JOURNAL OF CATALYSIS 50, 205–219 (1977)

The Effect of Surface Diffusion on the Catalytic Selectivity of Concurrent and Consecutive Reactions

S. M. M. AKHTAR,[1] K. BLACKMORE, S. A. SHAH, AND W. J. THOMAS[2]

School of Chemical Engineering, University of Bath, Bath BA2 7AY, England

Received October 13, 1976; revised April 24, 1977

The effect which surface diffusion has on the selectivity of certain concurrent and consecutive catalytic reactions is investigated numerically by analysis of a simple mathematical model of the parallel chemical kinetic and physical transport processes occurring in the porous catalyst medium. Nonisothermal and interparticle mass transfer effects are considered in the analysis. For exothermic concurrent reactions selectivity is enhanced by surface diffusion when the preferred product is formed by the reaction with the greater activation energy. Convection of heat away from the catalyst particle, on the other hand, reduces the selectivity. Although the selectivity of exothermic consecutive reactions is also enhanced by surface diffusion for low values of the Thiele modulus, when the reaction occurs in a diffusion-limited region, surface diffusion further exacerbates the already restricted selectivity. Increased heat transfer also has a deleterious effect on the reaction selectivity. Diametrically opposed to the results obtained for exothermic reaction are the trends observed for endothermic reactions, the selectivities of which are explained in terms of the magnitude of the intra- and interparticle mass and heat transport processes. The study concludes with a preliminary examination of the manner in which selectivity is affected when resistance to heat transfer is confined to a relatively stagnant boundary layer of fluid bathing the catalyst pellet. It is shown that, for certain ranges of parameters, multiple solutions exist.

INTRODUCTION

Intraparticle transport effects often have an important and sometimes limiting influence on overall chemical reaction rates in porous heterogeneous catalysts. The particular circumstances which ameliorate transport of reactants and products by surface translation rather than molecular or Knudsen diffusion through the pore volume have been the subject of recent discussion. DeBoer (*1*) has asserted that the transport of large molecules, with dimensions comparable with the width of micropores of which many catalysts are composed, is almost entirely due to surface diffusion rather than diffusion in the vapor phase contained by the porous catalyst structure. The significance of such an observation is that surface diffusion may play an important role in determining the catalytic selectivity of reactions of organic vapors in microporous solids often utilized for reforming and processing in the petroleum and petrochemicals industry.

Surface diffusion cannot be important unless adsorption occurs to an appreciable extent. On the other hand, strong chemisorption will exacerbate free two-dimensional translation. It is not surprising therefore that surface diffusion has been observed to contribute to the transport mechanism in cases of the physical adsorp-

---

[1] S. M. M. Akhtar made an initial and significant contribution to this work but died before it was completed.

[2] To whom reprint requests should be addressed.

ISSN 0021-9517

tion of gases at low or moderate temperatures (*2, 3*). A correlation of surface diffusion coefficients with the strength of adsorption has been suggested by Sladek *et al.* (*4*) and also reported by Satterfield (*5*). A high value for the surface diffusion coefficient, for example, reflects a low value of the heat of adsorption and a less polar interaction between adsorbate and adsorbent. Although the magnitude of the surface diffusion coefficient for chemisorbed components is likely to be smaller than that for physically adsorbed gases or vapors, surface diffusion has been cited as a contributory factor in effecting the catalytic dehydration of ethanol (*6*) where the partial pressure of the reactant is usually an appreciable fraction of the vapor pressure. It has also been invoked to explain why experimental effectiveness factors observed for the *ortho–para* hydrogen conversion (*7*) at about 2-bar pressure and 76 K, and also for the dehydration of isopropanol at 473 to 523 K on γ-alumina (*8*), are substantially larger than calculated. Some consequences of the occurrence of surface transport during concurrent catalytic reactions have briefly been alluded to by England and Thomas (*9*) in a paper which suggest that selectivity is affected by surface diffusion. In a more extensive analysis (*10*) of concurrent and consecutive reactions involving one zero-order step, it was demonstrated that selectivity is a monotonic increasing function of effective diffusivity. The functional relationship between selectivity and effective diffusivity is determined not only by the kinetic model and its associated boundary conditions but also by the transport processes that occur. Therefore, when surface diffusion is an integral part of the transport processes within a porous medium in which chemical reactions are concomitantly occurring, it is important to investigate the extent to which surface diffusion influences selectivity.

Butt and Foster (*11, 12*), in two important papers which lay the foundations for considering quantitatively the manner in which transport by surface diffusion can enhance catalytic reaction, show that when adsorption is sufficiently extensive and two-dimensional transport has a significant activation energy, the rate of chemical reaction is increased. They restrict their treatment to a simple first-order reaction in a porous pellet and include nonisothermal effects but do not consider the influence of interparticle heat and mass transfer. Wicke and Voigt (*13*) have also shown how the difference between calculated and observed rates of catalytic reactions can be accounted for by surface diffusion enhancement. The purpose of the present paper is to extend the work of Butt and Foster (*11, 12*) to include concurrent and consecutive reactions and to consider how catalytic selectivity is affected by surface diffusion effects within the porous catalyst pellet. We include nonisothermal conditions in our model and choose boundary conditions which reflect the possibility of interparticle transport.

THEORY

For the purpose of analyzing the effects of surface diffusion on catalytic selectivity, we choose a wafer-shaped porous pellet, the properties within which are isotropic. Either Maxwellian or Knudsen diffusion may occur through the void space of the solid permeated by a honeycomb of fine pores, but two-dimensional surface translation may also be a mode of transport for reactants and products. The flux per unit concentration gradient of a component through the void space is characterized by an effective diffusivity D_e,[3]

$$N = -D_e(dc/dx), \qquad (1)$$

the concentration c decreasing in the direction x of diffusion. We do not need to specify in advance whether Maxwellian or

---

[3] See Appendix for explanation of symbols.

Knudsen diffusion is prominent but may assess the relative contributions, if desired, by the simple formula of Bosanquet (*14*) or alternatively apply some other appropriate form (*15*). The surface flux, on the other hand, is described in terms of a decreasing surface concentration c_s

$$N_s = -D_s(dc_s/dx), \tag{2}$$

so that the total flux due to the combined effects of gas phase and surface transport is

$$\epsilon N_T = \epsilon N + \rho_p S_g N_s, \tag{3}$$

where ϵ is the pellet voidage, ρ_p its density, and S_g the specific surface area over which two-dimensional translation occurs. The summation of fluxes in Eq. (3) implies that an effective diffusion coefficient $\hat{D}_e$ can be defined for any component as the total flux per unit concentration gradient:

$$\hat{D}_e = D_e + (\rho_p S_g/\epsilon)\cdot[D_s(dc_s/dx)/(dc/dx)]. \tag{4}$$

To a first approximation, the ratio of the gas-phase and local surface concentration gradient in Eq. (4) may be regarded as the gradient of the adsorption isotherm. Because, in catalysis, surface concentrations are usually low, the isotherm gradient should be computed for the initial portion of the curve. If it is linear and the Henry's law constant is K, Eq. (4) may then be rewritten

$$\hat{D}_e = D_e + (\rho_p S_g K/\epsilon)\cdot D_s, \tag{5}$$

the form we adopt for the purpose of this discussion. As chemisorption is activated and the strength of the adsorbate–adsorbent interaction is sufficiently high to consider that two-dimensional surface translation requires an activation energy E_s, we write the temperature dependence of D_s as

$$D_s = D_{s0}\exp(-E_s/RT). \tag{6}$$

Application of the Clausius–Clapeyron equation to the adsorption isotherm leads one to a relation

$$K = K_0 \exp(q/RT), \tag{7}$$

describing the temperature dependence of the Henry's law constant where q is the heat of adsorption of the component considered. The variation of the Maxwellian or Knudsen effective diffusivity D_e with temperature is weak in comparison with that of K and D_s and is ignored in this analysis. It is also assumed that both E_s and q are independent of surface coverage. It would not be difficult to incorporate such a variation in principle, although the complexity of the computations would be considerably increased because conservation equations for both the gas phase and the adsorbed phase would then have to be written and solved.

The general steady state conservation equation describing the intraparticle transport of mass with chemical reaction in a porous medium is

$$-\mathrm{Div}\,\{-\hat{D}_{ei}\,\mathrm{Grad}\,c_i\} + (\rho_p S_g/\epsilon) \times \sum_{j=1}^{n} \alpha_{hj} r_j(c_h) = 0, \tag{8}$$

for each of the i components participating in reaction. The summation of reaction rates $r_j(c_h)$ is taken over the n kinetic pathways (each one designated j) in which component i features. The α_{hj} are stoichiometric coefficients. It is not uncommon for the rate of the surface reaction to be the rate-controlling step in the sequence chemisorption, surface reaction, and desorption. If we adopt such an assumption then, for a first-order surface reaction, each pathway j will have a chemical rate

$$r_j = k_j c_{sh} = k_j K_h c_h, \tag{9}$$

where the subscript h refers to a component h (not necessarily the same as i), the concentration of which is a function of the kinetic equation describing the rate of pathway j. The surface concentration c_s

will be directly related to the gas-phase concentration c because adsorption equilibrium is tacitly assumed. Provided the surface concentration is low, as is usually the case in catalysis, the linear form of the adsorption isotherm is justified in writing Eq. (9). The temperature dependence of the rate constant k_j is of Arrhenius form

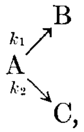
$$k_j = A_j \exp(-[E_j/RT]). \qquad (10)$$

Analogously, the equation representing the steady state conservation of heat within the porous medium is

$$-\mathrm{Div}\,\{-\lambda\,\mathrm{Grad}\,T\} + (\rho_p S_g/\epsilon) \times \sum_{j=1}^{n} \alpha_{hj}(-\Delta H_j) r_j(c_h) = 0. \qquad (11)$$

Because the heat of reaction is usually only a weak function of temperature compared with the reaction rate, $(-\Delta H_j)$ is considered to be constant.

We apply the conservation Eqs. (8) and (11) first to the concurrent reaction scheme,



and secondly to the consecutive reactions,

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C,$$

occurring in a slab-shaped porous pellet. For convenience of computation and scaling, we define the dimensionless quantities

$$\delta_{ij} = (E_j - q_i)/RT_0$$

and

$$\delta_{si} = (E_{si} - q_i)/RT_0, \qquad (12)$$

where T_0 represents the temperature of the gas phase bathing the pellet. It is also expedient to introduce a dimensionless variable ψ_i to describe the magnitude of the surface effect. Accordingly we put

$$\psi_i = (\rho_p S_g/\epsilon)\cdot[D_{s0i}K_{0i}\exp(-\delta_{si})/D_{ei}] = (\rho_p S_g/\epsilon)\cdot(D_{si}{}^{\circ}K_i{}^{\circ}/D_{ei}) \qquad (13)$$

where $D_{si}{}^{\circ}$ and $K_i{}^{\circ}$ are the values of D_{si} and K_i, respectively, at $T = T_0$. The Thiele modulus (*16, 17*) is also employed, in a modified form, as a dimensionless parameter. Because we consider the problem of catalyst selectivity for conditions when pellet temperature is not constant, we define a Thiele modulus[4] which is evaluated at the temperature T_0 and put

$$\phi_{ij} = a[(\rho_p S_g/\epsilon)(K_i{}^{\circ}k_j{}^{\circ}/D_{ei})]^{\frac{1}{2}}, \qquad (14)$$

where $k_j{}^{\circ}$ is the surface reaction velocity constant evaluated at T_0 and $a(= V_p/S_x)$ is the nominal pellet size definable in terms of pellet volume V_p and external surface area S_x. An additional parameter β_{ij},[4] introduced by Weisz and Hicks (*18*), serves to correlate the results presented with the degree of exothermicity or endothermicity of reaction. This parameter is defined by

$$\beta_{ij} = [(-\Delta H_j)D_{ei}c_{io}/\lambda T_0], \qquad (15)$$

where c_{io} is the concentration of component i in the bulk gas phase.

Concurrent Reaction

The pair of dimensionless material balance equations representing two first-order concurrent reactions in a pellet thus become

$$\begin{aligned}&\{1 + \psi_A \exp[\delta_{sA}(1 - 1/\theta)]\}(d^2\gamma_A/d\rho^2)\\&\quad + \{(\delta_{sA}\psi_A/\theta^2)\exp[\delta_{sA}(1 - 1/\theta)]\}\\&\quad \times (d\theta/d\rho)\cdot(d\gamma_A/d\rho) - \phi_{A1}{}^2\gamma_A\\&\quad \times \exp[\delta_{A1}(1 - 1/\theta)] - \phi_{A2}{}^2\gamma_A\\&\qquad\qquad \times \exp[\delta_{A2}(1 - 1/\theta)] = 0 \qquad (16)\end{aligned}$$

and

$$\begin{aligned}&\{1 + \psi_B \exp[\delta_{sB}(1 - 1/\theta)]\}(d^2\gamma_B/d\rho^2)\\&\quad + \{(\delta_{sB}\psi_B/\theta^2)\exp[\delta_{sB}(1 - 1/\theta)]\}\\&\quad \times (d\theta/d\rho)\cdot(d\gamma_B/d\rho) + \Delta_{AB}\phi_{A1}{}^2\gamma_A\\&\qquad\qquad \times \exp[\delta_{A1}(1 - 1/\theta)] = 0, \qquad (17)\end{aligned}$$

in which Δ_{AB} is the ratio (D_{eA}/D_{eB}). In

---

[4] Although the double suffix notation for ϕ an β is not essential for the reaction schemes considered in this paper, its use nonetheless facilitates extension of this work to more complex schemes.

the above equations the subscript 1 refers to the kinetic path A → B, while subscript 2 describes the route A → C. The corresponding dimensionless heat balance equation is

$$(d^2\theta/d\rho^2) + \beta_{A1}\phi_{A1}^2\gamma_A \exp[\delta_{A1}(1 - 1/\theta)] + \beta_{A2}\phi_{A2}^2\gamma_A \exp[\delta_{A2}(1 - 1/\theta)] = 0 \tag{18}$$

Due to the symmetry of the problem the boundary conditions at the particle center ($\rho = 0$) are common and are

$$\rho = 0, \; (d\gamma_A/d\rho) = (d\gamma_B/d\rho) = (d\theta/d\rho) = 0 \tag{19}$$

On the other hand, at the particle periphery ($\rho = 1$) the boundary conditions will depend on whether or not interparticle transport effects are considered important. When interparticle mass and heat transfer effects are neglected and the whole of the catalyst pellet is bathed in a uniform temperature and concentration field, the boundary conditions at $\rho = 1$ are

$$\rho = 1, \quad \gamma_A = 1, \quad \gamma_B = \Gamma, \quad \theta = 1, \tag{20}$$

where Γ is the ratio c_{B0}/c_{A0}.

Should, however, mass and heat transfer between the catalyst pellet and the surrounding fluid be considered an influence on the temperature and concentration profiles within the pellet and hence modify the catalytic selectivity, the appropriate boundary conditions are then

$$\rho = 1, \begin{cases} (d\gamma_i/d\rho) = \mathrm{Sh}_i(1 - \gamma_i) \text{ for } i = A. \\ (d\gamma_i/d\rho) = \mathrm{Sh}_i(\Gamma - \gamma_i) \text{ for } i = B, \\ (d\theta/d\rho) = \mathrm{Nu}\,(1 - \theta) \end{cases} \tag{21}$$

where the dimensionless modified Sherwood and Nusselt numbers (Sh_i and Nu, respectively) reflect the extent of interparticle transport.

If the selectivity σ of reaction is defined as the ratio of the rates of formation of components B and C, then for the steady state we may write

$$\sigma = [\hat{D}_{eB}(dc_B/dx)_{x=a}/\hat{D}_{eC}(dc_C/dx)_{x=a}] \tag{22}$$

which, in view of the stoichiometric relationship between components and the form of Eq. (5), becomes in dimensionless form

$$\sigma = -\frac{\Delta_{BC}}{\left\{\dfrac{1 + \psi_C \exp\left[\delta_{sC}\left(1 - \dfrac{1}{\theta}\right)\right]}{1 + \psi_B \exp\left[\delta_{sB}\left(1 - \dfrac{1}{\theta}\right)\right]}\right\}\left\{\dfrac{(d\gamma_A/d\rho)_{\rho=1}}{(d\gamma_B/d\rho)_{\rho=1}} + 1\right\}} \tag{23}$$

where Δ_{BC} is the ratio (D_{eB}/D_{eC}). Thus numerical solution of the coupled ordinary differential Eqs. (16), (17), and (18), subject to the boundary constraints (19) and (20) when there are no interparticle effects, or to the conditions (19) and (21) when interphase transport is significant, enables the selectivity, formulated by Eq. (23), to be computed.

Consecutive Reaction

Application of the general mass and heat balance Eqs. (8) and (11) to two first-order consecutive reactions in a porous pellet produces the three dimensionless equations

$$\{1 + \psi_A \exp[\delta_{sA}(1 - 1/\theta)]\}(d^2\gamma_A/d\rho^2) + \{(\delta_{sA}\psi_A/\theta^2)\exp[\delta_{sA}(1 - 1/\theta)]\} \times (d\theta/d\rho)\cdot(d\gamma_A/d\rho) - \phi_{A1}^2\gamma_A \times \exp[\delta_{A1}(1 - 1/\theta)] = 0 \tag{24}$$

$$\{1 + \psi_B \exp[\delta_{sB}(1 - 1/\theta)]\}(d^2\gamma_B/d\rho^2) + \{(\delta_{sB}\psi_B/\theta^2)\exp[\delta_{sB}(1 - 1/\theta)]\} \times (d\theta/d\rho)\cdot(d\gamma_B/d\rho) - \phi_{B2}^2\gamma_B \times \exp[\delta_{B2}(1 - 1/\theta)] + \Delta_{AB}\phi_{A1}^2\phi_A \times \exp[\delta_{A1}(1 - 1/\theta)] = 0 \tag{25}$$

and

$$(d^2\theta/d\rho^2) + \beta_{A1}\phi_{A1}^2\gamma_A \times \exp[\delta_{A1}(1-1/\theta)] + (\beta_{A2}/\Delta_{AB})\phi_{B2}^2\gamma_B \times \exp[\delta_{B2}(1 - 1/\theta)] = 0. \quad (26)$$

These will be subject to the same alternative boundary conditions as described for the concurrent reaction scheme. The catalytic selectivity may be computed from Eq. (23) once the coupled ordinary differential Eqs. (24), (25), and (26), together with the appropriate boundary conditions, have been solved numerically.

RESULTS AND DISCUSSION

Computations

Computation of the catalytic selectivity from Eq. (23) demands solution of the three coupled nonlinear second-order simultaneous ordinary differential Eqs. (16), (17), and (18) for a concurrent reaction path, or the Eq. (24), (25), and (26) for a consecutive reaction path. Butt and Foster (*11*, *12*), when solving their equations associated with a single reaction, applied a boundary value technique approximating the ordinary differential equations by means of a finite difference formulation. The resulting set of simultaneous nonlinear algebraic equations was solved by an iterative method in which each cycle of computation required the solution of three sets of linear simultaneous equations, each with a tridiagonal matrix of coefficients. Butt and Foster did, however, encounter convergence difficulties when dealing with some particular cases. In an attempt to avoid convergence problems we employ the shooting method with Newton correction of boundary conditions (*19*). Accordingly, we first reduce the three second-order differential equations to a set of six first-order differential equations subject to the boundary conditions already specified at $\rho = 0$ and $\rho = 1$. Using a Runge–Kutta–Merson (*19*) algorithm with an automatic step adjustment, the step-by-step forward integration routine is started at $\rho = 0$.

Now we know derivative values at this boundary but not the initial values of the three functions which must therefore be guessed. The initial values of γ_A, γ_B, and θ are thus treated as adjustable parameters and are varied until the forward integration process yields terminal values which match the specified conditions at $\rho = 1$. A Newton–Raphson method (*19*) of parameter adjustment was employed which yielded improved initial values for γ_A, γ_B, and θ. A few iterations (one, two, or three) generated the functions γ_i and θ satisfying the boundary conditions.

The partial derivatives required in the Newton–Raphson process were approximated by difference quotients, calculated by performing forward integration using small perturbations of the initial values of the parameters. As a check, the derivatives were also obtained (but with more computing effort) by differentiating the original equations with respect to the parameters and solving the enlarged set of differential equations by the initial value technique.

For convenience of display, presentation of the results of computations is restricted to a few typical values of some of the system parameters. Thus we assume no difference between the Maxwellian (or Knudsen) diffusivities for components and put $\Delta_{AB} = \Delta_{BC} = 1$. Similarly we select $\Gamma = \frac{1}{4}$ to represent the ratio of component concentrations exterior to the particle. Such a value might be typical of a particle situated not far from the entrance to a packed tubular reactor. Further along the reactor after significant conversion of the reactant has occurred, Γ would be substantially smaller. The ratio k_1/k_2 was always set at 2, whereas the parameters δ_{ij}, given by Eq. (12), are set at values of 10 and 15. For a reaction at about 300°C, such numerical values of δ_{ij} would mean a difference of approximately 45 kJ mol^{-1} between the overall chemical activation energy associated with a given kinetic path and the heat of adsorption. On the other hand, all δ_{si} are set at 2, representing a difference of only 8 to 12 kJ mol^{-1} between the activation energy associated with the surface reaction and the heat of adsorption.

Results are presented in the form of continuous curves representing the selectivity σ as a function of the Thiele modulus ϕ_{A1} describing the formation of product B (assumed to be the desired product). The effect which surface diffusion has on selectivity is portrayed by plotting families of curves with $\psi_A (= \psi_B)$ as a parameter.

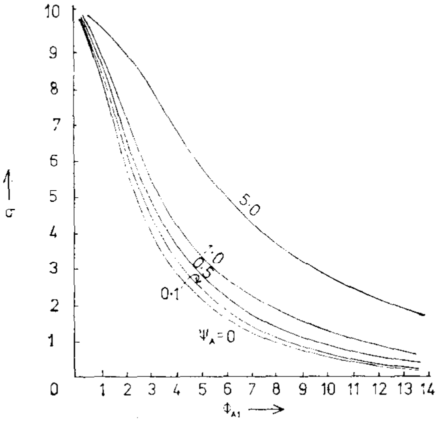


FIG. 1. Selectivity σ as a function of Thiele modulus ϕ_{A1}: isothermal concurrent reaction A → B, first order; A → C, zero order; $k_1c_{A0}/k_2 = 10$; $\beta = 0$; Nu = Sh = ∞; ψ_A as parameter.

Concurrent Reaction

For isothermal conditions, if the kinetic orders of the two competing reactions are equal, it is obvious that the selectivity will be unaffected by any type of intraparticle diffusion. When the reactions differ in kinetic order, selectivity will be a monotonic decreasing function of the Thiele modulus. This has previously been demonstrated either directly or implicitly in various discussions (*9, 17, 20–22*), but the effect of surface diffusion was excluded from the analysis. As an illustration of the effect which surface diffusion has on isothermal concurrent reactions of different kinetic orders we consider briefly a situation where the desired product (say B) is formed by a first-order isothermal reaction and the wasteful product C by a zero-order isothermal reaction. The appropriate differential equations describing diffusion and reaction in a slab shaped pellet may be derived by application of Eq. (8). In dimensionless form they become

$$(1 + \psi_A)(d^2\gamma_A/d\rho^2) - \phi_{A1}{}^2\gamma_A = \phi_{A2}{}^2/c_{A0} \tag{27}$$

and

$$(1 + \psi_B)(d^2\gamma_B/d\rho^2) + \Delta_{AB}\phi_{A1}{}^2\Gamma\gamma_A = 0. \tag{28}$$

These equations now include the parameters ψ_i accounting for the contribution which surface translation makes to the total diffusive flux of each component. The solution may immediately be written for boundary conditions which either include or exclude interparticle mass transfer. Because resistance to interparticle mass transfer is so often negligible in comparison with resistance to intraparticle diffusion, we confine our attention to the boundary conditions

$$\rho = 0,\ (d\gamma_i/d\rho) = 0;$$
$$\rho = 1,\ \gamma_i = 1 \text{ for } (i = \text{A, B}), \tag{29}$$

in which the isothermal pellet is bathed in the uniform concentration c_{i0}. The selectivity, as previously defined by Eq. (22), is easily shown to be

$$\sigma = (1 + k_1c_{A0}/k_2)[(1 + \psi_A)^{\frac{1}{2}}/\phi_{A1}] \times \tanh[\phi_{A1}/(1 + \psi_A)^{\frac{1}{2}}] - 1. \tag{30}$$

Figure 1 shows clearly that the reaction selectivity is enhanced by the surface transport of reactant A over the whole range of Thiele moduli for a given value of the kinetic parameter k_1c_{A0}/k_2 and is therefore in accord with the conclusion of Butt and Foster (*11, 12*) that surface diffusion enhances the rate of chemical reaction. For a 50-fold increase in surface diffusion, for example, selectivity is enhanced by a factor between 1.5 and 3 for Thiele moduli in the range 1 to 5.

When the competing concurrent reactions are nonisothermal, then the reaction

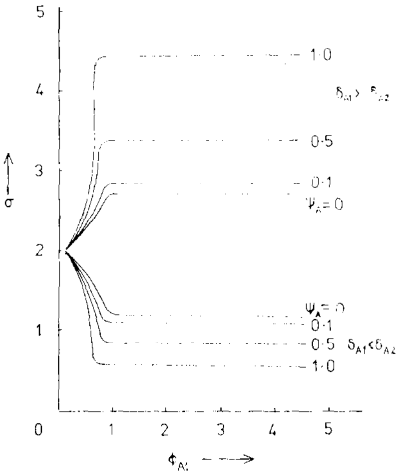


FIG. 2. Selectivity σ as a function of Thiele modulus ϕ_{A1}: exothermic first-order concurrent reaction, $\beta_{A1} = \beta_{A2} = 0.2$; Nu = Sh = ∞; ψ_A as parameter. Upper family of curves, $\delta_{A1} = 15$, $\delta_{A2} = 10$; lower family of curves, $\delta_{A1} = 10$, $\delta_{A2} = 15$.

selectivity is not necessarily a monotonic decreasing function of the Thiele modulus. If we first consider two competing first-order exothermic reactions, we find (Fig. 2) that the selectivity increases with an increase in Thiele modulus provided the dimensionless parameter δ_{ij} (which is a measure of the difference between the activation energy E_j and the heat of adsorption q_i) describing the desired reaction exceeds that for the undesired reaction. Such behavior has also been described by Østergaard (*23*). We further find that the selectivity is enhanced when surface diffusion of the reactant occurs, a greater selectivity for formation of the desired product B being attainable the more extensive is the amount of surface diffusion. Particularly noticeable is the very sharp increase in selectivity with increase in Thiele modulus for the whole range of surface diffusion considered and the abrupt transition to an asymptotic limit at a Thiele modulus between 0.5 and 1.0. Even at moderate values of the Thiele modulus, therefore, where pore diffusion limits the reaction rate, any increase in surface translation is extremely effective in improving selectivity. At values of the Thiele modulus greater than about 1.0, the selectivity is approximately doubled for a tenfold increase in surface diffusion. Indeed, for $\phi_{A1} > 1$, the only mode by which selectivity may be further enhanced is by surface translation rather than diffusion through the now very fine pores. In diametric contrast, the case when $\delta_{A1} < \delta_{A2}$ reveals that the selectivity decreases with an increase in Thiele modulus, surface diffusion now exacerbating the formation of desired product B and ameliorating the production of C. In such an instance, Fig. 2 indicates that the smallest particle size compatible with pressure drop restrictions is to be preferred.

If we now turn our attention to endothermic reactions it is apparent from Fig. 3 that, for the same parameters Δ and Γ as are considered for exothermic reactions, when $\delta_{A1} > \delta_{A2}$ the selectivity is a monotonic decreasing function of the Thiele modulus and is suppressed by an increase in surface diffusion of the reactant. On the other hand, when $\delta_{A1} < \delta_{A2}$ the selectivity increases with the Thiele modulus and is enhanced by the surface translation

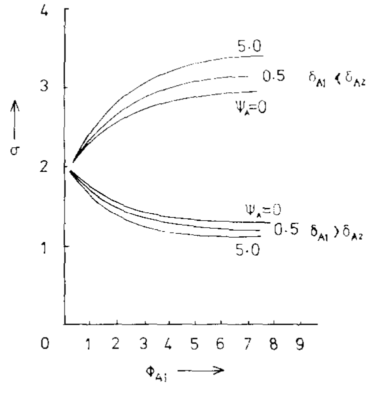


FIG. 3. Selectivity σ as a function of Thiele modulus ϕ_{A1}: endothermic first-order concurrent reaction, $\beta_{A1} = \beta_{A2} = -0.2$; Nu = Sh = ∞; ψ_A as parameter. Upper family of curves, $\delta_{A1} = 10$, $\delta_{A2} = 15$; lower family of curves, $\delta_{A1} = 15$, $\delta_{A2} = 10$.

of A. Thus when B is the desired product and yield is an important consideration, moderate size pellets should be chosen when $\delta_{A1} < \delta_{A2}$ so that gaseous and surface diffusion of reactant can favor the selective formation of B. One might expect that a 20% increase in selectivity would occur when ϕ_{A1} is increased from 1.0 to 2.0. Pellets which are too large would, of course, tend to be a disadvantage since the reaction would then be severely diffusion-limited for large Thiele moduli and much of the internal surface of the pellet would not be utilized. Small pellets, however, would be advantageous for the selective formation of B when $\delta_{A1} > \delta_{A2}$ but again the choice of particle size will be constrained by reactor operation.

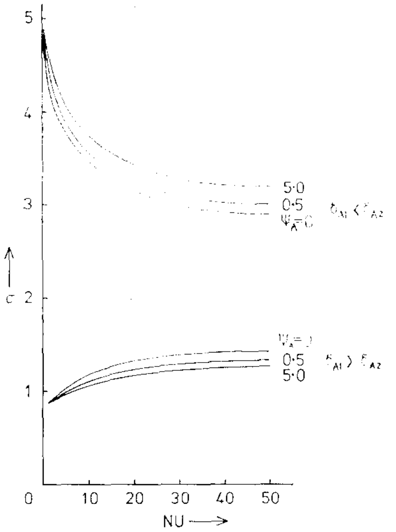


FIG. 5. Selectivity σ as a function of modified Nusselt group Nu: endothermic first-order concurrent reactions, $\beta_{A1} = \beta_{A2} = -0.2$; $\phi_{A1} = 3.0$; ψ_A as parameter. Upper family of curves, $\delta_{A1} = 10$, $\delta_{A2} = 15$; lower family of curves, $\delta_{A1} = 15$, $\delta_{A2} = 10$.

When we examine the effect of interparticle mass and heat transfer on the above results it is clear that the transfer of either heat or mass from the fluid phase to the porous material can have a marked influence on the selectivity. Figure 4 thus demonstrates that when interparticle heat transfer is an important consideration, then, for a given Thiele modulus describing an exothermic reaction, selectivity decreases monotonically with an increase in the magnitude of the modified dimensionless Nusselt group (depicting the relative ability of the fluid phase to transport heat by a convective mechanism) whenever $\delta_{A1} > \delta_{A2}$ but increases monotonically when $\delta_{A1} < \delta_{A2}$. Thus, for a reaction in which the activation energy for the formation of the desired product exceeds that for the wasteful product, the selectivity might easily be halved by only a three or fourfold increase in the interparticle heat transfer coefficient. This somewhat surprising result may be interpreted more easily when it is recalled that if the activation energy E_1 for the reaction responsible for formation of the desired product is greater than the activation energy E_2 ascribed to the reaction producing the wasteful product, then the reaction with the highest temperature coefficient will be favored whenever there is a tendency to accumulate heat within the pellet. For a given Thiele modulus and surface mobility, the selectivity for forma-

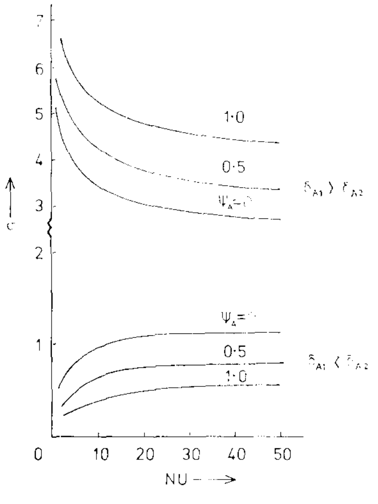


FIG. 4. Selectivity σ as a function of modified Nusselt group Nu: exothermic first-order concurrent reactions, $\beta_{A1} = \beta_{A2} = 0.2$; $\phi_{A1} = 1.5$; ψ_A as parameter. Upper family of curves, $\delta_{A1} = 15$, $\delta_{A2} = 10$; lower family of curves, $\delta_{A1} = 10$, $\delta_{A2} = 15$.

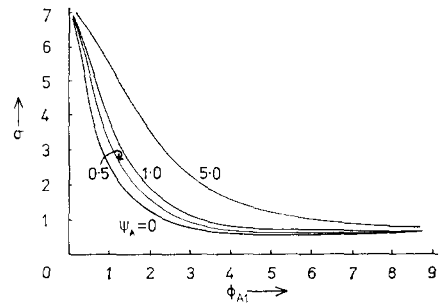


FIG. 6. Selectivity σ as a function of Thiele modulus ϕ_{A1}: isothermal consecutive first-order reactions, $\beta = 0$; Nu = Sh = ∞; ψ_A as parameter.

tion of B by an exothermic reaction would therefore be decreased by more effective particle to fluid heat transfer because any retention of heat by the particle would otherwise favor its formation. Precisely the opposite situation will apply when $E_1 < E_2$. If the competing reactions within the pellet are endothermic then, as Fig. 5 shows, the complete argument is reversed.

Similar computations were completed to investigate the effect of fluid to pellet mass transport, and the results indicate that for competing reactions which are exothermic the selectivity increases with increase in Sherwood number (a measure of the effectiveness of transport between fluid and particle) when $\delta_{A1} > \delta_{A2}$, surface diffusion enhancing the effect. For $\delta_{A1} < \delta_{A2}$, the selectivity decreases with increase in Sherwood number, and this decrease is more exaggerated the greater the extent of surface diffusion of reactant. These results are not displayed because resistance to mass transfer from pellet to fluid is usually unimportant in comparison with diffusion within the pellet and also less significant than interparticle resistance to heat transfer. Nevertheless the effects noted are explicable simply in terms of the relative ease with which the competing reactions can proceed and as influenced by the magnitude of the kinetic rate constants determined by the respective activation energies. For competing reactions which are endothermic, diametrically opposite results were obtained as would be expected.

Consecutive Reaction

For consecutive reactions which are isothermal the selectivity for the formation of the intermediate component B (which will be regarded as the desired product) is a monotonic decreasing function of the Thiele modulus (*20*, *21*). The effect which surface diffusion has on the selectivity may be determined, once again, by application of Eq. (*8*). The appropriate differential equations will not be written here but may be derived by analogy with the derivation of Eqs. (27), (28), and (29) describing isothermal concurrent reactions in a pellet. Figure 6 traces the form of the function describing how the selectivity of two consecutive and isothermal first-order kinetic reactions varies with Thiele modulus and includes the effect of surface diffusion. The result for $\psi = 0$ has already been discussed elsewhere (*20*, *21*). It is clear from the family of curves that, at Thiele moduli between 0.5 and 2.0, selectivity is approximately doubled for a tenfold increase in surface diffusion.

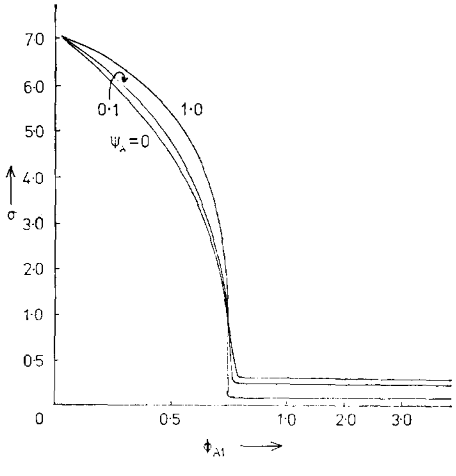


FIG. 7. Selectivity σ as a function of Thiele modulus ϕ_{A1}: exothermic consecutive first-order reactions, $\beta_{A1} = 0.2$, $\beta_{A2} = 0.2$; Nu = Sh = ∞; ψ_A as parameter; $\delta_{A1} = \delta_{B2} = 10$.

It transpires that the result is not quite as straightforward for two consecutive first-order exothermic reactions as it is for isothermal reactions. Thus Fig. 7 shows that, although the selectivity decreases by a factor of about 10 when the Thiele modulus (based on the decomposition of reactant A) increases from 0.1 to about 0.7, there is an asymptotic limit to the decline in selectivity at a Thiele modulus just exceeding 0.75, albeit the selectivity is reduced to values as low as 0.5. It is thus somewhat academic to consider further the effect of surface diffusion at values of $\phi_{A1} > 0.75$, although it is interesting to note that, while surface diffusion clearly enhances selectivity when $\phi_{A1} < 0.75$, it has the reverse effect when $\phi_{A1} > 0.75$. In practice then, it is an advantage to operate with relatively small particle size and with a catalyst which adsorbs the reactant to an extent sufficient to promote surface transport. Such transport can be further encouraged, of course, by fine pores but if the pore structure is too fine the selectivity will suffer a marked decrease on account of severe Knudsen diffusion limitation.

Turning to consecutive first-order endothermic reactions, Fig. 8 shows that the selectivity decreases monotonically with increase in Thiele modulus, surface diffusion of the reactant favoring the preferential formation of the desired intermediate product B. If, therefore, surface transport predominates it is evident that it becomes immaterial whether large or small particles are selected for operation since the selectivity hardly changes with increase in Thiele modulus at large values of ψ. When there is a relatively small amount of transport by surface translation, on the other hand, the choice of particle size would be dictated by other considerations including the rapid fall off in selectivity with increasing Thiele modulus.

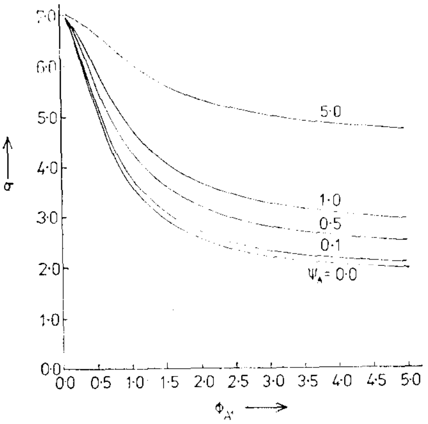


FIG. 8. Selectivity σ as a function of Thiele modulus ϕ_{A1}: endothermic consecutive first-order reaction, $\beta_{A1} = \beta_{A2} = -0.2$; Nu = Sh = ∞; ψ_A as parameter; $\delta_{A1} = \delta_{B2} = 10$.

We also consider the effect of interparticle mass and heat transfer on the selectivity of two first-order consecutive reactions. Figure 9 reveals that, for exothermic reactions, selectivity falls off sharply with an increase in the modified Nusselt group, surface diffusion exacerbating the decrease in selectivity. For a twofold increase in the interparticle heat transfer coefficient, for example, the selectivity is reduced by about 20%. This behavior is in contrast to that found for concurrent reactions for which the selectivity can be either greater or less than the limiting value at $\phi_{ij} = 0$ depending on the relative magnitudes of the activation energies of the competing reactions. For consecutive reactions, the relative magnitude of the activation energies of each reaction merely increases or diminishes the effect noted. Better selectivities can be attained at moderate Thiele values (diffusion-limited reaction) when the modified Nusselt group is low so that poor heat transfer from particle to fluid causes the temperature within the pellet to rise. If the activation energy of the reaction producing the desired product is greater than that for its subsequent reaction, then the selectivity will be better than it would have been if heat were easily transferred to the fluid,

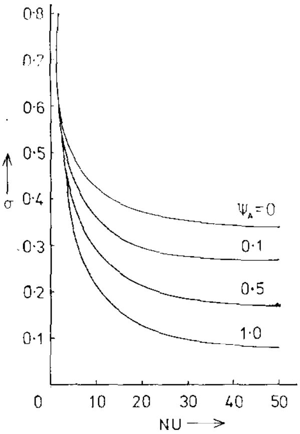


FIG. 9. Selectivity σ as a function of modified Nusselt group Nu: exothermic consecutive first-order reactions, $\beta_{A1} = 0.2$, $\beta_{A2} = 0.2$; $\delta_{A1} = \delta_{B2} = 10$; $\phi_{A1} = 1.5$; ψ_A as parameter.

as any temperature rise within the pellet favors the formation of B rather than C when $E_1 > E_2$. This is the case illustrated in Fig. 9. An increase in surface diffusion tends to be detrimental to such a situation. It is possible that a previously localized temperature rise will now be dispersed over a larger number of active catalyst sites and the favorable effect thus diluted. At lower Thiele moduli, where only mild diffusion limitation occurs, selectivity is improved at high Nusselt values, for now there is relatively less impedance to diffusion of reactants and products within the particle, and it is an advantage to the formation of B when not only is the desired product able to move outward freely through the porous structure, but any temperature rise likely to cause its further decomposition to C can be quickly dissipated. The behavior of consecutive first-order endothermic reactions is less complicated. Figure 8 shows that the selectivity falls off with an increase in Thiele modulus, surface diffusion retarding the decrease. This effect is found at both low and moderately high values of the Nusselt group.

The effect of interparticle mass transfer was found to enhance selectivity, an increase in surface mobility tending to nullify such enhancement for exothermic consecutive reactions but to further increase selectivity for endothermic consecutive reactions. Because interparticle mass transport is usually unimportant in comparison with intraparticle diffusion, this point is not developed further here.

Resistance to Heat Transfer Confined to Pellet Exterior

An important class of problems arises if it is considered that resistance to heat transfer is confined to regions exterior to the pellet. For a wide range of parameters resistance to mass transfer is primarily due to difficulties associated with diffusive transport within the porous pellet, while resistance to heat transfer is caused principally by the relatively stagnant boundary layer of fluid bathing the particle (*24*, *25*). Under such circumstances, although the general mass conservation equations such as (8) have to be included in the model, the differential heat conservation Eq. (11) is replaced by a steady-

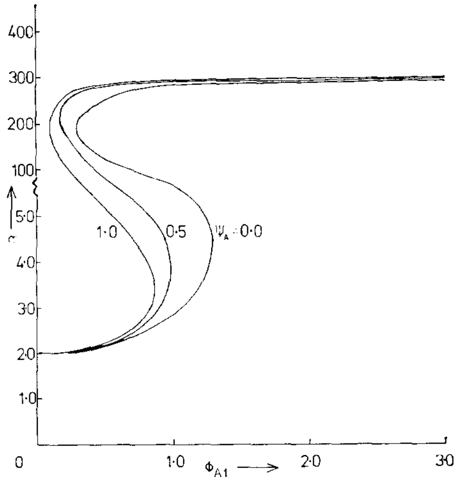


FIG. 10. The existence of multiplicity when resistance to heat transfer confined to stagnant fluid surrounding particle: exothermic concurrent first-order reactions, $\beta_{A1} = 0.2$, $\beta_{A2} = 0.2$; $\delta_{A1} = 15$, $\delta_{A2} = 10$; Nu $= 5.0$; ψ as parameter.

state algebraic heat balance over the fluid film exterior to the catalyst particle. Thus for the concurrent reaction scheme considered, the problem is defined by the mass balance differential Eqs. (16) and (17) (with the term $d\theta/d\rho$ set equal to zero) together with the algebraic equation

$$\begin{aligned}\mathrm{Nu}(1-\theta_s) &= -(\tanh\kappa/\kappa)\{\phi_{A1}{}^2\beta_{A1} \\ &\quad\times\exp[\delta_{A1}(1-1/\theta_s)]+\phi_{A2}{}^2\beta_{A2} \\ &\quad\times\exp[\delta_{A2}(1-1/\theta_s)]\}\end{aligned}\tag{31}$$

in place of the differential Eq. (18). In the above equation

$$\begin{aligned}\kappa^2 &= \{\phi_{A1}{}^2\exp[\delta_{A1}(1-1/\theta_s)] \\ &\quad+\phi_{A2}{}^2\exp[\delta_{A2}(1-1/\theta_s)]\}/ \\ &\quad(1+\psi_A\exp[\delta_{A1}(1-1/\theta_s)]),\end{aligned}\tag{32}$$

and θ_s describes the dimensionless constant pellet temperature now replacing θ in the mass balance equations. Thus the value of θ_s must be sought iteratively. The boundary conditions applicable are similar to (19) and (21) except that the imposition of temperature constraints is no longer necessary.

To conclude this paper we merely outline, in the briefest manner, some of the interesting results generated. A fuller treatment of the problem will be given elsewhere. Attention is especially drawn to results obtained for concurrent and consecutive exothermic reactions. For certain ranges of the parameters, multiple solutions exist. This is illustrated in Fig. 10 which shows, for a concurrent exothermic reaction with $E_1 > E_2$, how selectivity varies with the Thiele modulus and the surface diffusion parameter. For a modified Nusselt number of 5 and an exothermicity β of 0.2, multiple solutions are evident between Thiele moduli of 0.3 and 1.3 when there is no surface diffusion. Beyond the upper bound of ϕ a very high selectivity is possible, formation of the undesirable product being almost entirely suppressed. This high selectivity is, however, at the cost of severe diffusion limitation and consequently throughput of desired product. When surface diffusion is a mode of intraparticle transport, the bounds on ϕ are displaced to smaller values of ϕ, and so a high selectivity is more easily attainable when surface diffusion intrudes. Consecutive exothermic reactions also display similar regions of multiplicity.

Calculations for concurrent endothermic reactions with $E_1 > E_2$ revealed a monotonic decline in selectivity with an increase in Thiele modulus, surface diffusion magnifying the decline.

APPENDIX

NOMENCLATURE

Symbol	*Interpretation*	*Dimensions*
A	Reactant	
A_j	Arrhenius constant for kinetic pathway j	T^{-1}
a	Particle dimension	L
B	Desired product	
C	Wasteful product	
c	Concentration of component	ML^{-3}
D_e	Effective Knudsen or Maxwellian diffusivity	L^2T^{-1}
$\hat{D}_e$	Effective diffusion coefficient	L^2T^{-1}
$\acute{D}_s$	Surface diffusion coefficient	L^2T^{-1}
D_{s0}	Temperature-independent surface diffusion coefficient	L^2T^{-1}
E	Activation energy	HM^{-1}
E_s	Activation energy for surface translation	HM^{-1}
K	Henry's Law constant	L
K_0	Temperature-independent constant of Henry's Law	L

k	Chemical kinetic constant	T^{-1} (for first-order reaction)
N	Molar flux	$ML^{-2}T^{-1}$
N_s	Molar surface flux	$ML^{-1}T^{-1}$
N_T	Total molar flux	$ML^{-2}T^{-1}$
q	Heat of adsorption	HM^{-1}
R	Gas law constant	$HM^{-1}\theta^{-1}$
r	Rate of reaction	$ML^{-3}T^{-1}$
T	Absolute temperature	θ
T_0	Absolute temperature of gas phase bathing the pellet	θ
$(-\Delta H)$	Heat of reaction	HM^{-1}
β	Thermicity defined by Eq. (15)	
Γ	Ratio of gas phase concentrations c_{B0}/c_{A0}	
γ_i	Dimensionless concentration of component defined as c_i/c_{A0}	
Δ_{AB}	Ratio of effective diffusivities D_{eA}/D_{eB}	
δ, δ_s	Defined by Eq. (12)	
ϵ	Pellet voidage	
λ	Effective thermal conductivity	$HL^{-1}T^{-1}\theta^{-1}$
κ	Defined by Eq. (32)	
θ	Dimensionless temperature T/T_0	
σ	Selectivity defined by Eq. (22)	
ρ	Dimensionless length variable x/a	
ϕ	Thiele modulus defined by Eq. (14)	
ψ	Surface diffusion parameter defined by Eq. (13)	
Nu	Modified Nusselt group based on particle diameter	
Sh	Modified Sherwood group based on particle diameter	

Subscript

h i	Chemical components
j	Reaction path
0	Conditions in fluid phase
s	Conditions at the pellet/fluid interface

Superscript

0	Parameter calculated at T_0

REFERENCES

1. de Boer, J. H., "Proceedings 4th International Congress on Catalysis (Moscow, 1968)," Vol. I, p. 9. Akadémiai Kiadó, Budapest, 1971.
2. Masamune, S., and Smith, J. M., *Amer. Inst. Chem. Eng. J.* **10**, 246 (1964).
3. Thomas, W. J., and Qureshi, A. R., *Trans. Inst. Chem. Eng.* **49**, 60 (1971).
4. Sladek, K. J., Gilliland, E. W., and Baddour, R. F., *Ind. Eng. Chem. Fundam.* **13**, 100 (1974).
5. Satterfield, C. N., "Mass Transfer in Heterogeneous Catalysis," p. 50. MIT Press, Cambridge, Massachusetts, 1970.
6. Krasuk, J. H., and Smith, J. M., *Ind. Eng. Chem. Fundam* **4**, 102 (1965).
7. Sterret, J. S., and Brown, L. F., *Amer. Inst. Chem. Eng. J.* **14**, 696 (1968).
8. Bienert, R., and Gelbin, D., *Chem. Techol. (Berlin)* **19**, 207 (1967).
9. England, R., and Thomas, W. J., *Trans. Inst. Chem. Eng.* **54**, 115 (1976).
10. Blackmore, K., Luckett, P., and Thomas, W. J., *Chem. Eng. Sci.* **30**, 1285 (1975).
11. Butt, J. B., and Foster, R. N., *Ind. Eng. Chem. Fundam.* **6**, 481 (1967).
12. Butt, J. B., and Foster, R. N., *Ind. Eng. Chem. Fundam.* **8**, 171 (1969).
13. Wicke, E., and Voigt, U., *Angew. Chem. Int. Ed. Engl.* **319**, 94 (1947).
14. Bosanquet, C. H., British TA Report BR/507, September 12, 1944.
15. Scott, D. S., and Dullien, F. A. L., *Amer. Inst. Chem. Eng. J.* **8**, 113 (1962).
16. Thiele, E. W., *Ind. Eng. Chem.* **31**, 916 (1939).
17. Aris, R., "The Mathematical Theory of Diffusion and Reaction in Permeable Catalysts," Vol. 1, p. 123. Clarendon Press, Oxford, 1975.
18. Weisz, P. B., and Hicks, J. S., *Chem. Eng. Sci.* **17**, 265 (1962).

19. Fox, L., "Numerical Solution of Ordinary and Partial Differential Equations." Pergamon Press, London/New York, 1962.

20. Wheeler, A., *Advan. Catal.* **3**, 249 (1951).

21. Thomas, J. M., and Thomas, W. J., "Introduction to the Principles of Heterogeneous Catalysis," p. 335. Academic Press, New York, 1967.

22. Thomas, W. J., *in* "Chemical Engineering," (J. M. Coulson and J. F. Richardson, Eds.), Vol. 3, p. 111–116. Pergamon Press, London/New York, 1971.

23. Østergaard, K., "Proceedings 3rd International Congress on Catalysis (Amsterdam)," **2**, 1348 (1960).

24. McGreavy, C., and Thornton, J. M., *Canad. J. Chem. Eng.* **48**, 187 (1970).

25. Carberry, J. J., *Ind. Eng. Chem.* **58**, 40 (1966)