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 $\times 10^4$, 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

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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

$$\frac{1}{r^n}\frac{d}{dr}\left(r^n\frac{dy}{dr}\right) = -\psi_0^2\,(1+\beta-y)\exp\left[\gamma\left(1-\frac{1}{y}\right)\right] = -\psi_0^2 f(y) \qquad (1)$$

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