Effectiveness Factors for General Reaction Rate Forms

KENNETH B. BISCHOFF
The University of Texas, Austin, Texas

The great utility of the effectiveness factor concept to account for intraparticle diffusion lies in its simplicity of application. Unfortunately, the standard formulation leads to a separate relationship for each type of reaction rate form, which greatly complicates practical computations.

A general asymptotic solution is given here which leads to the definition of a general modulus somewhat different in form from the standard one. The use of this general modulus tends to approximately bring together all of the various curves.

To illustrate its use, a few new exact solutions for simple order reactions are derived and combined with existing solutions for both simple order and adsorption reaction rate forms. It is seen that all of the curves lie within a relatively narrow range. Thus the general modulus permits one to estimate the effectiveness factor for any arbitrary reaction from the existing curves.

BACKGROUND

The concept of effectiveness factor for considering the importance of intraparticle diffusion in porous catalyst pellets has been found to be very useful for many years, as recently discussed by Hougen (*1*). Much of the practical value stems from the fact that it is a simple concept and very easy to use in practical applications for those cases in which it has been developed. These cases have previously consisted mainly of single reactions of simple order (first order is most widely used). Effectiveness factors can also be obtained for more complicated cases, but here it is probably easier to directly solve the basic mass and energy balances for each special problem rather than attempting to cast the results into the effectiveness factor form. In other words, the effectiveness factor is most useful as a rough estimate of intraparticle diffusion effects, to be used in lieu of extensive numerical calculations. The detailed calculations can always be made, but often the most important type of information, especially in view of the inaccuracy of most kinetic data, is that poor catalyst effectiveness will be obtained with a given catalyst and alternate designs might be considered.

For these reasons, it would seem to be useful to have values of effectiveness factors available, possibly only approximate, for any general type of reaction rate form. As will be discussed in detail shortly, the developments to date do not provide this, since each type of reaction gives a different effectiveness factor relationship.

Thiele (*2*) and Zeldovich (*3*) in 1939 gave the early, and now classical, treatments. Thiele considered a few simple order reaction rate forms and presented various curves of the effectiveness factor as a function of a dimensionless modulus. This modulus was a grouping of the important parameters of the system (reaction rate coefficient, diffusivity in the particle, reactant concentration in the surrounding fluid, average pore size, and average pore length which is related to the particle size) of the form, for a first-order reaction, $m = L\sqrt{k_v/D}$.

Nonisothermal reactions, bimodal pore size distributions, surface fluid film resistance, and other extensions have also been derived and are reviewed by Wheeler (*4*) and more recently by Carberry (*5*), Hougen (*1*), and Satterfield and Sherwood (*6*). These complications will not be considered here, and interest will be centered on the simplest basic case.

Recently, Chu and Hougen (*7*) showed that even for isothermal reactions in catalysts with simple geometry, a complex form of reaction rate with many parameters, such as the Langmuir-Hinshelwood-Hougen-Watson adsorption type, gives rise to a multitude of curves when plotted in the standard fashion. Thus, for the purposes discussed above, the usefulness of the effectiveness factor concept is greatly decreased. Again, it can be stated that a general solution would be very desirable. The purpose of this work is to show how this can be approximately realized.

GENERAL SOLUTION FOR FINITE PARTICLE

A solution of the general problem for an arbitrary reaction rate form will first be given. The problem stated mathematically then is to solve the diffusion equation describing the system with an arbitrary reaction occurring and where the boundary conditions are that the surface concentration is C_o and the mass flux is zero at the end of the pore (or center of slab), $x = L$. The mathematics will be developed only for cartesian coordinates (or a single pore), but Aris (*8*) has shown that by choosing appropriate characteristic lengths, other geometrical shapes give approximately similar results.

The steady state, one-dimensional mass balance for this case of diffusion then is

$$\frac{d}{dx} D(C) \frac{dC}{dx} = r(C) \tag{1}$$

with boundary conditions

$$C(0) = C_o \tag{2}$$

$$\frac{dC(L)}{dx} = 0 \tag{3}$$

The parameter $D(C)$ is the effective diffusivity for the particle and is often a function of concentration as recently discussed by Wakao and Smith (9). It can also be used to represent changes in volume with reaction, which will be discussed later.

Equation (1) can be solved by defining the new variable

$$p = \frac{dC}{dx}$$

so that

$$\frac{d}{dx} = \frac{dC}{dx}\frac{d}{dC} = p\frac{d}{dC}$$

Thus Equation (1) becomes

$$p\frac{d}{dC}[D(C)p] = r(C) = \frac{1}{2}\frac{1}{D(C)}\frac{d}{dC}[D(C)p]^2 \tag{4}$$

This can be easily integrated to give

$$[D(C)p]^2 = 2\int_{C_L}^{C} D(\alpha)\, r(\alpha)\, d\alpha \tag{5}$$

where Equation (3) has been used and C_L is the (as yet unknown) concentration at $x = L$. Using the definition of p one gets

$$\frac{dC}{dx} = -\frac{\sqrt{2}}{D(C)}\left[\int_{C_L}^{C} D(\alpha)\, r(\alpha)\, d\alpha\right]^{1/2} \tag{6}$$

The relationship between concentration and position can be found by another integration:

$$x = \frac{1}{\sqrt{2}}\int_{C}^{C_o} D(\beta)\left[\int_{C_L}^{\beta} D(\alpha)\, r(\alpha)\, d\alpha\right]^{-1/2} d\beta \tag{7}$$

If one sets $x = L$ in Equation (7), one obtains an implicit solution for C_L in terms of the measurable variables

$$L = \frac{1}{\sqrt{2}}\int_{C_L}^{C_o} D(\beta)\left[\int_{C_L}^{\beta} D(\alpha)\, r(\alpha)\, d\alpha\right]^{-1/2} d\beta \tag{8}$$

The effectiveness factor is now found using Equation (6):

$$\mathcal{E} = \frac{\text{total rate considering diffusion}}{\text{total rate if all reactants were available at } C_o}$$

$$= \frac{-SD\,(C_o)\,\dfrac{dC(o)}{dx}}{SLr(C_o)}$$

$$= \frac{\sqrt{2}}{Lr(C_o)}\left[\int_{C_L}^{C_o} D(\alpha)\, r(\alpha)\, d\alpha\right]^{1/2} \tag{9}$$

For a given $D(C)$ and $r(C)$, Equation (9) gives the effectiveness factor as a function of measurable variables and C_L which can be found from Equation (8). The integral in Equation (9) can often be evaluated (especially for constant D), but the second integration of Equation (8) is usually difficult. Thus, although in principle Equations (8) and (9) completely solve the general finite particle problem, numerical values are often difficult to compute because of integration difficulties.

GENERAL SOLUTION FOR SEMI-INFINITE PARTICLE

Frank-Kamenetskii (*10*) gives the treatment of Zeldovich for an n^{th} order reaction for this case. Consider an arbitrary reaction rate form which also includes this case. The problem is then to solve Equation (1) with the surface boundary condition (2), but with Equation (3) replaced by

$$C(\infty) = 0 = \frac{dC(\infty)}{dx} \tag{10}$$

This condition essentially assumes that the pore is very long, the reaction is very rapid, or the diffusion is very slow. All of these decrease the penetration of reactant so that the infinite condition is approximately valid.

The solution method is the same as that given above, and the analogue of Equation (9) is

$$\mathcal{E}_\infty = \frac{\sqrt{2}}{Lr(C_o)}\left[\int_{o}^{C_o} D(\alpha)\, r(\alpha)\, d\alpha\right]^{1/2} \tag{11}$$

The value of C_L no longer appears, and so Equation (11) is a complete, explicit solution.

In order to better interpret Equation (11), consider the special case of a first-order reaction with constant diffusivity:

$$r(C) = k_v C$$

Equation (11) becomes

$$\mathcal{E}_\infty = \frac{1}{LC_o}\sqrt{\frac{2D}{k_v}}\left[\int_{o}^{C_o} \alpha\, d\alpha\right]^{1/2}$$

$$= \frac{1}{L}\sqrt{\frac{D}{k_v}}$$

$$= \frac{1}{m} \tag{12}$$

Equation (12) thus indicates that the effectiveness factor for a semi-infinite particle is the reciprocal of the modulus, which is what Thiele found from the exact solution for large m. Thus it appears that the author's semi-infinite assumption leads to an asymptotic solution valid for large m, which again means small penetration of reactant. Therefore take Equation (11) to be the general asymptotic solution and define the general modulus as

$$m \equiv \frac{Lr(C_o)}{\sqrt{2}}\left[\int_{o}^{C_o} D(\alpha)\, r(\alpha)\, d\alpha\right]^{-1/2} \tag{13}$$

This will then essentially force the portion of the curves for large m to coincide for all types of reactions. The entire length of the curves for all values of m will not then necessarily coincide, but it will be seen below that the differences are relatively small.

When one uses this definition of the general modulus, Equations (8) and (9) may be rewritten as

$$m = \frac{r(C_o)}{2}\,\frac{\displaystyle\int_{C_L}^{C_o} D(C)\left[\int_{C_L}^{\beta} D(\alpha)\, r(\alpha)\, d\alpha\right]^{-1/2} dC}{\left[\displaystyle\int_{o}^{C_o} D(C)\, r(C)\, dC\right]^{-1/2}} \tag{14}$$

$$\mathcal{E} = \frac{1}{m}\left[\frac{\displaystyle\int_{C_L}^{C_o} D(C)\, r(C)\, dC}{\displaystyle\int_{o}^{C_o} D(C)\, r(C)\, dC}\right]^{1/2} \tag{15}$$

Equation (15) gives the effectiveness factor as a function of the modulus, measurable variables, and the concentration C_L, which must be found implicitly from Equation (14) as a function of measurable variables and the modulus. As mentioned above, the integrals in Equation (14) are often difficult to evaluate. Certain cases are possible, however, and some of the available ones will be considered next.

SIMPLE ORDER REACTION RATE FORM WITH CONSTANT DIFFUSIVITY

The reaction rate here is given by

$$r(C) = k_v C^n \tag{16}$$

Equation (13) becomes

$$\begin{aligned} m &= L(C_o)^n \sqrt{\frac{k_v}{2D}} \left[\int_o^{C_o} C^n dC \right]^{-1/2} \\ &= L\sqrt{(n+1)\frac{k_v C_o^{n-1}}{2D}} \end{aligned} \tag{17}$$

A form of modulus similar to Equation (17), but with only the term C_o^{n-1} for dimensional consistency, has been used by many of the above investigators for n^{th} order reactions. Equation (14) becomes

$$\begin{aligned} m &= \frac{C_o^n}{2} \frac{\int_{C_L}^{C_o} \left[\int_{C_L}^{C} \alpha^n d\alpha \right]^{-1/2} dC}{\left[\int_o^{C_o} C^n dC \right]^{1/2}} \\ &= \frac{n+1}{2} (C_o)^{\frac{n-1}{2}} \int_{C_L}^{C_o} \frac{dC}{\sqrt{C^{n+1} - C_L^{n+1}}} \end{aligned} \tag{18}$$

Equation (15) becomes

$$\begin{aligned} \mathcal{E} &= \frac{1}{m} \left[\frac{\int_{C_L}^{C_o} C^n dC}{\int_o^{C_o} C^n dC} \right]^{1/2} \\ &= \frac{1}{m} \sqrt{1 - \left(\frac{C_L}{C_o} \right)^{n+1}} \end{aligned} \tag{19}$$

The integral in Equation (18) cannot be evaluated for arbitrary n. In terms of the variable $t = C/C_L$, Equation (18) can be written as

$$m = \frac{n+1}{2} \left(\frac{C_o}{C_L} \right)^{\frac{n-1}{2}} \int_1^{C_o/C_L} \frac{dt}{\sqrt{t^{n+1} - 1}} \tag{20}$$

For a given m, Equation (20) could be solved for C_o/C_L and then these values used in Equation (19) to finally calculate $\mathcal{E}(m)$.

For certain values of n one can readily evaluate the integral in Equation (20). With $n = 1$, the integral is elementary, and one finds from Equation (20)

$$m = \int_1^{C_o/C_L} \frac{dt}{\sqrt{t^2 - 1}} = \ln\left[\frac{C_o}{C_L} + \sqrt{\left(\frac{C_o}{C_L} \right)^2 - 1} \right]$$

or

$$\frac{C_o}{C_L} = \cosh m$$

which when substituted into Equation (19) gives

$$\begin{aligned} \mathcal{E} &= \frac{1}{m} \sqrt{1 - \frac{1}{\cosh^2 m}} \\ &= \frac{\tanh m}{m} \end{aligned} \tag{21}$$

the well-known result which is plotted in Figure 1.

For $n = 0$, the integral is elementary and reduces to the solution of Wheeler (*4*):

$$\mathcal{E} = \begin{cases} 1, & m < 1 \\ \frac{1}{m}, & m > 1 \end{cases} \tag{22}$$

Equation (22) is also plotted in Figure 1. For $n = 2$, the integral is

$$I = \int_1^{C_o/C_L} \frac{dt}{\sqrt{t^3 - 1}}$$

which can be changed by the substitution

$$t = 1 + \sqrt{3}\,\frac{1 - \cos\phi}{1 + \cos\phi}$$

into an elliptic integral of the first kind (*11, 12*), which is essentially the solution found by Thiele (*2*):

$$\begin{aligned} I &= \frac{1}{\sqrt[4]{3}} \int_0^\phi \frac{d\psi}{\sqrt{1 - k^2 \sin^2\psi}} \\ &= \frac{1}{\sqrt[4]{3}} F(\phi, k) \end{aligned}$$

where

$$\sin\phi = \frac{\sqrt{4\sqrt{3}\left(\frac{C_o}{C_L} - 1 \right)}}{\sqrt{3} - 1 + \frac{C_o}{C_L}}$$

and

$$k = \sin 15\text{ deg.} = \frac{\sqrt{2 - \sqrt{3}}}{2}$$

Thus Equation (20) becomes

$$m = \frac{3}{2} \sqrt{\frac{C_o}{C_L}} \frac{1}{\sqrt[4]{3}} F(\phi, k) \tag{23}$$

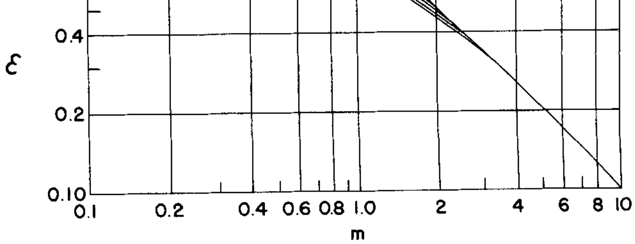

Fig. 1. General plot for simple order reactions.

and Equation (19) becomes

$$\mathcal{E} = \frac{1}{m}\sqrt{1-\left(\frac{C_L}{C_o}\right)^3} \qquad (24)$$

Figure 1 shows the curve calculated with Equations (23) and (24) with using the tables of Jahnke and Emde (*13*).

For $n = 3$, similar manipulations lead to a solution in terms of an elliptic integral of the first kind:

$$m = \sqrt{2}\left(\frac{C_o}{C_L}\right)F(\phi, k) \qquad (25)$$

$$\mathcal{E} = \frac{1}{m}\sqrt{1-\left(\frac{C_L}{C_o}\right)^4} \qquad (26)$$

where

$$\sin\phi = \sqrt{1-(C_L/C_o)^2}$$

and

$$k = \sin 45 \text{ deg.} = 1/\sqrt{2}$$

Figure 1 shows the curve calculated from Equations (25) and (26).

For $n = ½$, the solution consists of elliptic integrals of the first and second kinds:

$$m = \frac{3}{2}\sqrt{\frac{C_L}{C_o}}\frac{1}{\sqrt[4]{3}}\Big[(1+\sqrt{3})\,F(\phi, k) - 2\sqrt{3}\,E(\phi, k)$$

$$+ 2\sqrt{3}\frac{\sin\phi\sqrt{1-k^2\sin^2\phi}}{1+\cos\phi}\Big] \qquad (27)$$

$$\mathcal{E} = \frac{1}{m}\sqrt{1-\left(\frac{C_L}{C_o}\right)^{3/2}} \qquad (28)$$

where

$$\sin\phi = \frac{\sqrt{4\sqrt{3}\left(\frac{C_o}{C_L}-1\right)}}{\sqrt{3}-1+\frac{C_o}{C_L}}$$

and

$$k = \sin 15 \text{ deg.} = \frac{\sqrt{2-\sqrt{3}}}{2}$$

Figure 1 shows the curve calculated from Equations (27) and (28).

A few other cases could also be found in this fashion; $n = 1/3$ leads to elliptic integrals, and $n = 5$, $1/5$ leads to particular hyperelliptic integrals which can be reduced to the tabulated elliptic integrals. These will not be presented, since the above five cases suffice to cover a wide range of reaction types.

By inspecting the various curves on Figure 1, one can see that, as mentioned previously, the asymptotic (large m) parts of all the curves coincide. The intermediate range gives results that are not exactly the same for all reaction orders, but the spread is only about 15% for the most interesting cases of one-half- to third-order reactions and is about 30% when zero-order reactions are included. Thus, by using the proper generalized modulus m, one could get a reasonably good estimate of the effectiveness factor for any other reaction order from the existing curves.

ADSORPTION REACTION RATE FORM

This type of reaction has been recently treated by Chu and Hougen (*7*). The form of rate equation used was

$$r(C) = \frac{k_v C}{\zeta + C}$$

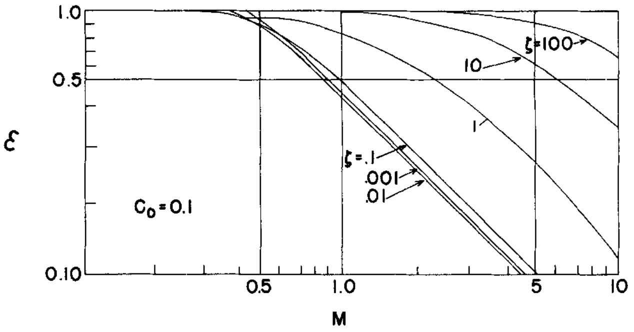

Fig. 2a. Standard plot for adsorption reaction.

The general modulus, Equation (13), then becomes

$$m = L\sqrt{\frac{k_v}{2D}}\frac{C_o}{\zeta + C_o}\left[\int_o^{C_o}\frac{CdC}{\zeta + C}\right]^{-1/2}$$

$$= L\sqrt{\frac{k_v}{D}}\frac{1}{\sqrt{2}}\frac{C_o}{\zeta + C_o}\left[C_o - \zeta\ln\left(1+\frac{C_o}{\zeta}\right)\right]^{-1/2} \qquad (29)$$

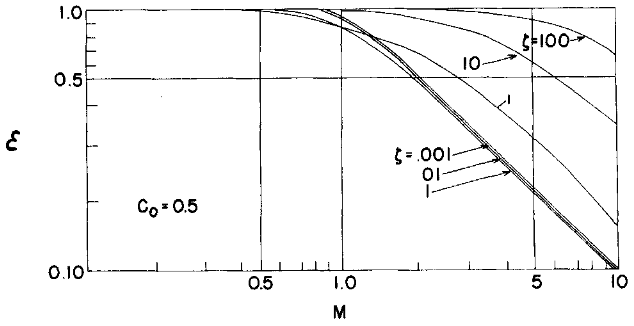

Fig. 2b. Standard plot for adsorption reaction.

Chu and Hougen used a standard modulus

$$M = L\sqrt{\frac{k_v}{D}} \qquad (30)$$

Therefore, for this case, the relationship of the general modulus to the standard one used by Chu and Hougen is

$$m = \frac{M}{\sqrt{2}}\frac{C_o}{\zeta + C_o}\left[C_o - \zeta\ln\left(1+\frac{C_o}{\zeta}\right)\right]^{-1/2} \qquad (31)$$

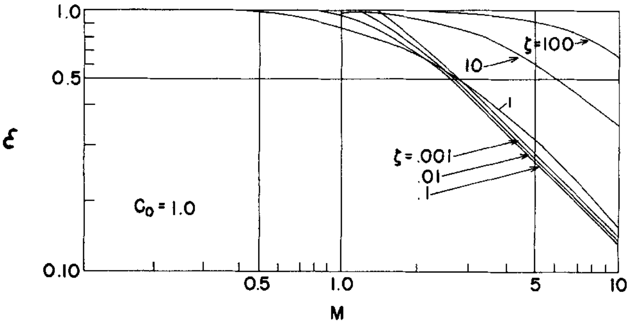

Fig. 2c. Standard plot for adsorption reaction.

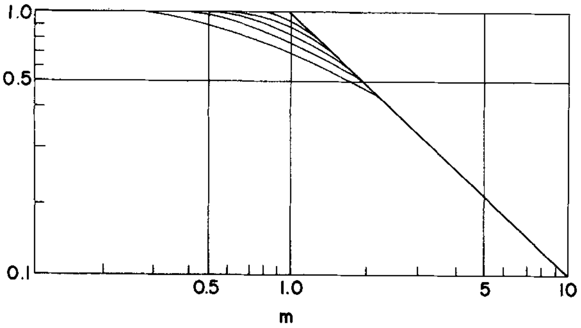

Fig. 3. General plot for adsorption reaction.

Equations (14) and (15) could be written down for this case, but the integrals are not available. Therefore, Chu and Hougen numerically integrated equivalent expressions in order to find the effectiveness factors, and this paper will directly use their curves, which are redrawn in Figure 2.

Since the standard modulus M contains only the factors L, k_v, and D, there are separate curves for each value of the two remaining parameters ζ and C_o. The general modulus m contains all of the parameters in a form that again forces the large m portions of all the curves to coincide. This is shown in Figure 3, where the data are replotted as a function of m. The spread is again about the same as for the simple order reactions.

FIRST-ORDER REACTION WITH VOLUME CHANGE

This case can be handled by using a variable diffusivity to take the volume expansion into account:

$$D(C) = \frac{D}{\omega C + 1} \tag{32}$$

Then Equation (13) becomes

$$m = LC_o \sqrt{\frac{k_v}{2D}} \left[\int_0^{C_o} \frac{CdC}{\omega C + 1} \right]^{-1/2}$$

$$= M \frac{|\omega C_o|}{\sqrt{2}} [\omega C_o - \ln(\omega C_o + 1)]^{-1/2} \tag{33}$$

Again, the general modulus provides a correction factor for the classical modulus that tends to bring the large m portions of all curves together. If the calculated curves of Thiele (2) are shifted in this way, it can be seen that they again fall within the range of Figure 1.

Hawthorn, as reported in reference 6, found an empirical correction factor that brought the curves together:

$$(m)_{\text{Hawthorn}} = M \left[\frac{\omega C_o}{\ln(1 + \omega C_o)} \right]^{0.7} \tag{34}$$

Table 1 shows a comparison between the correction factors calculated from Equations (33) and (34). It is seen that the two are essentially equivalent numerically, and so the general modulus again brought the curves together in a logical fashion.

TABLE 1. MODULUS CORRECTION FACTORS FOR VOLUME CHANGE

ωC_o	Equation (33)	Equation (34)
0.4	1.12	1.13
1.0	1.28	1.29
–0.5	0.804	0.796
–0.25	0.905	0.906

SUMMARY

From the above results, it is seen that the general modulus condenses the curves for a rather wide range of reaction types into a relatively narrow region. If reactions of order less than one-half are excluded, the spread between all the various curves is about 15%. This is probably a close enough estimate for many purposes, and so effectiveness factors for arbitrary reactions can be found from the existing curves in Figures 1 or 3.

A possible complication that could occur in the applications would be that the integral appearing in the general modulus, Equation (13), could not be easily evaluated. In all of the above cases (even with adsorption) this did not happen, but for some complicated rate expressions, especially if $D(C)$ is not constant, the problem might arise. In this case the integral would have to be numerically evaluated, which is somewhat more complicated, but still not as bad as having to solve the entire problem. Thus the use of the general modulus should enable one to quickly estimate the effectiveness factor for any type of reaction.

NOTATION

C = reactant concentration
C_o = reactant concentration at catalyst surface
C_L = reactant concentration at catalyst center
$D(C)$ = effective diffusivity in catalyst
$\mathcal{E}$ = effectiveness factor
$E(\phi, k)$ = elliptic integral of second kind
$F(\phi, k)$ = elliptical integral of first kind
k_v = reaction rate coefficient based on volume
L = catalyst half width (or pore length)
m = general modulus, Equation (13)
M = modulus
n = reaction rate order
$r(C)$ = reaction rate
S = cross-sectional area
t = dummy variable of integration (C/C_L)
x = length variable
α, β = dummy variables of integration
ζ = parameter in adsorption rate equation
ω = factor for volume expansion

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