi}}{1-\frac{1}{\xi_e}}\left[\frac{K^2}{6}(1-\xi_e^2) - \frac{\ln(1+m)}{m}\right]\right\} \tag{15}$$

According to definition, the effectiveness factor for the spherical case should be, generally, for n^{th}-order reaction

$$\eta' = \frac{4\pi R^2 \cdot N_{A_r}|_{r=R}}{\frac{4}{3}\pi R^3(-kac_{A_s}^n)} \tag{16}$$

where the prime denotes a quantity for reactions with volume change as distinguished from those without. Noting Equation (5) and reexpressing in dimensionless form, we obtain

$$\eta' = \frac{3\left(\frac{dC}{d\xi}\right)'_{\xi=1}}{K^2(1+m)} \tag{17}$$

Incidentally, the effectiveness factor for reactions without volume change can be deduced from this by making $m = 0$ while removing the prime:

$$\eta = \frac{3}{K^2}\left(\frac{dC}{d\xi}\right)_{\xi=1}$$

so that the effect of the volume change can be expressed in terms of the ratio

$$\frac{\eta'}{\eta} = \frac{1}{1+m}\left(\frac{dC}{d\xi}\right)'_{\xi=1} \Big/ \left(\frac{dC}{d\xi}\right)_{\xi=1} \tag{18}$$

Differentiating Equation (15) and using it in Equation (17), we have

$$\eta' = 1 + \frac{\frac{1}{2}(1 - \xi_e^2) - \frac{3}{K^2} \cdot \frac{\ln(1+m)}{m}}{1 - \frac{1}{\xi_e}} \tag{19}$$

or

$$\eta' = 1 - \xi_e \left[\frac{1 + \xi_e}{2} - \frac{3}{K^2(1 - \xi_e)} \cdot \frac{\ln(1+m)}{m} \right] \tag{19a}$$

This equation is shown in two different forms because the first one can be shown to be similar to those for cylindrical and thin-disk geometries, while the second one can be easily seen to be reducible to the special case worked out by Weekman and Gorring (*26*) for no volume change. This will be further discussed in a later section.

Equation (19) can be simplified if we find the relationship between K and ξ_e by requiring that $dC/d\xi = 0$ at $\xi = \xi_e$ since the concentration, and thus the concentration gradient, of the reactant must gradually diminish as it nears the point of exhaustion. Again, from Equation (15) this gives us

$$K^2 = \frac{3 \frac{\ln(1+m)}{m}}{(1 - \xi_e)\left[\frac{1}{2}(1 + \xi_e) - \xi_e^2\right]} \tag{20}$$

which, when substituted into Equation (19), yields

$$\eta' = 1 - \xi_e^2 \tag{21}$$

Equation (21) is exactly the same as that for the no-volume-change case (*26*), while Equation (20) differs from its counterpart only by the factor $\left(\frac{\ln(1+m)}{m}\right)$.

REACTANT NOT EXHAUSTED

When the combination of particle size, reaction, and diffusion rates is such that the reactant will *not* be completely spent when it reaches the center, the boundary conditions are

$$\text{B.C.1} \qquad \text{at} \quad \xi = 1, \quad C = 1$$

$$\text{B.C.2} \qquad \text{at} \quad \xi = 0, \quad \frac{dC}{d\xi} = 0$$

The particular solution to Equation (14) then becomes

$$\ln \frac{1 + mC}{1 + m} = -m \frac{K^2}{6}(1 - \xi^2) \tag{22}$$

which, when used in Equation (17), gives

$$\eta' = 1$$

This result is entirely reasonable, since now all of the porous surface areas are used for the reaction and, although there is a reactant concentration decline toward the center, the reaction rate does not depend on the concentration and is uniform everywhere. For this situation the effectiveness factor should naturally be unity.

The criterion for whether or not the reactant will be exhausted before reaching the center can be established by requiring $\xi_e = 0^+$ in Equation (20), which gives

$$K_e = \sqrt{6 \frac{\ln(1+m)}{m}} \tag{23}$$

This means that if $K < K_e$, the diffusion is so efficient, the available catalytic surface area so small, the surface concentration so large, particle size so small, and/or catalytic reaction so slow, we will have no logistical problem in continually supplying the reactant for the reaction, in which case $\eta' = 1$. On the other hand, if $K > K_e$, the supply will run short because of slow diffusion, small surface concentration, excessively large particle size, large available catalytic surface area, and/or rapid consumption (reaction). In other words, $\xi_e > 0$, which means that the inner part of the spherical particle with radius equal to ξ_e will never be used at all for the reaction. This criterion will also tell us such things as how to choose the proper particle size once the diffusional and reaction constants are set.

With Equation (23), Equations (15), (19), and (20) can be rewritten as

$$\ln \frac{1 + mC}{1 + m} = -\frac{K^2 m}{6}\left\{(1 - \xi^2) - \frac{1 - \frac{1}{\xi}}{1 - \frac{1}{\xi_e}}\left[(1 - \xi_e^2) - \left(\frac{K_e}{K}\right)^2\right]\right\} \tag{24}$$

$$\eta' = 1 + \frac{1}{2} \frac{(1 - \xi_e^2) - \left(\frac{K_e}{K}\right)^2}{1 - \frac{1}{\xi_e}} \tag{25}$$

and

$$K^2 = \frac{K_e^2}{(1 - \xi_e)\left[(1 + \xi_e) - 2\xi_e^2\right]} \tag{26}$$

TABLE 1. GENERALIZED EXPRESSION FOR THE CONCENTRATION PROFILES, THIELE MODULUS, AND EFFECTIVENESS FACTOR FOR VARIOUS GEOMETRIES, ZERO-ORDER REACTION

Reactant exhausted at ξ_e (K K_e):

$$\ln \frac{1 + mC}{1 + m} = -M_j \left\{ f(\xi) - \frac{g(\xi)}{g(\xi_e)} \cdot h\left(\xi_e, \frac{K_e}{K}\right) \right\}$$

$$\left(\frac{K}{K_e}\right)^2 = \frac{1}{2\xi_e^j \cdot g(\xi_e) + f(\xi_e)}$$

$$\eta' = 1 + \frac{h(\xi_e, K_e/K)}{2g(\xi_e)} = 1 - \xi_e^j$$

Reactant not exhausted (K K_e):

$$\ln \frac{1 + mC}{1 + m} = -M_j \cdot f(\xi)$$

where

$$f(\xi) = 1 - \xi^2$$

$$h\left(\xi_e, \frac{K_e}{K}\right) = f(\xi_e) - \left(\frac{K_e}{K}\right)^2$$

$$K_e = \sqrt{2j \frac{\ln(1+m)}{m}}$$

$$M_j = \frac{mK^2}{2j}$$

and

	Thin disk	Infinite cylinder	Sphere
$g(\xi)$	$\xi - 1$	$\ln \xi$	$1 - 1/\xi$
j	1	2	3

†Note that Equation (22) can also be obtained by imposing this condition on Equation (15).

THIN-DISK AND CYLINDRICAL GEOMETRIES

Following a similar procedure, one can work out equivalent quantities for thin disks and infinite cylinders. The results are shown to vary from thin-disk to cylindrical and then to spherical geometries in a highly systematic manner. We can summarize them into a single set of generalized equations while defining specific factors or terms for the different geometries, as shown in Table 1.

GRAPHICAL REPRESENTATION

The concentration profiles for the thin-disk, infinite-cylinder, and spherical geometries can be plotted at various m and ξ_e for the cases of $K > K_e$ (with reactant exhaustion), and at various m and K for the cases of $K < K_e$ (without reactant exhaustion) using formulas generated from Table 1. For the sake of brevity we only select a few here (Figures 1, 2, 3) to show the effect of geometry, volume-change modulus m, reactant exhaustion radius ξ_e, and Thiele modulus K. Other charts can be similarly drawn.

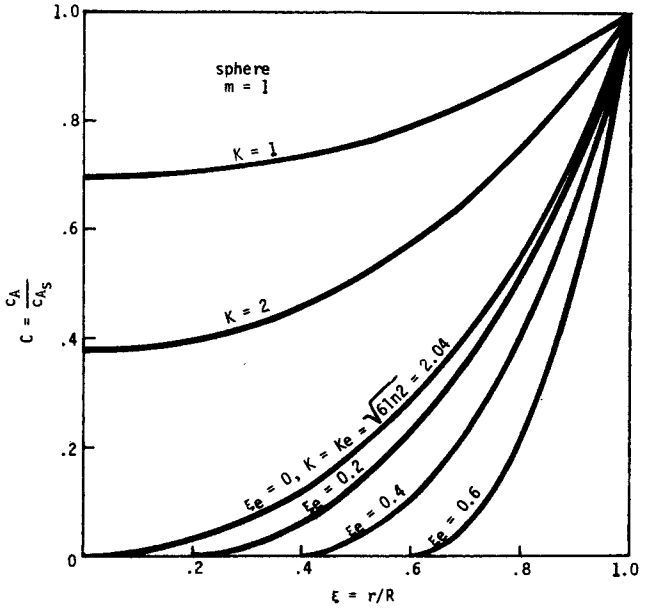

Fig. 1. Concentration profiles at various Thiele moduli and exhaustion radii; zero-order reaction with volume change.

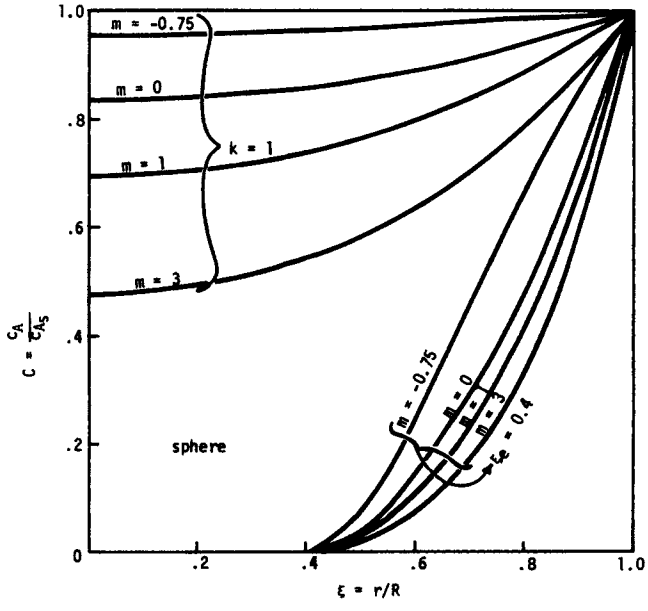

Fig. 2. Effect of volume-change modulus on concentration profile; zero-order reaction.

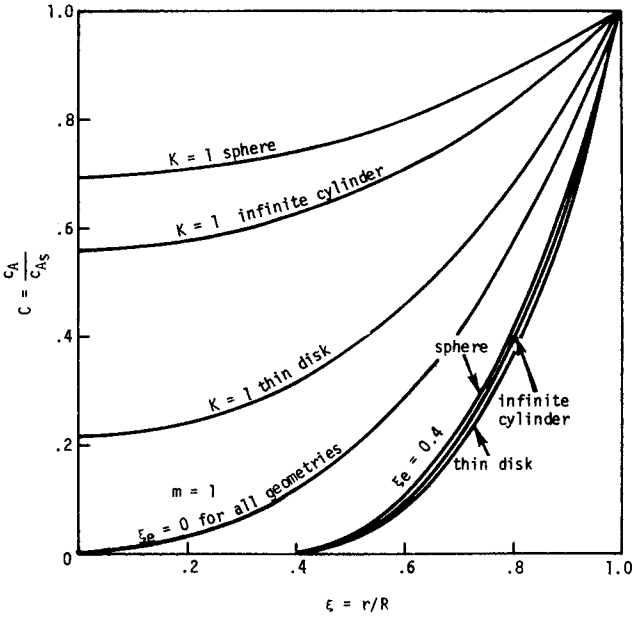

Fig. 3. Effect of geometry on concentration profile; zero-order reaction. Note the significant effect at the same Thiele modulus but relatively small effect at the same exhaustion radius. Also note that when the reactant is barely exhausted at the center, $\xi_e = 0$, curves for all geometries converge to $C = 2\xi^2 - 1$. But this means different K's for the various geometries.

Effectiveness factors for the various geometries are plotted in Figures 4*a*, *b*, and *c*. In these graphs we have incorporated ξ_e into the traditional η' versus K chart. This way we can obtain η' from K and m, or from ξ_e alone. In addition, we can also interrelate ξ_e and K through the two sets of curves, as indicated by the dotted lines on the chart and explained in the caption of Figure 4*a*.

DISCUSSIONS

The expressions developed are strictly theoretical and thus should be applicable and exact for the conditions prescribed. As a verification, the graphical representation given herein for the spherical particle has been found to agree with that obtained by numerical solution (*26*). Furthermore, by setting $m = 0$, the expressions for spherical geometry can be shown to reduce to those for no volume change [Equations (13) to (17); *25*] if we note that

$$\lim_{m\to 0}\left\{\frac{\ln(1+m)}{m}\right\} = 1 \quad \text{and} \quad \lim_{m\to 0}\left\{\frac{\ln\dfrac{1+mC}{1+m}}{m}\right\} = C - 1$$

To show the advantage offered by the analytic solutions we can quickly calculate, for example, the maximum particle size to maintain an η' of unity. Knowing the stoichiometry (m) and exact geometry, we can compute K_e using the proper formula. Then by knowing k, $\mathfrak{D}_{\text{eff}}$, and a, we can promptly find out the upper limit of R before K reaches a value of K_e. Moreover, summarizing and sectioning these expressions make computer programming much more systematic and easier.

It is of interest but should not be surprising to note in Table 1 that the different quantities for the different geometries are in their characteristic forms. For example, it is well known that the second derivative

$$\frac{1}{\xi^{j-1}} \frac{d}{d\xi}\left(\xi^{j-1} \frac{du}{d\xi}\right)$$

is characteristic of thin-disk, cylindrical, or spherical geometry, depending on whether $j = 1$, 2, or 3, respectively. Moreover, the logarithmic function for $g(\xi)$ is usually expected for cylindrical geometry. It is equally well known that solutions for thin-disk (or infinite-plate) and spherical geometries under otherwise identical conditions differ only by a factor ξ, as is the present case.

We look forward to being able to solve analytically similar problems for more complex geometries, such as finite cylinders, as well as for nonzero-order reactions. We further believe that we will then find the entire set of equations highly systematic, with the "general" equations in Table 1 only special cases (such as for $n = 0$, $L = \infty$, with L being the length of the cylinder) for the even more (and truly) general equations. Irregular geometries should be able to be accounted for by using the equivalent radius (*1*) in place of the regular circular radius $R_{eq} = 3V/S$, where V and S are, respectively, the volume and external surface

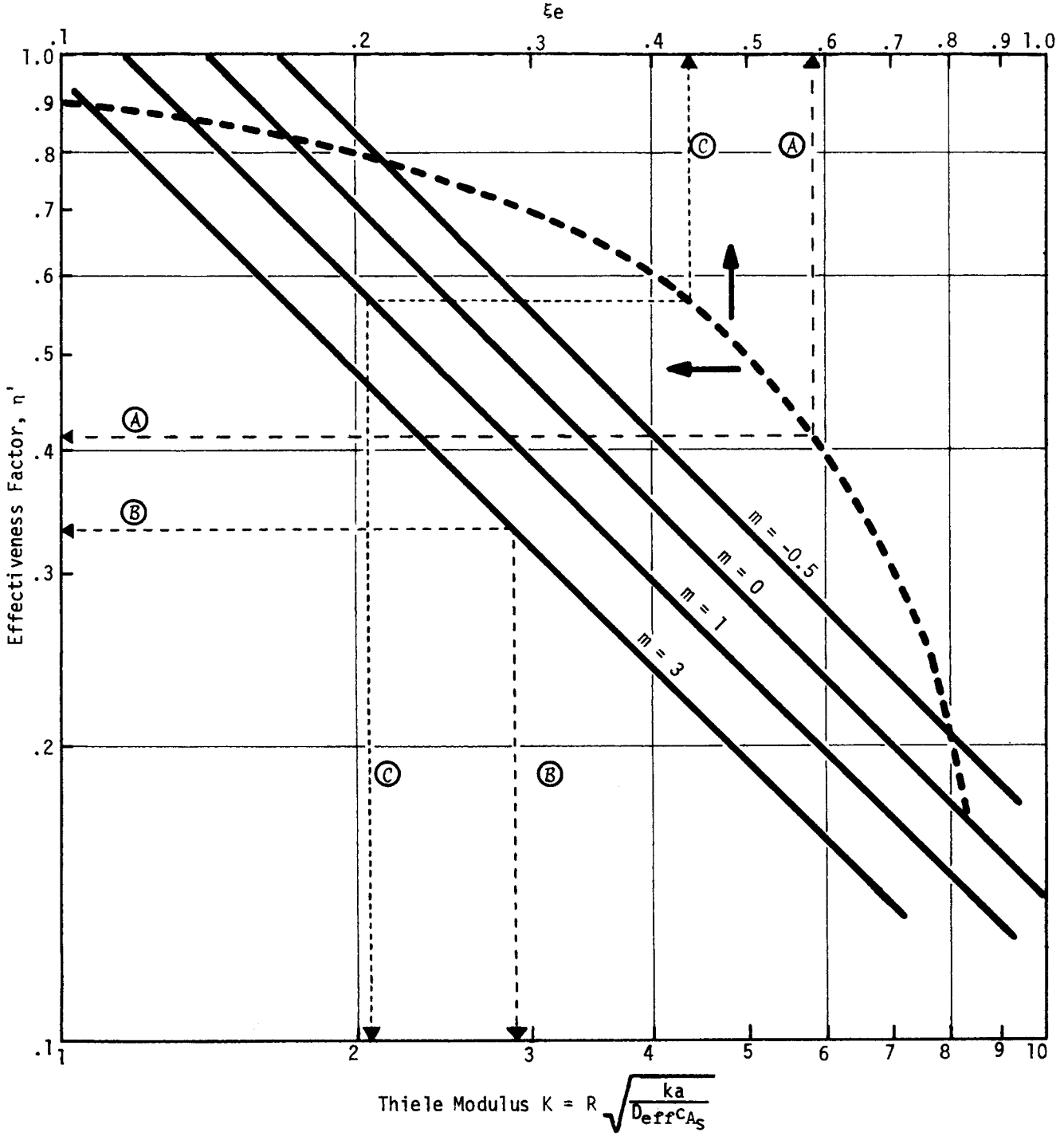

Fig. 4a. Effectiveness factor for thin disks, zero-order reaction with volume change. *A*, Relates η' and ξ_e directly. *B*, Relates η' and K through m. *C*, Relates ξ_e and K through m.

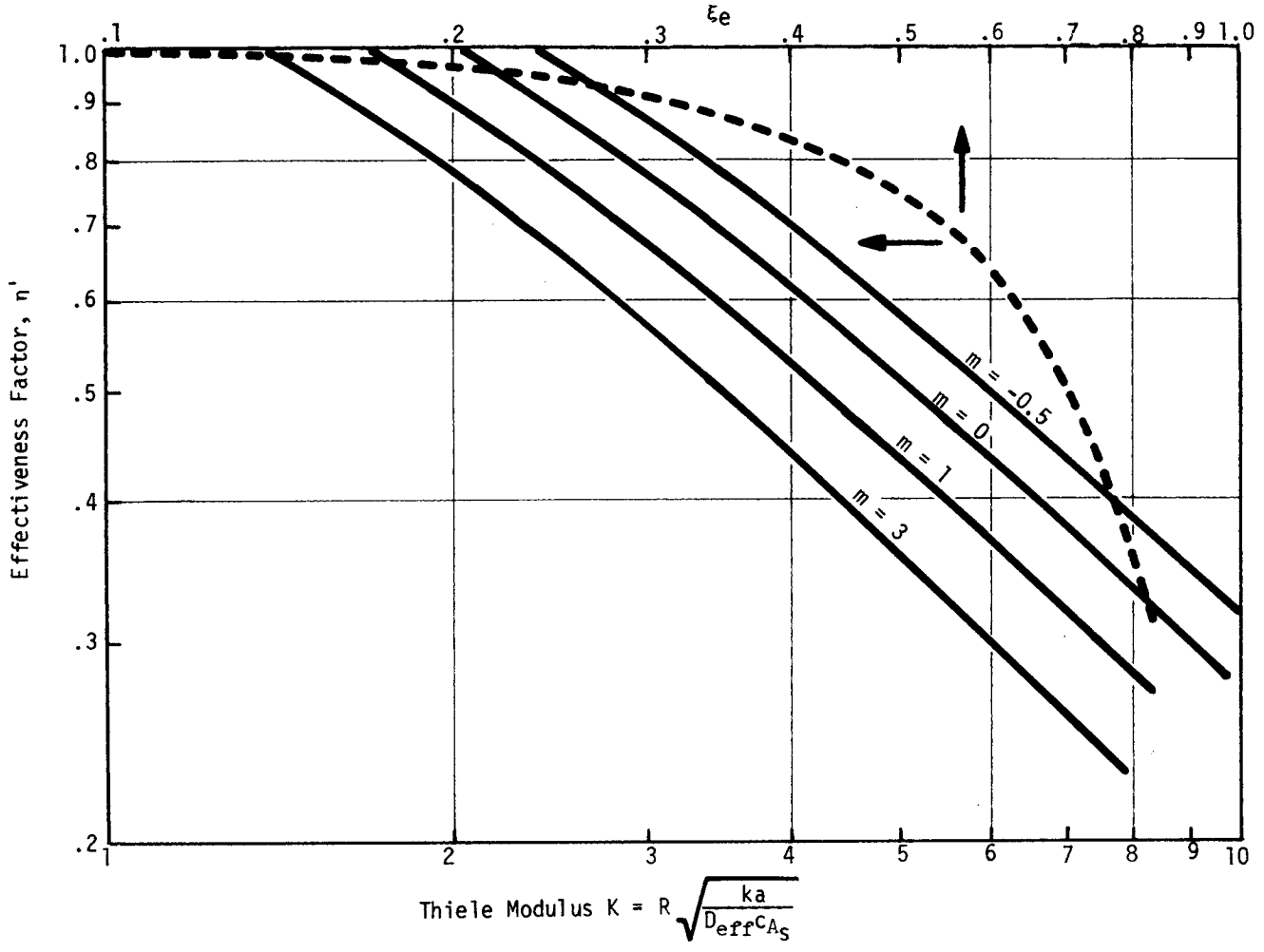

Fig. 4b. Effectiveness factor for infinite cylinders, zero-order reaction with volume change.

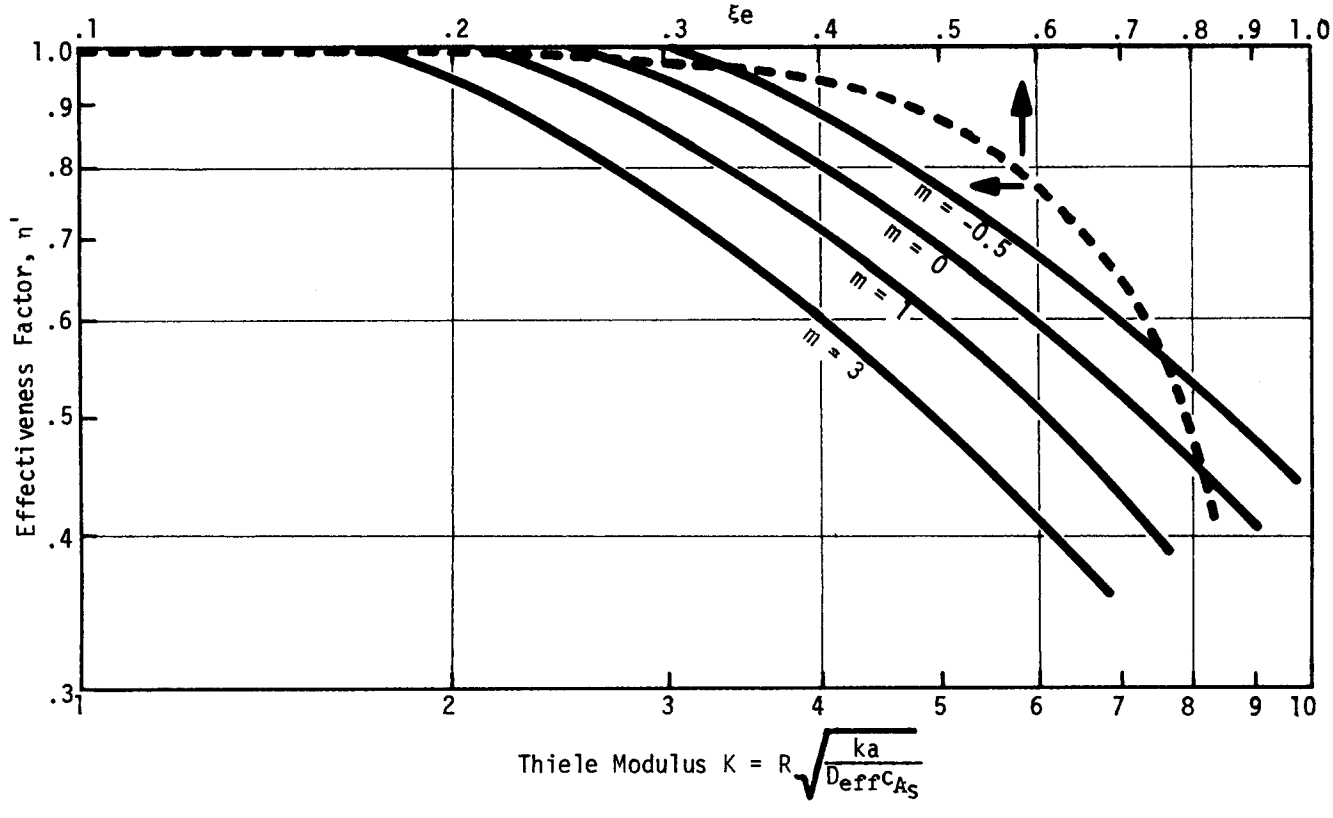

Fig. 4c. Effectiveness factor for spheres, zero-order reaction with volume change.

area of the typical single catalyst particle. This definition stems from the special case when $R_{eq} = R$ for spherical particles.

CONCLUSIONS

A generalized set of equations for concentration profiles, Thiele modulus, and effectiveness factor has been developed for a zero-order heterogeneous chemical reaction occurring in the fine pores of thin-disk, infinite-cylinder, and spherical particles with volume change during the reaction. The development is entirely theoretical and the results are expected to hold exactly for the conditions prescribed. Graphical representations are also given so as to facilitate their application to actual problems.

In addition to having discovered a variable transformation and mathematical procedure to solve this problem, the main significance of the present work is that we have been able to systematize the results for the various geometries into a single set of general expressions. By breaking each of these expressions into its components and alternately substituting appropriate quantities for them for the different geometries, an entire set of specific equations can be generated. This is analogous to breaking up the Hougen-Watson catalytic reaction rate equations (*14*) into the kinetic, potential, and adsorption terms (*31*) and using appropriate quantities for the various rate-controlling mechanisms and types of reactions. We would be amiss if we did not acknowledge Professor Hougen's influence. Such sectioning greatly systematizes and facilitates computer programming of these functions to obtain numerical results, in addition to giving us better insight into the problem and making us appreciate the beauty of the mathematical language.

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NOTATION

$A = K^2 m^{1-n}$

a = catalytic surface area per unit volume of catalyst

b = stoichiometric coefficient for species B (number of moles of B produced per mole of A reacted)

$C = c_A/c_{A_s} = x_A/x_{A_s}$, dimensionless concentration

c = total molar concentration of mixture

c_A = local molar concentration of reactant A within the catalyst particle

c_i = molar concentration of species i

$\mathcal{D}_{eff}$ = effective diffusivity of reactant A in porous catalyst particle

$f(\xi) = 1 - \xi^2$

$g(\xi)$ = general function for thin-disk $(\xi - 1)$, infinite-cylinder $(\ln \xi)$, and spherical $1 - \frac{1}{\xi}$ geometries

j = geometrical index, 1 for thin disk, 2 for infinite cylinder, and 3 for sphere

K = Thiele modulus, $R\sqrt{\dfrac{kac_{A_s}^{n-1}}{\mathcal{D}_{eff}}}$

K_e = critical Thiele modulus at which reactant exhaustion starts, $\sqrt{2j\dfrac{\ln(1+m)}{m}}$

k = reaction rate constant

$M_j = K^2 m/2j$

$m = (b-1)x_{A_s}$, volume-change modulus

$\mathbf{N}_i$ = total (diffusional plus bulk-flow) molar flux of species i

n = order of reaction

R = radius or, in the case of thin-disk, half-thickness of disk

R_i = rate of production of species i

r = radial coordinate or, in the case of thin-disk, coordinate from centerplane

S_1, S_2 = integration constants

$u = 1 + mC$

$v = \dfrac{1}{u}\dfrac{du}{d\xi}$

x_i = mole fraction of species i

Greek Letters

∇ = differential operator

η = effectiveness factor

ξ = dimensionless radial coordinate, r/R

Subscripts

A = reactant A

B = product B

e = reactant exhaustion

j = geometrical index

r = radial

s = surface

Superscripts

$'$ = with volume change

$*$ = dimensionless

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