Effective Diffusivities for the Ortho-Para Hydrogen System

NORMAN STEISEL, RICHARD N. FOSTER, and JOHN B. BUTT

Yale University, New Haven, Connecticut

Sterrett and Brown (*1*) have compared the predictions of three procedures (*2* to *4*) for estimation of effective diffusivity values in porous media to corresponding experimental values based on measurements in the presence of reaction for the ortho-para hydrogen system. A microporous ferric oxide gel catalyst with a rather narrow range of pore sizes was employed for the reaction at 1 atm. and 76°K. Of particular interest in the work of Sterrett and Brown (as they point out), is the examination of the question of whether these predictive methods, all developed on the basis of theory and experiment in the absence of chemical reaction, can be applied to reacting systems.

The purpose of this paper is to add to the results of Sterrett and Brown effective diffusivities computed for their system from the pore structure simulation of Foster and Butt (*5*). The general procedure for this in application to a catalytic reaction has been described previously (*6*). The diffusivities are computed from mass flux calculations, except that the 1:1 stoichiometry required by the ortho-para reaction is employed for the simulation rather than inverse square root of molecular weight ratio pertaining to isothermal, isobaric counter diffusion. The pore size distribution data reported by Sterrett (*7*) were used to establish the geometry of the pore arrays of the simulation, and the correlation for values of the mixing efficiency parameter of the simulation (*8*) is bounded at 100% for the small micropores involved.

The effective diffusivities so calculated are reported in Table 1. The values are very similar to those determined by the other methods tested by Sterrett and Brown, about 40% below the experimental diffusivity of 19.3×10^{-4} sq.cm./sec. The similarity in results obtained by these four different methods is striking, and tends to lend substance to the speculation that differences between computed and experimental values may be the result of some mode of surface migration.

TABLE 1. PREDICTED EFFECTIVE DIFFUSIVITIES FROM CONVERGENT—DIVERGENT PORE MODEL
(Diffusivity × 10^4, sq.cm/sec)

Catalyst 30-02		
To a radius of 10 Å.	—	10.3
To a radius of 5.2 Å.	—	10.7
Catalyst 80-02		
To a radius of 10 Å.	—	10.9
To a radius of 5.2 Å.	—	11.4

ACKNOWLEDGMENT

We are most indebted to J. S. Sterrett and L. F. Brown for their help in furnishing the detailed data required for the simulation calculations.

LITERATURE CITED

1. Sterrett, J. S., and L. F. Brown, *AIChE J.*, **14**, 000 (1968).
2. Weisz, P. B., and A. B. Schwartz, *J. Catalysis*, **1**, 399 (1962).
3. Wakao, N., and J. M. Smith, *Chem. Eng. Sci.*, **17**, 825 (1962).
4. Johnson, M. F. L., and W. E. Stewart, *J. Catalysis*, **4**, 248 (1965).
5. Foster, R. N., and J. B. Butt, *AIChE J.*, **12**, 180 (1966).
6. Steisel, N., and J. B. Butt, *Chem. Eng. Sci.*, **22**, 469 (1967).
7. Sterrett, J. S., MS thesis, Univer. Colorado, Boulder (1967).
8. Foster, R. N., J. B. Butt, and H. Bliss, *J. Catalysis*, **7**, 191 (1967).

Bounds on the Effectiveness Factors for Exothermic Catalytic Reaction

DAN LUSS

University of Houston, Houston, Texas

The effectiveness factors (E.F.) for a single irreversible reaction that occur in a spherical catalyst have been reported by Weisz and Hicks (*9*). It was shown that the E.F. is a function of three dimensionless groups: β (dimensionless heat of reaction), γ (dimensionless activation energy), and ψ_0 (the Thiele modulus). Their work has been extended by Weekman and Gorring (*7*), and Weekman (*8*) to include the effect of volume change of the reactants. Butt (*3*) extended it for the case of two reactions. Tinkler and Metzner (*6*) proposed to use a simplified exponential approximation, which enabled them to obtain the E.F. as a function of the Thiele modulus and the product $\epsilon = \gamma\beta$. This reduced largely the amount of computational effort needed for a parametric study. Moreover, it enables the analytical estimation of the asymptotic value of the E.F. for large Thiele modulus (*4*, *5*).

It was shown (*2*, *8*) that the T.-M. (Tinkler-Metzner) approximation can cause rather large errors in the values of the E.F., especially in the region of multiple solutions. Moreover, this approximation leads to wrong values for the asymptotic E.F. A method will be described in this paper, by which the simple T.-M. approximation can be modified to obtain an upper and lower bound on the exact values of the E.F. These bounds enable one to estimate the range in which the T.-M. approximation is valid, and obtain an improved analytical estimate of the asymptotic E.F.

EQUATIONS AND METHOD OF SOLUTION

The differential equation describing a single irreversible first order reaction occurring in a catalyst pellet is

$$\frac{1}{r^n}\frac{d}{dr}\left(r^n\frac{dy}{dr}\right)=$$

$$-\psi_0{}^2\,(1+\beta-y)\exp\left[\gamma\left(1-\frac{1}{y}\right)\right]=-\psi_0{}^2 f(y) \quad (1)$$

where

$$n\begin{cases}0 \text{ for an infinite slab}\\ 1 \text{ for an infinite cylinder}\\ 2 \text{ for a sphere}\end{cases}$$

$$\beta=\frac{(-\Delta H)Dc_o}{\lambda T_o} \qquad y=\frac{T}{T_o}$$

$$\psi_0=R\sqrt{k(T_o)/D} \qquad \gamma=\frac{E}{RT_o}$$

subject to the boundary conditions

$$y'(0) = 0 \tag{2}$$

$$y(1) = 1 \tag{3}$$

The effectiveness factor is defined as

$$\text{E.F.} = \eta = -\frac{n+1}{\psi_0^2\beta} y'(1) \tag{4}$$

A very simple numerical procedure to solve Equation (1) has been described (9), and was used for the numerical computations of this work.

By the transformation

$$y - 1 = \beta z = \frac{\epsilon z}{\gamma} \tag{5}$$

Equation (1) can be transformed into

$$\frac{1}{r^n}\frac{d}{dr}\left(r^n \frac{dz}{dr}\right) = -\psi_0^2 z \exp\frac{\epsilon z}{y} \tag{6}$$

subject to the boundary conditions

$$z'(0) = 0 \tag{7}$$

$$z(1) = 0 \tag{8}$$

Tinkler and Metzner suggested the use of approximation

$$\frac{\epsilon z}{y} \approx \epsilon z \qquad 1 \leqq y \leqq 1 + \beta \tag{9}$$

This enabled them to obtain the E.F. as a function of the two dimensionless groups ϕ_0 and $\epsilon = \gamma\beta$ instead of the three groups ϕ_0, γ and β needed by Weisz and Hicks (9).

Aris has shown (2) that in the case of spherical particles, the E.F. obtained by the T.-M. approximation are larger than those obtained by the exact solution. Figures 1 and 2 show that the same phenomena occur for slabs and cylindrical particles. The discrepancy is largest for high values of ϵ, and for a given value of ϵ it is increasing with β. It is clear from Figures 1 and 2 that such a procedure may lead to a large error.

DETERMINATION OF BOUNDS ON THE EFFECTIVENESS FACTOR

In this section a simple technique will be developed to determine upper and lower bounds on the E.F. This will enable us to check in which range the T.-M. approximation is valid and to obtain better bounds on the asymptotic E.F.

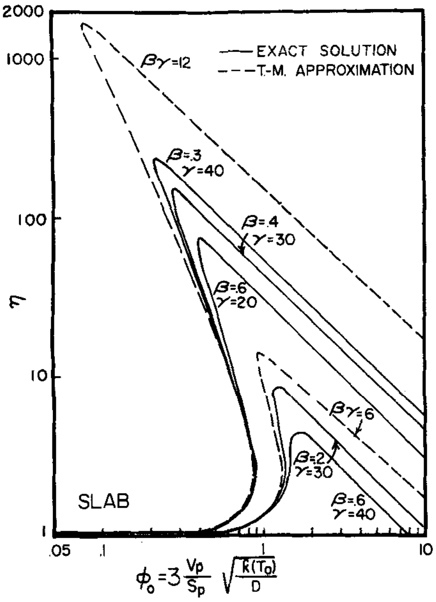

Fig. 1. Variations of effectiveness factor for a slab with Thiele modulus for two groups of parameter values.

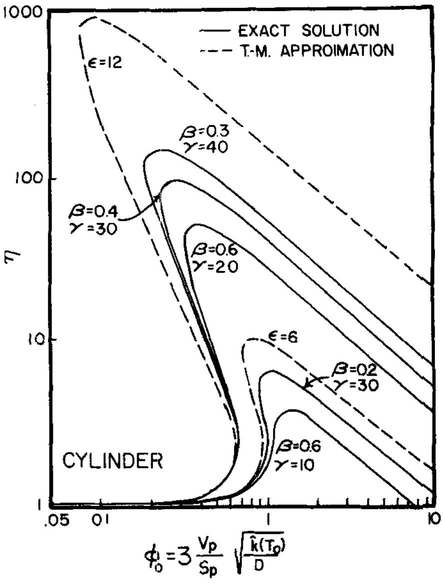

Fig. 2. Variations of effectiveness factor for a cylinder with Thiele modulus for two groups of parameter values.

In case of a slab, Equation (1) can be rewritten as

$$\frac{dy}{dr} = w \tag{10}$$

$$\frac{dw}{dr} = -\psi_0^2 f(y) \tag{11}$$

subject to the boundary conditions

$$w(0) = 0 \tag{12}$$

$$y(1) = 1 \tag{13}$$

The trajectories in the phase plane $w - y$ are described by

$$\frac{dw}{dy} = -\frac{\psi_0^2 f(y)}{w} \tag{14}$$

The steady state solutions are given by trajectories passing between the lines $w = 0$ and $y = 1$. A schematic description of that part of the phase plane is given in Figure 3.

Define:

$l_{(a)}$ = the trajectory for which $y = a$ for $w = 0$

$w[l_{(a)}]$ = the value of $w = dy/dx$ along the trajectory $l_{(a)}$

Clearly the steady states are represented by all trajectories for which

$$\int_a^1 \frac{dy}{w[l_{(a)}]} = 1 \tag{15}$$

In the range of interest $w \leqq 0$ $1 < y \leqq 1 + \beta$ there is no singular point and hence the trajectories cannot intersect. Suppose that $l_{(a_1)}$, $l_{(a_2)}$, and $l_{(a_3)}$ represent the trajectories which satisfy Equation (1) and its boundary conditions (2, 3). It is clear from Figure 3 that at $y = 1$

$$-\frac{dy}{dx}\bigg|_{l_{(a_1)}} < -\frac{dy}{dx}\bigg|_{l_{(a_2)}} < -\frac{dy}{dx}\bigg|_{l_{(a_3)}} \qquad \text{if } a_1 < a_2 < a_3 \tag{16}$$

Thus, it can be concluded that among the possible steady states, the largest (smallest) E.F. is obtained for the one with the highest (lowest) temperature at the center of the catalyst.

Consider now the steady state trajectory with largest E.F., that is, a_3. If we replace in Equation (11) $f(y)$ by

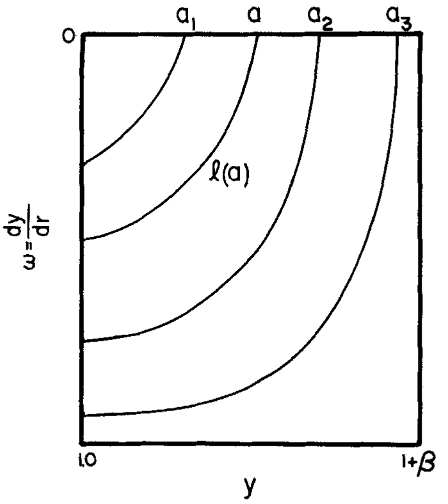

Fig. 3. Schematic description of phase plane of equations. (A1) (A2).

$f^*(y)$, such that

$$f(y) < f^*(y) \qquad 1 < y < 1+\beta \tag{17}$$

then instead of $l_{(a_3)}$ a new trajectory $l^*_{(a)}$ will be obtained (see Figure 4) for which

$$-w[l^*_{(a_3)}] > -w[l_{(a_3)}] \quad 1 \leq y \leq a_3 \tag{18}$$

Hence

$$\int_1^{a_3} \frac{dy}{w[l^*_{(a_3)}]} = \int_1^{a_3} \frac{dy}{-w[l^*_{(a_3)}]} < \int_1^{a_3} \frac{dy}{-\mathrm{w}[l_{(a_3)}]} = 1 \tag{19}$$

Hence $l^*_{(a_3)}$ is not a steady state solution for $f^*(y)$. Since

$$\lim_{a_3 \longrightarrow 1+\beta} \int_{a_3}^{1} \frac{dy}{w[l^*_{(a_3)}]} = \infty \tag{20}$$

there exists a value, say a_4 ($a_3 < a_4 < 1+\beta$) for which the trajectory $l^*_{(a_4)}$ is a steady state solution, that is, it satisfies Equation (15). Now at $y = 1$

$$-\frac{dy}{dr}\bigg|_{l_{(a_3)}} < -\frac{dy}{dr}\bigg|_{l^*_{(a_3)}} < -\frac{dy}{dr}\bigg|_{l^*_{(a_4)}} \tag{21}$$

We define $\underset{i}{\mathrm{Max}}\ \eta[f(y)]$ as the largest E.F. among all i solutions of the steady state Equation (1) by using the kinetic expression $f(y)$. Similarly $\underset{i}{\mathrm{Min}}\ \eta[f(y)]$ is the smallest E.F. among all i solutions.

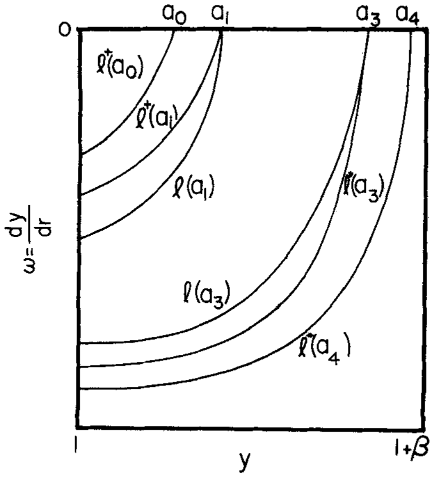

Fig. 4. Schematic of phase plane.

Since the E.F. is a linear function of dy/dr at $y = 1$ [Equation (4)], it follows from Equation (21), that

$$\underset{i}{\mathrm{Max}}\,\eta[f(y)] < \underset{i}{\mathrm{Max}}\,\eta[f^*(y)] \tag{22}$$

Consider the steady state with the lowest E.F., $l_{(a_1)}$. If we replace in Equation (11) $f(y)$ by $f^+(y)$ such that

$$f^+(y) < f(y) \qquad 1 < y < 1+\beta \tag{23}$$

then it can be shown that there exists a steady state solution $l^+_{(a_0)}$, where $1 < a_0 < a_1$. It is clear from the phase plane shown in Figure 4 that

$$-\frac{dy}{dr}\bigg|_{l^+_{(a_0)}} < -\frac{dy}{dr}\bigg|_{l^+_{(a_1)}} < -\frac{dy}{dr}\bigg|_{l_{(a_1)}} \tag{24}$$

It follows from Equation (24) that

$$\underset{i}{\mathrm{Min}}\,\eta[f(y)] > \underset{i}{\mathrm{Min}}\,\eta[f^+(y)] \tag{25}$$

Clearly,

$$\exp\frac{\gamma(y-1)}{1+\beta} < \exp\frac{\gamma(y-1)}{y} < \exp\gamma(y-1) \qquad 1 < y < 1+\beta \tag{26}$$

By use of Equation (5) this can be transformed into

$$\exp\,\epsilon' z < \exp\frac{\epsilon z}{y} < \exp\epsilon z \qquad 1 < y < 1+\beta \tag{27}$$

Where

$$\epsilon' = \frac{\gamma\beta}{1+\beta}$$

From Equations (22) and (25) we arrive at the following theorem.

The E.F. are bounded from above by the upper E.F. computed by the T.-M. approximation [$\exp\gamma(y-1)/y \approx \exp\epsilon z$], and from below by the lowest E.F. computed by the T.-M. approximation for ϵ'. [$\exp(\gamma(y-1)/y) \approx \exp\epsilon' z$].

The validity of the theorem is clearly demonstrated in Figure 5. It is shown for example that the exact E.F. curve for $\gamma = 24$ and $\beta = 0.5$ is bounded between the T.-M. curves computed for $\epsilon = 12$ and $\epsilon = 8$. (This relatively high value of ϵ was chosen in order to enable a clear distinction between the various E.F. curves). Since

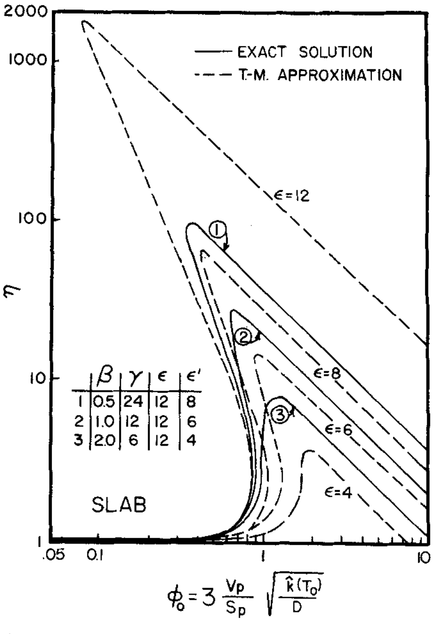

Fig. 5. Bounds on the effectiveness factor for slab.

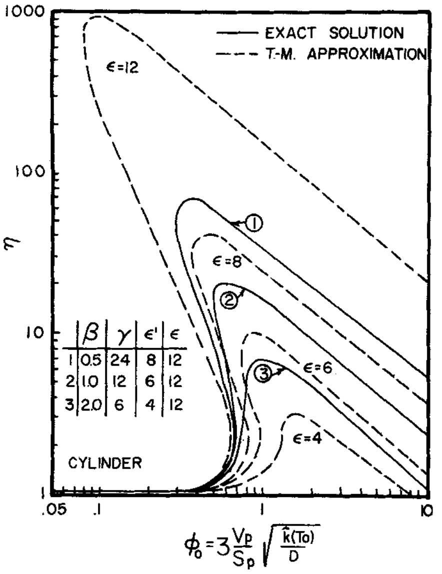

Fig. 6. Bounds on the effectiveness factor for cylinder.

the exact E.F. curve is bounded by the curves for ϵ and ϵ', it can be concluded that the Tinkler-Metzner method yields a good approximation in the range in which the curve for $\epsilon = \beta\gamma$ and $\epsilon' = \beta\gamma/(1 + \beta)$ are close together.

Thus, the approximation is good for low values of $\epsilon (\epsilon < 4)$. Figures 1 and 2 indicate that for any value of ϵ the approximation is better for smaller values of β.

It is seen from Figure 5 that the asymptotic E.F. is better described by the ϵ' curve than by the ϵ curve. The reason being that for large values of ϕ_0 most of the reaction is completed in a narrow zone near the interface and the dimensionless temperature throughout most of the volume is much closer to $1 + \beta$ than to one. Analytical methods to estimate the asymptotic E.F. by use of the T.-M. approximation are discussed (*4*, *5*).

It should be noted that the theorem is proved here only for slab. It was shown by Aris (*1*) and Petersen (*5*) that all catalyst particles of arbitrary shape have the same asymptotic value of the E.F. if the characteristic length is V_p/S_p. Thus, it is clear that the bounds on the asymptotic E.F. obtained for a slab can be used also for other configurations.

Surprisingly, it was found that the theorem is valid also for cylinders (Figure 6) and spheres [Figure 2 in (*2*)] for all values of the Thiele modulus. However, no proof of this fact was found.

CONCLUSIONS

1. It is shown that for large values of $\epsilon = \gamma\beta$ the Tinkler-Metzner approximation yields large errors in the computed values of the effectiveness factors.
2. A simple method is developed by which the Tinkler-Metzner approximation can be used to obtain upper and lower bounds on the exact value of the effectiveness factor for an exothermic catalytic reaction.
3. It is shown that the asymptotic effectiveness factor curve computed by the T. M. method for $\epsilon' = \gamma\beta/(1 + \beta)$ yields a better estimate than does the curve for $\epsilon = \gamma\beta$.

ACKNOWLEDGMENT

The author is indebted to M. Strand who performed most of the computations.

NOTATION

c_o = concentration of reactant
D = effective diffusivity
E = activation energy
$f(y)$ = kinetic expression
ΔH = heat of reaction
k = reaction rate constant
r = radial position
R = radius, or half thickness of slab
S_p = surface area of particle
T = temperature
V_p = volume of particle
y = T/T_o
w = dy/dr
z = $(y - 1)/\beta$

Greek Letters

β = $(-\Delta H)Dc_o/\lambda T_o$
γ = E/RT_o
ϵ = $\beta\gamma$
ϵ' = $\beta\gamma/(1 + \beta)$
η = effectiveness factor
λ = thermal conductivity
ϕ_0 = $3V_p/S_p\sqrt{k(T_o)/D}$
ψ_0 = $R\sqrt{k(T_o)/D}$

LITERATURE CITED

1. Aris, R., *Chem. Eng. Sci.*, **6**, 262 (1957).
2. ———, *Ind. Eng. Chem.*, **58**, 32 (1966).
3. Butt, J. B., *Chem. Eng. Sci.*, **21**, 275 (1966).
4. Petersen, E. E., *ibid.*, **17**, 987 (1962).
5. ———, "Chemical Reactor Analysis", Prentice Hall, Englewood Cliffs, N. J. (1965).
6. Tinkler, J. D., and A. B. Metzner, *Ind. Eng. Chem.*, **53**, 663 (1961).
7. Weekman, V. W., and R. L. Gorring, *J. Cat.*, **4**, 260 (1965).
8. *Ibid.*, **5**, 44 (1966).
9. Weisz, P. B., and J. S. Hicks, *Chem. Eng. Sci.*, **17**, 265 (1961).

Diffusion Coefficients for Oxygen Transport in Whole Blood

DANIEL HERSHEY
University of Cincinnati, Cincinnati, Ohio
and
TERRY KARHAN
Union Carbide Corp., Bound Brook, New Jersey

The rate of oxygen uptake by blood has been the object of much study. Early researchers hypothesized that the oxygen molecules, after traversing a multistage diffusion path in the lungs, would then combine with the hemo-