JOURNAL OF CATALYSIS 6, 186–193 (1966)

Effectiveness Factors for Second Order Reactions

J. A. MAYMÓ AND R. E. CUNNINGHAM

From the Departamento de Industrias, Facultad de Ciencias Exactas y Naturales, Buenos Aires, Argentina

Received July 7, 1965; revised January 31, 1966

Effectiveness factors are computed for a second order reaction of the type $A + B \rightleftarrows R + S$ for both irreversible and reversible cases. The influence of different reactant diffusivities, of a nonstoichiometric relationship of reactant concentration, and of equilibrium constant upon effectiveness factor are analyzed. Computed results are compared with those from analytic asymptotic solutions.

INTRODUCTION

The effectiveness factor of a catalyst pellet has been extensively studied for the case of first order irreversible reaction (*3, 6, 7, 8, 10*); the first order reversible reaction (*1*) and other orders than one (*2, 4, 9*) have also been taken into account. Isothermal behavior of the catalyst pellet has been assumed in these cases.

However, no reference exists for a second order reaction of the type $r = kc_Ac_B$. In this paper the effectiveness factor for this type of reaction has been computed including those cases in which reactant concentrations on the pellet surface are not equal or those in which reactant diffusivities are different. A criterion is also presented to decide when the assumption of a first order (or pseudo first order) can be made.

The more complicated reaction of the type

$$r = k(c_Ac_B - c_Rc_S/K) \qquad (1)$$

is also analyzed. No generalized results are presented here because of the high number of variables that arise for this case. But a few examples have been selected showing the relative influence of the different variables.

From the comparison of the irreversible reaction with the reversible one some interesting remarks follow.

NOMENCLATURE

c	Concentration
C	Dimensionless concentration of A, defined by Eq. (7)
D_{eff}	Effective diffusivity
D	Dimensionless diffusivity, defined by Eq. (9)
E	Dimensionless concentration, defined by Eq. (8)
J	Molal flux
k	Second order reaction rate constant
k'	Pseudo-first-order reaction rate constant
K	Equilibrium constant
r	Reaction rate
x	Distance
x_0	Pellet radius
X	Dimensionless distance
ϕ_L	Thiele modulus for second order reaction
ϕ'_L	Thiele modulus for pseudo-first-order reaction
η	Effectiveness factor

Subscripts

A, B, R, S	Reaction components
0	Pellet surface conditions

Superscripts

*	Chemical equilibrium conditions

FORMULATION OF EQUATIONS

The following restrictions are taken: (1) steady state; (2) stoichiometry: $A + B = R + S$; (3) kinetics: $r = k(c_Ac_B - c_Rc_S/K)$; (4) no temperature gradients inside the pellet; (5) effective diffusivities are constant through the pellet; (6) the pellet is spherical.

As concentration gradients are not independent among them the following equations can be written for every point:

$$J_A = J_B = -J_R = -J_S \tag{2}$$

$$\begin{aligned} -D_{\mathrm{eff,A}}(dc_A/dx) &= -D_{\mathrm{eff,B}}(dc_B/dx) \\ &= D_{\mathrm{eff,R}}(dc_R/dx) \\ &= D_{\mathrm{eff,S}}(dc_S/dx) \end{aligned} \tag{3}$$

provided the steady state has been reached. Integration of Eq. (3) between x and x_0 allows us to write all the concentrations as a function of one taken as a reference

$$c_B = c_{A0}[E_B - (1 - C)/D_B] \tag{4}$$

$$c_R = c_{A0}[E_R + (1 - C)/D_R] \tag{5}$$

$$c_S = c_{A0}[E_S + (1 - C)/D_S] \tag{6}$$

in which

$$C = c_A/c_{A0} \tag{7}$$

$$E_B = c_{B0}/c_{A0} \qquad E_R = c_{R0}/c_{A0} \qquad E_S = c_{S0}/c_{A0} \tag{8}$$

$$D_B = D_{\mathrm{eff,B}}/D_{\mathrm{eff,A}} \qquad D_R = D_{\mathrm{eff,R}}/D_{\mathrm{eff,A}} \qquad D_S = D_{\mathrm{eff,S}}/D_{\mathrm{eff,A}} \tag{9}$$

it is seen that reactant A has been taken as reference.

Hence, by combining Eq. (1) with Eqs. (4), (5), (6), and (7), the reaction rate at any point inside the pellet can be written

$$r = kc_{A0}^2\left\{C\left[E_B - \frac{(1-C)}{D_B}\right] - \left(\frac{1}{K}\right)\left[E_R + \frac{(1-C)}{D_R}\right]\left[E_S + \frac{(1-C)}{D_S}\right]\right\} \tag{10}$$

where the only variable which depends upon x is C.

At the same time the mass balance for the sphere reads

$$x^2(d^2c_A/dx^2) + 2x(dc_A/dx) - rx^2/D_{\mathrm{eff,A}} = 0 \tag{11}$$

If a dimensionless distance $X = x/x_0$ and a Thiele modulus $\phi_L = (x_0/3)(kc_{A0}/D_{\mathrm{eff,A}})^{1/2}$ are introduced and c_A and r are replaced as given in Eqs. (7) and (10), Eq. (11) turns to dimensionless form

$$0 = \frac{d^2C}{dX^2} + \frac{2}{X}\left(\frac{dC}{dX}\right) - 9\phi_L^2\left\{C\left[E_B - \frac{(1-C)}{D_B}\right] - \left(\frac{1}{K}\right)\left[E_R + \frac{(1-C)}{D_R}\right]\left[E_S + \frac{(1-C)}{D_S}\right]\right\} \tag{12}$$

with the following boundary conditions:

$$X = 0 \qquad dC/dX = 0$$

$$X = 1 \qquad C = 1$$

Numerical integration of Eq. (12) will provide C as a function of X. This relationship will be used to compute the effectiveness factor of the pellet defined as follows:

$$\eta = \bar{r}/r_0 = \frac{\text{mean reaction rate in the pellet}}{\text{reaction rate at surface pellet conditions}} \tag{13}$$

$$\bar{r} = \int_0^{x_0} 4\pi x^2 r\,dx \Big/ (\tfrac{4}{3})\pi x_0^3 = 3\int_0^1 rX^2\,dX \tag{14}$$

over pellet surface $C = 1$ and Eq. (10) can be written as

$$r = kc_{A0}^2(E_B - E_R E_S/K) \tag{15}$$

Replacing Eqs. (14) and (15) in (13) the relationship of Eq. (16) (below) arises. Equation (16) can be integrated numerically once $C = C(X)$ is known. Hence, the final result will be of the form

$$\eta = \eta(\phi_L, K, E_B, E_R, E_S, D_B, D_R, D_S)$$

THE IRREVERSIBLE REACTION

In this case Eq. (12) reduces to

$$(d^2C/dX^2) + (2/X)(dC/dX) - 9\phi_L^2 C[E_B - (1 - C)/D_B] = 0 \tag{17}$$

and Eq. (16) simplifies to

$$\eta = 3\int_0^1 [E_B - (1 - C)/D_B]CX^2\,dX \Big/ E_B \tag{18}$$

$$\eta = \frac{3\int_0^1 \{[E_B - (1 - C)/D_B] - (1/K)[E_R + (1 - C)/D_R][E_S + (1 - C)/D_S]\}\, CX^2\,dX}{E_B - (1/K)E_R E_S} \tag{16}$$

A limiting case for which there is an analytical solution is that of $D_B = \infty$, because in this case there are no concentration gradients for the reactant B, namely, $c_B = c_{B0}$. This reaction can be studied as a pseudo-first-order one with a reaction rate constant $k' = kc_{B0} = kc_{A0}E_B$. The Thiele modulus for the first order case is

$$\begin{aligned}\phi'_L &= (x_0/3)(k'/D_{\mathrm{eff,A}})^{1/2} \\ &= (x_0/3)(kc_{A0}/D_{\mathrm{eff,A}})^{1/2}(E_B)^{1/2} = \phi_L E_B^{1/2}\end{aligned} \tag{19}$$

and the effectiveness factor will be

$$\eta = (3/\phi'_L)[(1/\tanh \phi'_L) - (1/\phi'_L)] \tag{20}$$

Figures 1, 2, 3, and 4 show the effectiveness factor for the second order reaction as a function of E_B, ϕ_L, and D_B.

The Reversible Reaction

The influence of the Thiele modulus, equilibrium constant, and conversion upon the effectiveness factor has been computed under the following assumptions: (1) the relationship of reactant concentrations at reactor inlet is the stoichiometric one; hence, $c_{A0} = c_{B0}$ and $c_{R0} = c_{S0}$ at any place of the catalyst bed. For the same reason $E_B = 1$ and $E_R = E_S$. (2) The diffusivities are all the same, namely, $D_B = D_R = D_S = 1$. The maximum value that $c_{R0} = c_{S0}$ can reach is that of equilibrium conditions.

The equilibrium constant is

$$K = c_{R0}{}^* c_{S0}{}^*/c_{A0}c_{B0} = c_{R0}{}^{*2}/c_{A0}{}^2 = E_R{}^{*2}$$

hence

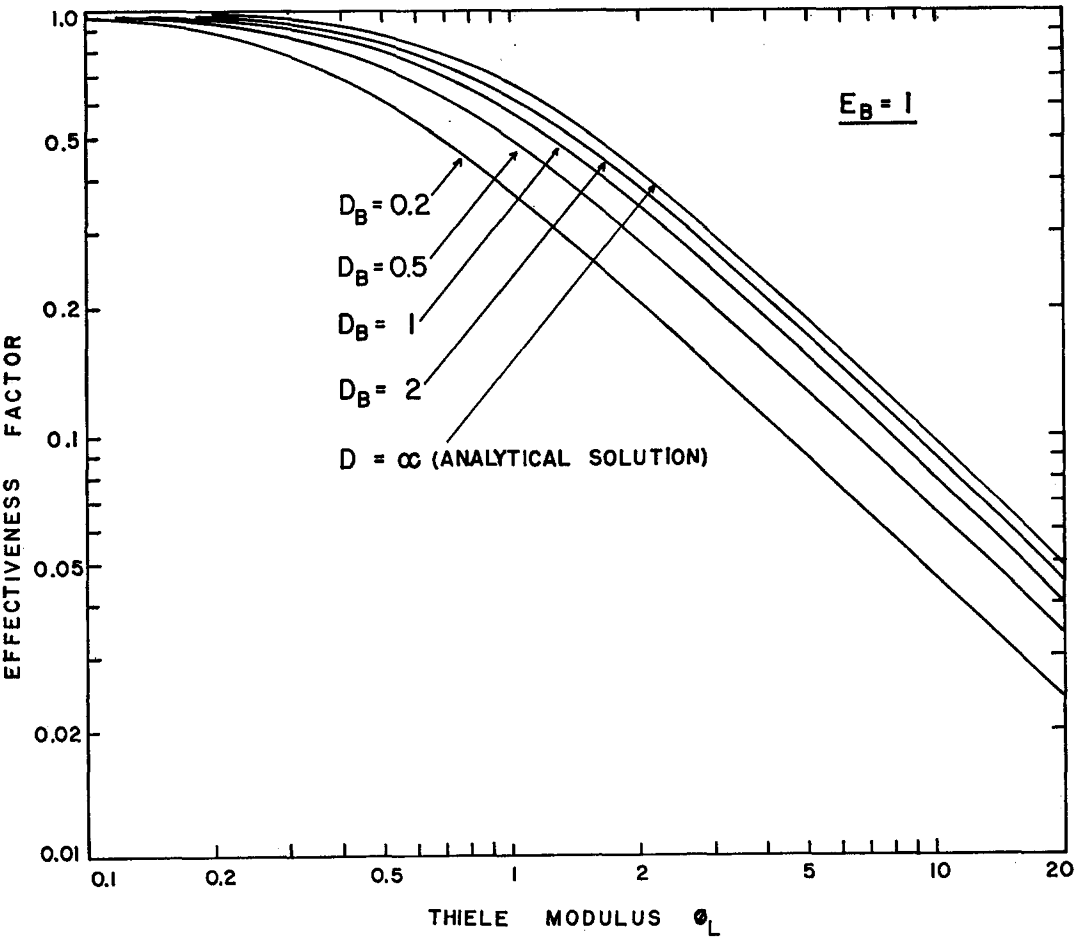

FIG. 1. Effectiveness factor vs. Thiele modulus for irreversible reaction: $E_B = 1$.

$$E_R^* = K^{1/2}$$

The E_R/E_R^* ratio is a measure of the actual conversion with respect to the equilibrium one.

Figures 5, 6, and 7 show the influence of ϕ_L, K, and E_R/E_R^* upon the effectiveness factor.

CONCLUSIONS

From Figs. 1, 2, 3, and 4 it is seen that effectiveness factor for irreversible reaction approaches the pseudo-first-order solution [Eq. (20)] when the stoichiometric ratio E_B and the diffusivity ratio D_B increase. As a practical criterion we can say that pseudo-first-order assumption can be used when $E_BD_B \geqslant 2$. In such a case the error involved is less than 10%.

From Fig. 7 two interesting remarks can be made for the reversible case:

(a) The effectiveness factor for the reversible reaction is less than that for the irreversible case (dotted line) even when conversion at pellet surface is null. This is so because zero conversion at pellet surface means there is a negligible product concentration in the gas phase; however, product concentration inside the pellet is not zero provided effective diffusivities are finite. The difference between reversible and irreversible reaction rates is going to be higher as the equilibrium constant decreases. This fact indicates that a reversible catalytic reaction cannot be handled as an irreversible one when working at very low conversion unless diffusional effects are negligible. The same conclusion

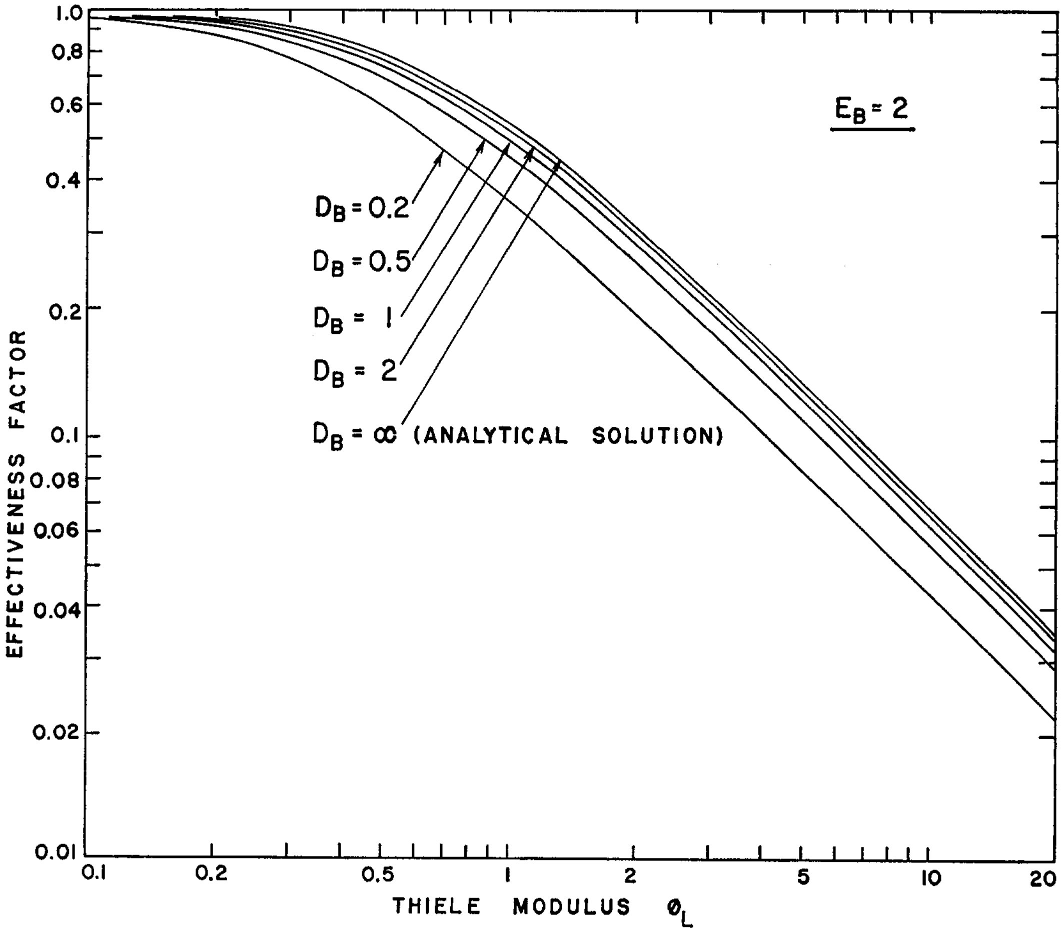

FIG. 2. Effectiveness factor vs. Thiele modulus for irreversible reaction: $E_B = 2$.

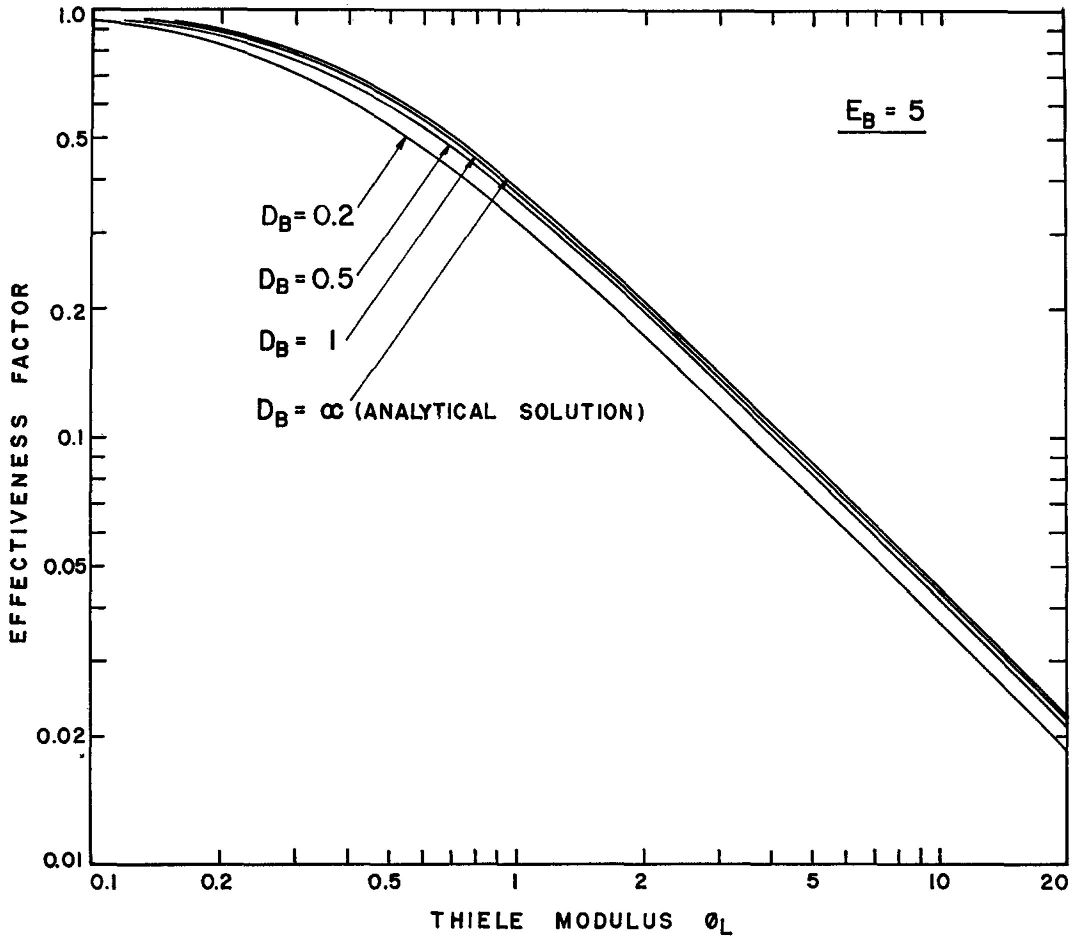

FIG. 3. Effectiveness factor vs. Thiele modulus for irreversible reaction: $E_B = 5$.

can be obtained for the case in which one or more of the products decreases reaction rate because of strong adsorption on the catalyst.

(b) For a given value of the Thiele modulus, reaction rate approaches zero when conversion approaches one. However, the effectiveness factor does not approach unity (Fig. 7). This can be explained in the following way: The reaction rate driving force decreases very much as equilibrium is approached and very low concentration gradients very much decrease the reaction rate inside the pellet. This implies that when dealing with a reversible reaction near equilibrium conditions diffusional effects should be very carefully estimated.

ASYMPTOTIC SOLUTIONS

The effectiveness factor can also be expressed in terms of the concentration gradient at the pellet surface

$$\eta = \frac{(dC/dX)_{X=1}}{3\phi_L^2[E_B - E_R E_S/K]} \tag{21}$$

In general the concentration gradient should be evaluated by numerical integration of Eq. (12), since analytic solutions exist only for a few cases.

However, Petersen (*5*) has shown that for high values of the Thiele modulus the first derivative may be neglected with respect to the second one in Eqs. (12) and (17). This makes possible the analytic calcu-

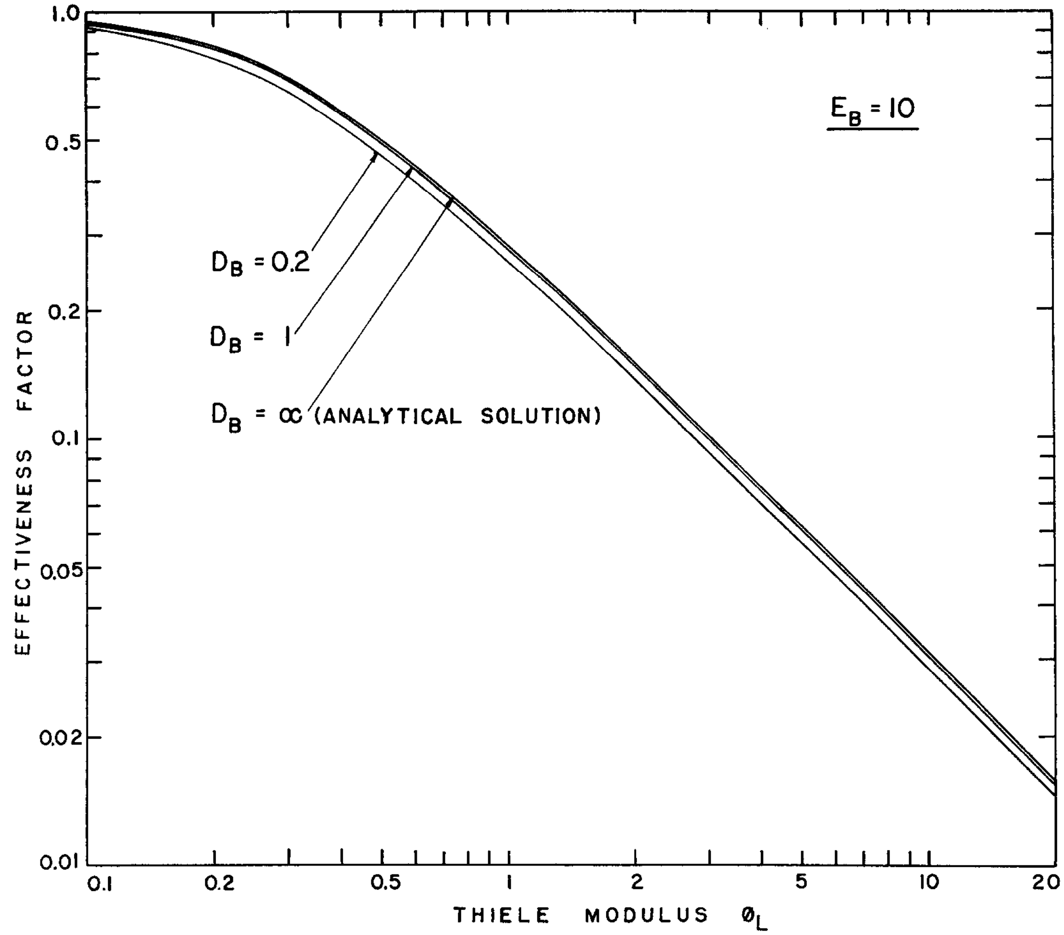

FIG. 4. Effectiveness factor vs. Thiele modulus for irreversible reaction: $E_B = 10$.

lation of the concentration gradient at the pellet surface, which combined with Eq. (21) gives an asymptotic solution for the effectiveness factor.

For the irreversible case the integration of Eq. (17) (neglecting the first derivative) is made by Clairaut substitution, taking into account that at the pellet center both the concentration and the concentration gradient are zero. Hence, from Eqs. (17) and (21) it follows that

$$\eta = \frac{\sqrt{2}}{\phi_L E_B}\left(\frac{E_B}{2} - \frac{1}{6D_B}\right)^{1/2} \qquad (22)$$

This result checks well with the asymptotic values of Figs. 1 to 4.

For the reversible case it is taken into account that now the concentration C is not zero at the pellet center. It has an equilibrium value which depends upon the dimensionless concentrations E, diffusivities D, and equilibrium constant K. It can be calculated from Eq. (10) making $r = 0$.

By the same procedure as before it follows that

$$(dC/dX)_{X=1} = 3\phi_L\sqrt{2}(\mathrm{M} - \mathrm{N})^{1/2} \qquad (23)$$

where

$$M = \frac{E_B}{2} - \frac{1}{6D_B} - \frac{1}{K}$$
$$\times \left(E_R E_S + \frac{E_R}{2D_S} + \frac{E_S}{2D_R} + \frac{1}{3D_R D_S}\right)$$

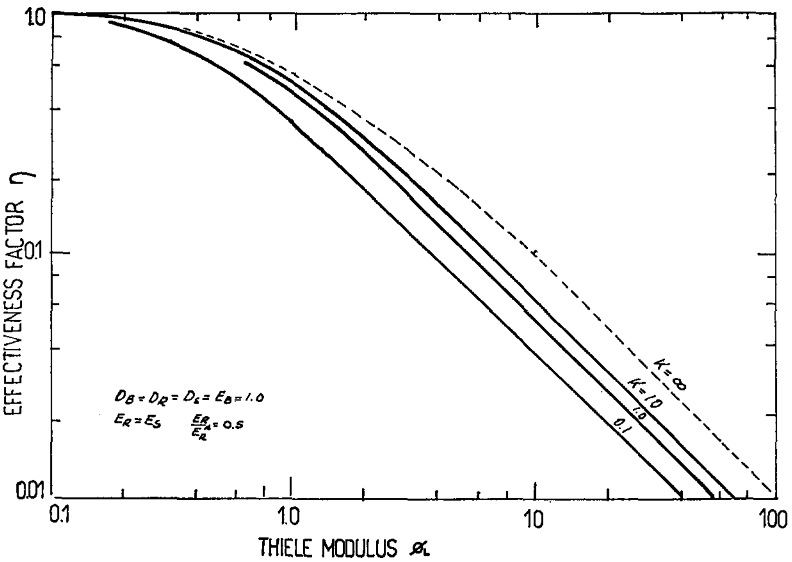

FIG. 5. Thiele modulus influence on effectiveness factor for reversible reaction.

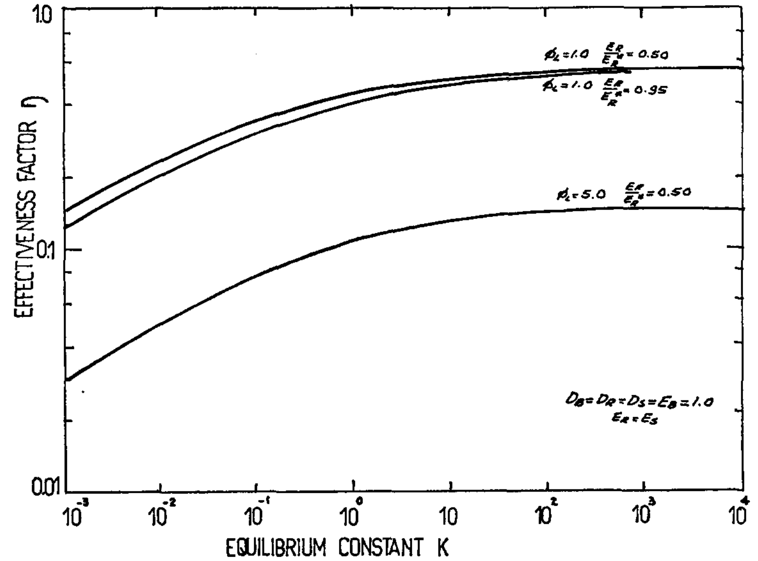

FIG. 6. Equilibrium constant influence on effectiveness factor for reversible reaction.

$$
\begin{aligned}
N = {} & C_{\mathrm{eq}}{}^{3}\left(\frac{1}{3D_{\mathrm{B}}} - \frac{1}{3KD_{\mathrm{R}}D_{\mathrm{S}}}\right) \\
& + C_{\mathrm{eq}}{}^{2}\left(\frac{E_{\mathrm{B}}}{2} - \frac{1}{2D_{\mathrm{B}}} + \frac{E_{\mathrm{R}}}{2KD_{\mathrm{S}}} \right. \\
& \left. + \frac{E_{\mathrm{S}}}{2KD_{\mathrm{R}}} + \frac{1}{KD_{\mathrm{R}}D_{\mathrm{S}}}\right) \\
& - C_{\mathrm{eq}}\left(\frac{E_{\mathrm{R}}E_{\mathrm{S}}}{K} + \frac{E_{\mathrm{R}}}{KD_{\mathrm{S}}} + \frac{E_{\mathrm{S}}}{KD_{\mathrm{R}}} + \frac{1}{KD_{\mathrm{R}}D_{\mathrm{S}}}\right)
\end{aligned}
$$

We have computed the case for $D_{\mathrm{B}} = D_{\mathrm{R}} = D_{\mathrm{S}} = E_{\mathrm{B}} = 1$; $E_{\mathrm{R}} = E_{\mathrm{S}}$; $(E_{\mathrm{R}}/E_{\mathrm{R}}{}^{*}) = 0.5$; $K = 10^{-1}$, $K = 1$, and $K = 10$ for $10^{-1} \leq \phi_L \leq 10^{2}$, which is represented in Fig. 5. We observe here that for $K = 10^{-1}$ and $K = 10$, Eq. (12) needs to be integrated numerically. For $K = 1$ Eq. (12) is linear and there is an analytic solution; in this case the effectiveness factor is represented by

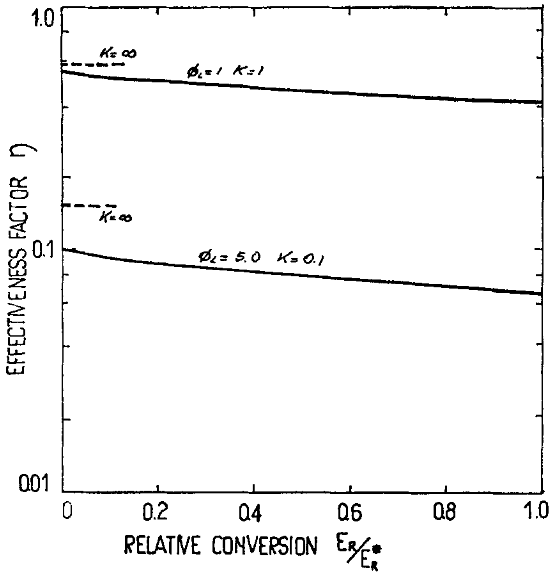

FIG. 7. Relative conversion influence on effectiveness factor for reversible reaction.

$$\eta = \frac{(27)^{1/2}}{9\phi_L}\left(\frac{1}{\tanh \phi''_L} \quad \frac{1}{\phi''_L}\right) \quad (24)$$

$$\phi''_L = (27)^{1/2}\phi_L$$

These solutions can be compared with those given by Eqs. (21) and (23), which represent the asymptotic ones

$$\eta = 0.40/\phi_L \qquad \text{for } K = 10^{-1}$$

$$\eta = 0.57/\phi_L \qquad \text{for } K = 1$$

$$\eta = 0.68/\phi_L \qquad \text{for } K = 10$$

These asymptotic solutions compare very well with Fig. 5.

ACKNOWLEDGMENTS

The calculations involved in this article were performed with the aid of the Mercury Ferranti digital computer of the Instituto del Calculo of the University of Buenos Aires, to whom we are indebted. The suggestions of Prof. E. E. Petersen are also gratefully acknowledged.

REFERENCES

1. CARBERRY, J. J., *A.I.Ch.E. J.* **8**, 557 (1962).
2. CHIEH CHU, AND HOUGEN, O. A., *Chem. Eng. Sci.* **17**, 167 (1962).
3. DAMKÖHLER, G., *D. Chem. Ing.* **3**, 430 (1937).
4. KUBOTA, H., AND SHINDO, M., *Chem. Eng. (Japan)* **20**, 11 (1956).
5. PETERSEN, E. E., *Chem. Eng. Sci.* **17**, 987 (1962).
6. THIELE, E. H., *Ind. Eng. Chem.* **31**, 316 (1939).
7. WAGNER, K., *Z. Physik. Chem.* **A193**, 1 (1943).
8. WEISZ, P. B., *Z. Physik. Chem. (Frankfurt)* **11**, 1 (1957).
9. WHEELER, A., *Catalysis* **2**, 105 (Reinhold, New York, 1955).
10. ZELDOVICH, J. B., *Acta Physicochim. URSS* **10**, 583 (1939).