Equation (7)

Λ = integral scale; Λ_x^+, integral scale in dimensionless units in the x direction

μ = fluid viscosity

ν = fluid kinematic viscosity

ρ = density; ρ_s, density of wall material; ρ_f, density of the fluid

τ = shear stress; $\bar{\tau}_w$, the time averaged wall shear stress

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Manuscript received October 8, 1968; revision received March 17, 1969; paper accepted March 19, 1969.

Simultaneous Noncatalytic Solid-Fluid Reactions

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Solid-fluid reactions often involve two or more simultaneous reactions because either the feed contains multiple fluid reactants or the fluid products are reactive with the solid. Three types of simultaneous reactions, independent, parallel, and consecutive, are examined in terms of the selectivity and the effectiveness factor based on the unreacted core shrinking model under isothermal conditions. Criteria for high selectivities are derived, and effects of diffusion and chemical reaction are discussed.

Noncatalytic, solid-fluid reactions are of considerable industrial importance and are readily found in chemical and metallurgical industries. A large number of examples of this system involving a single fluid reactant have been discussed (*2, 3, 6*). In many of the industrial operations, however, we often encounter situations in which more than two reactions are involved either because the feed contains multiple fluid reactants or because the products are reactive with the solid. For example, in the gasification of carbonaceous matter by steam and hydrogen, more than two simultaneous reactions are involved. It has been observed (*7*) that reaction of carbon with hydrogen is first order with respect to hydrogen and that with steam is approximately zero order with respect to steam. The treatment involving simultaneous multiple reactions is much more complicated than that for a single reaction.

Actually there is a more important reason for studying such complex reactions. The interactions among the reactant, intermediate, and product species at the reacting surface of a solid particle, manifest themselves in some cases by striking changes in the magnitude of the overall reaction rate. Three commonly encountered systems for the complex reactions are independent reactions, parallel reactions, and consecutive reactions. In fact, all real systems fall either into one of the above classes, or a combination of the three. Some of the examples are:

Independent reactions:

$$\left\{\begin{aligned} &2F_2\ (g) + UO_2F_2\ (s) \rightarrow UF_6\ (g) + O_2\ (g) \\ &4BrF_5\ (g) + 5UO_2F_2\ (s) \rightarrow 5UF_6\ (g) + 2Br_2\ (g) \\ &\qquad\qquad\qquad\qquad\qquad\qquad + 5O_2\ (g) \end{aligned}\right.$$

$$\left\{\begin{aligned} &H_2S\ (g) + CaO\ (s) \rightarrow H_2O\ (g) + CaS\ (s) \\ &CO\ (g) + H_2O\ (g) + CaO\ (s) \rightarrow H_2\ (g) \\ &\qquad\qquad\qquad\qquad\qquad\qquad + CaCO_3\ (s) \end{aligned}\right.$$

Parallel reactions:

$$\left\{\begin{aligned} &CO\ (g) + MnSO_4\ (s) \rightarrow CO_2\ (g) + SO_2\ (g) \\ &\qquad\qquad\qquad\qquad\qquad\qquad + MnO\ (s) \\ &4CO\ (g) + MnSO_4\ (s) \rightarrow 4CO_2\ (g) + MnS\ (s) \end{aligned}\right.$$

Consecutive reactions:

$$\left\{\begin{aligned} &O_2\ (g) + C\ (s) \rightarrow CO_2\ (g) \\ &CO_2\ (g) + C\ (s) \rightarrow 2CO\ (s) \end{aligned}\right.$$

Since in many of the simultaneous reactions it is necessary to promote one reaction which is desired and to suppress other reactions which are undesired, design criteria which take into account the effect of diffusion and chemical reaction are needed. In this paper, a mathematical treatment of the three different types of simultaneous reactions listed above will be presented based on the unreacted core shrinking model under isothermal conditions. The analysis will be made based on the concept of the selectivity and effectiveness factor commonly used in the field of catalysis.

Many solid-gas reactions are either exothermic or endothermic. Therefore, it is also of prime importance to examine the effects of heats of reactions and the reaction temperature on effectiveness factor and selectivities. We intend to treat the simultaneous solid-gas reaction systems under nonisothermal conditions in another paper.

MATHEMATICAL MODEL FOR SIMULTANEOUS SOLID FLUID REACTIONS

For solid-fluid reactions, the unreacted core shrinking model (6) is applicable when the porosity of the unreacted solid is very small. Under this condition the solid is practically impervious to the fluid reactants, and the reaction will occur at the surface of the solid or at the interface between the unreacted solid and the porous product layer. The model is also applicable for fast reactions and at high temperatures so that the slow diffusion is the rate controlling factor. When the porosity of the solid particle is large, the homogeneous model must be used (3, 6). In addition, cases in which the particle size decreases without formation of inert solid product layer are treated.

However, this model is not applicable when the reacting particles undergo swelling, ablating, cracking, splitting, and sintering.

For a spherical particle, the fundamental equations relating the material balances and boundary conditions are written separately for the three cases of simultaneous solid-fluid reactions as follows:

Independent reactions:

$$aA\ (g) + S\ (s) \xrightarrow{k_1} eE\ (g) + S_1\ (s) \tag{1}$$

$$bB\ (g) + S\ (s) \xrightarrow{k_2} fF\ (g) + S_2\ (s) \tag{2}$$

Material balance for component A and B can be written as

$$\epsilon \frac{\partial C_i}{\partial t} = D_{ei}\left(\frac{\partial^2 C_i}{\partial r^2} + \frac{2}{r}\frac{\partial C_i}{\partial r}\right),\ R > r > r_c \tag{3}$$

where $i = A$ and B

The boundary conditions are:

at the solid particle surface R

$$D_{ei}\left(\frac{\partial C_i}{\partial r}\right)_R = k_{mi}\,(C_{io} - C_{is})\ \text{ where } i = A \text{ and } B \tag{4}$$

at the moving reacting surface r_c

$$\begin{aligned} D_{eA}\left(\frac{\partial C_A}{\partial r}\right) &= ar_{1j} \\ D_{eB}\left(\frac{\partial C_B}{\partial r}\right) &= br_{2j} \end{aligned} \tag{5}$$

where r_{1j} and r_{2j} are the consumption rates of solid reactant per unit reaction surface area for the first and the second reaction, respectively. The subscript j indicates the order of reaction with respect to the fluid reactant.

In this study, only cases involving zero order and/or first order with respect to fluid reactants and first order with respect to solid reactant are considered.

When the rates of diffusion through fluid-film and porous solid are both very fast, the overall rate of a solid-fluid reaction is solely controlled by the inherent chemical reactivity of the solid reactant. Based on the Langmuir adsorption isotherm, it is possible qualitatively to describe the mechanism of uncatalyzed heterogeneous solid-fluid reactions under this condition. However, depending on the mechanism, the resultant rate equation involves more than two arbitrary constants, some times as many as seven. In selecting these constants for each mechanism, the curve representing the rate equation of the favored mechanism which best fits the experimental data is chosen. Because of the unavoidable intrinsic scatter of the experimental data, it is rather clear that in many instances little meaning can be attributed to the magnitude of the adsorption equilibrium constants, the frequency factor, the apparent activation energy, etc., obtained by fitting the data to such multiconstant equations.

Often, the difference in fit may be so slight that it is very difficult to determine whether it is simply due to experimental error or truly due to the difference in mechanism. Furthermore, an alternative mechanism may fit the data equally well, necessitating an additional extensive experimental search for the correct mechanism. Although a correct mechanism will allow extrapolation to conditions not actually investigated, in view of the difficulty in obtaining a correct mechanism, there is no reason why simple rate equations which fit the data satisfactorily should not be used provided no extrapolation beyond the range investigated is allowed.

For design purposes, the n^{th} order rate equation can fit the data satisfactorily when the surface phenomenon controls the rate of a solid-fluid reaction. Based on adsorption isotherms, the order of solid-gas reactions can be shown to vary from 0 to 2 depending on whether the gas reactant is strongly adsorbed or weakly adsorbed. Experimental studies also indicate many solid-gas reactions to have the similar range of the order of reaction depending on conditions such as reactant reactivity, temperature, pressure, etc.

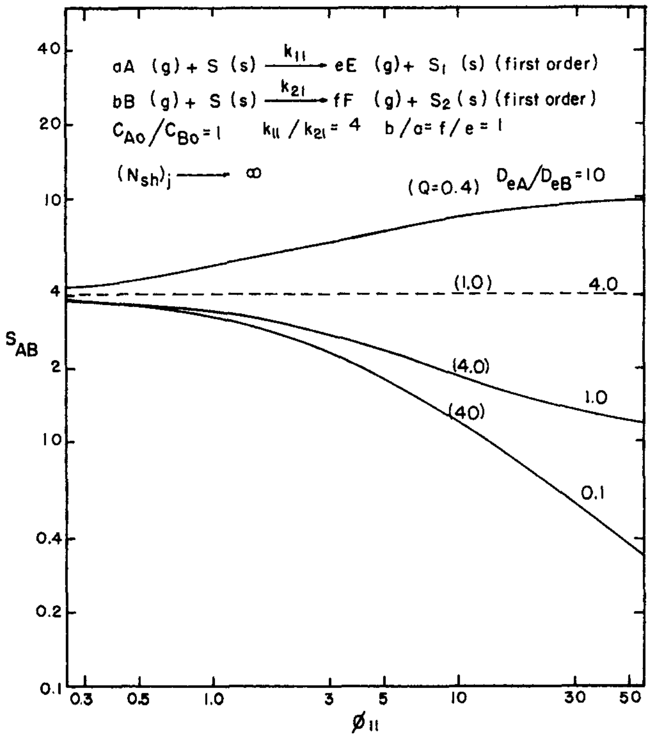

Fig. 1. The selectivity as a function of Thiele modulus at $\xi_c = 0.5$ for the independent first-order reactions (constant particle diameter).

Since the solid reactant is assumed to be distributed uniformly throughout the particle, the solid reactant concentration at the reacting surface is always C_{So}, the initial solid reactant concentration.

Therefore, r_{1j} and r_{2j} can be expressed as

$$r_{1j} = k_{1j}\, C_{So}\, (C_{AC})^j \quad j = 0 \text{ or } 1$$
$$r_{2j} = k_{2j}\, C_{So}\, (C_{BC})^j \quad j = 0 \text{ or } 1 \tag{6}$$

Here k_{1j}, k_{2j} are the j^{th} order reaction rate constants for the first and the second reaction.

Parallel reactions:

$$a_1A\ (g) + S\ (s) \overset{k_1}{\rightarrow} bB\ (g) + S_1\ (s) \tag{7}$$

$$a_2A\ (g) + S\ (s) \overset{k_2}{\rightarrow} fF\ (g) + S_2\ (s) \tag{8}$$

Material balance equations for components A, B, and F are the same as Equation (3) except that $i = A$, B, and F.

The boundary conditions at the solid particle surface R are the same as Equation (4) except that $i = A$, B, and F, and at the moving reacting surface r_c

$$\left.\begin{aligned} D_{eA}\left(\frac{\partial C_A}{\partial r}\right)_{r_c} &= a_1r_{1j} + a_2r_{2j} \\ D_{eB}\left(\frac{\partial C_B}{\partial r}\right)_{r_c} &= -\, br_{1j} \\ D_{eF}\left(\frac{\partial C_F}{\partial r}\right)_{r_c} &= -\, fr_{2j} \end{aligned}\right\} \tag{9}$$

where

$$r_{1j} = k_{1j}\, C_{So}\, (C_{AC})^j \quad j = 0 \text{ or } 1 \tag{10}$$

$$r_{2j} = k_{2j}\, C_{So}\, (C_{AC})^j \quad j = 0 \text{ or } 1 \tag{11}$$

Consecutive reactions:

$$aA\ (g) + S\ (s) \overset{k_1}{\rightarrow} b_1B\ (g) + S_1\ (s) \tag{12}$$

$$b_2B\ (g) + S\ (s) \overset{k_2}{\rightarrow} fF\ (g) + S_2\ (s) \tag{13}$$

Material balance equations for fluid components A, B, and F are the same as Equation (3), except that $i = A$, B, and F. Similarly, the boundary conditions at the solid particle surface R are the same as Equation (4) except that, $i = A$, B, and F, and at the moving intersurface r_c

$$\left.\begin{aligned} D_{eA}\left(\frac{\partial C_A}{\partial r}\right)_{r_c} &= ar_{1j} \\ D_{eB}\left(\frac{\partial C_B}{\partial r}\right)_{r_c} &= -\, b_1r_{1j} + b_2r_{2j} \\ D_{eF}\left(\frac{\partial C_F}{\partial r}\right)_{r_c} &= -\, fr_{2j} \end{aligned}\right\} \tag{14}$$

Here r_{1j} and r_{2j} have the same expressions as those given in independent reactions.

The effective diffusivities D_{eA} and D_{eB} for solid product layer may be based on an equivalent uniform diameter pore network which varies depending on the porosity, tortuosity, surface roughness, and other structural characteristics. The effective diffusivities of gases through porous pellets are experimentally shown to be roughly proportional to $\epsilon^{2\sim3}$.

Since all cases treated here involve more than two components, a rigorous solution of the problem would require use of multicomponent diffusivities. However, in the following derivations, it is assumed that reactants and products are sufficiently dilute so that the diffusivities may be approximated by those of the binary system consisting of the particular component and the solvent.

In solving the above equations, pseudo steady state approximation for the fluid reactant components is applied; that is, $\epsilon \dfrac{\partial C_i}{\partial t} = 0$, where $i = A$, B, and F. This assumption has been shown to be valid for most solid-gas reactions (6).

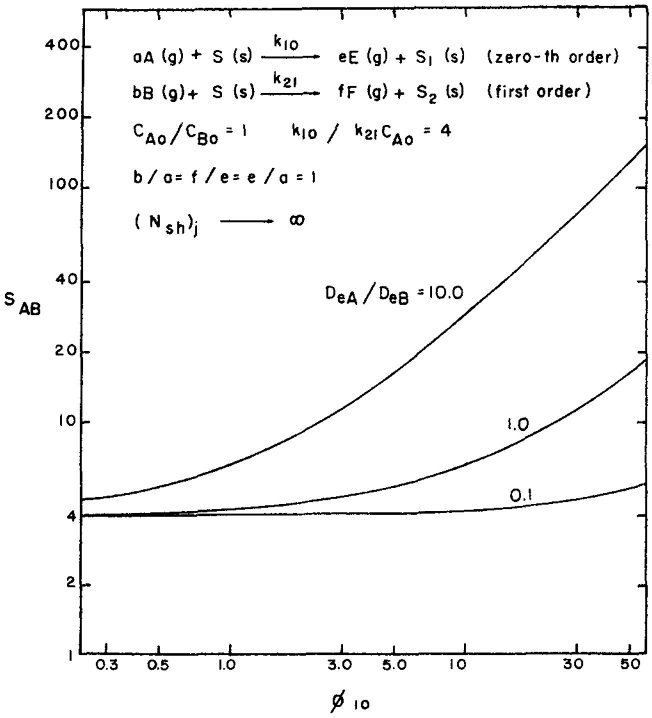

Fig. 2. The selectivity as a function of Thiele modulus at $\xi_c = 0.5$ for the independent reactions (constant particle diameter).

The selectivity defined here follows that of Petersen's (*4*) for catalytic reaction and is the ratio of the flux of the desired product to that of the undesired product at the surface of the solid particle. This is equal to the ratio of the surface reaction rate for the first reaction to that of the second reaction, both at the reacting surface of the shrinking core. The first reaction considered here is the desired reaction, while the second reaction is the undesired reaction. However, it is immaterial in many instances which of the two reactions is desired over the other. For these cases the selectivity defined simply becomes the indication of reactivity ratio or the effectiveness factor ratio of the two reactions.

Accordingly, for independent reactions:

$$S_{AB} = \frac{D_{eA}\left(\dfrac{\partial C_A}{\partial r}\right)}{D_{eB}\left(\dfrac{\partial C_B}{\partial r}\right)}\Bigg|_{\text{surface of solid particle}} = \frac{ar_{1j}}{br_{2j}}\Bigg|_{\text{reacting surface}} \quad (15)$$

for parallel reactions:

$$S_{BF} = \frac{D_{eB}\left(\dfrac{\partial C_B}{\partial r}\right)}{D_{eF}\left(\dfrac{\partial C_F}{\partial r}\right)}\Bigg|_{\text{surface of solid particle}} = \frac{br_{1j}}{fr_{2j}}\Bigg|_{\text{reacting surface}} \quad (16)$$

for consecutive reactions:

$$S_{BF} = \frac{D_{eB}\left(\dfrac{\partial C_B}{\partial r}\right)}{D_{eF}\left(\dfrac{\partial C_F}{\partial r}\right)}\Bigg|_{\text{surface of solid particle}}$$

$$= \frac{-b_1 r_{1j} + b_2 r_{2j}}{-fr_{2j}}\Bigg|_{\text{reacting surface}} \quad (17)$$

SELECTIVITIES

Selectivities as defined in Equations (15), (16), and (17) are derived for unreacted core shrinking model under pseudo steady state conditions for particles with constant diameter.

Independent reactions:

Both first order. (k_{11}, k_{21})

$$S_{AB} = \frac{D_{AB}\, C_{AB}\, Q_2}{Q_1} \quad (18)$$

Zero order with respect to A, first order with respect to B. (k_{10}, k_{21})

$$S_{AB} = D_{AB}\, C_{AB}\, Q_2\, \phi_{10}\, \xi_c^2 \quad (19)$$

First order with respect to A, zero order with respect to B. (k_{11}, k_{20})

$$S_{AB} = \frac{D_{AB}\, C_{AB}}{Q_1\, \phi_{20}\, \xi_c^2} \quad (20)$$

Both zero order. (k_{10}, k_{20})

$$S_{AB} = \frac{ak_{10}}{bk_{20}} \quad (21)$$

where

$$D_{AB} = (D_{eA}/D_{eB}),\ C_{AB} = (C_{Ao}/C_{Bo}),\ \xi_c = (r_c/R)$$

$$Q_1 = \frac{1}{\xi_c}\left(1 + \frac{1}{\xi_c\, \phi_{11}}\right) - 1 + \frac{1}{N_{ShA}}$$

$$Q_2 = \frac{1}{\xi_c}\left(1 + \frac{1}{\xi_c\, \phi_{21}}\right) - 1 + \frac{1}{N_{ShB}}$$

$$\phi_{11} = \frac{ak_{11}\, C_{So}\, R}{D_{eA}}, \quad \phi_{21} = \frac{bk_{21}\, C_{So}\, R}{D_{eB}}$$

$$\phi_{10} = \frac{ak_{10}\, C_{So}\, R}{D_{eA}\, C_{Ao}}, \quad \phi_{20} = \frac{bk_{20}\, C_{So}\, R}{D_{eB}\, C_{Bo}}$$

$$N_{ShA} = \frac{k_{mA}R}{D_{eA}}, \quad N_{ShB} = \frac{k_{mB}R}{D_{eB}}, \quad N_{ShF} = \frac{k_{mF}R}{D_{eF}}$$

Parallel reactions:

Both first order. (k_{11}, k_{21})

$$S_{BF} = \frac{bk_{11}}{fk_{21}} \quad (22)$$

Zero order with respect to A, first order with respect to B. (k_{10}, k_{21})

$$S_{BF} = \left(\frac{b\ a_2\ \phi_{10}}{f\ a_1\ \phi_{21}}\right) \Bigg/ \left\{1 + \frac{(\phi_{10} + \phi_{21})\left(1 - \dfrac{1}{N_{ShA}} - \dfrac{1}{\xi_c}\right)}{\dfrac{1}{\xi_c}\left(\phi_{21} + \dfrac{1}{\xi_c}\right) - \phi_{21}\left(1 - \dfrac{1}{N_{ShA}}\right)}\right\} \quad (23)$$

First order with respect to A, zero order with respect to B. (k_{11}, k_{20})

$$S_{BF} = \left(\frac{b\ a_2\ \phi_{11}}{f\ a_1\ \phi_{20}}\right) \left\{1 + \frac{(\phi_{11} + \phi_{20})\left(1 - \dfrac{1}{N_{ShA}} - \dfrac{1}{\xi_c}\right)}{\dfrac{1}{\xi_c}\left(\phi_{11} + \dfrac{1}{\xi_c}\right) - \phi_{11}\left(1 - \dfrac{1}{N_{ShA}}\right)}\right\} \quad (24)$$

Both zero order. (k_{10}, k_{20})

$$S_{BF} = \frac{bk_{10}}{fk_{20}} \quad (25)$$

Consecutive reactions:

Both first order reactions. (k_{11}, k_{21})

$$S_{BF} = \frac{QD_{AB}\, C_{AB}\, (A_2 - A_1/\xi_c)(b_1/a) - 1}{\left(\dfrac{f}{b_2}\right)(A_4 - A_3/\xi_c)\, A_5} \quad (26)$$

Zero order with respect to A, first order with respect to B. (k_{10}, k_{21})

$$S_{BF} = \frac{(b_1/a)\, D_{AB}\, QC_{AB} - 1}{(f/b_2)\left\{A_5 - \xi_c^2\,[(b_1/a)D_{AB}QC_{AB} - 1]\left(1 - \dfrac{1}{N_{ShB}} - \dfrac{1}{\xi_c}\right)\phi_{21}\right\}} \quad (27)$$

First order with respect to A, zero order with respect to B. (k_{11}, k_{20})

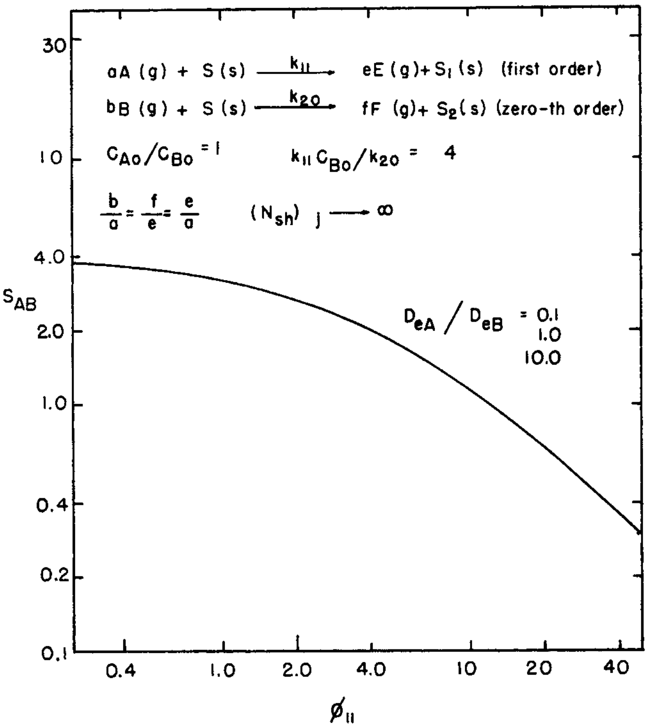

Fig. 3. The selectivity as a function of Thiele modulus at $\xi_c = 0.5$ for the independent reactions (constant particle diameter).

$$S_{BF} = \frac{(b_1/a)\, D_{AB} C_{AB}\, A_1 - \xi_c^2\, \phi_{20}}{(f/b_2)\, \xi_c^2\, \phi_{20}} \tag{28}$$

Both zero order. (k_{10}, k_{20})

$$S_{BF} = (b_2/f)\ [(b_1/a)\, D_{AB}\, Q\, C_{AB} - 1] \tag{29}$$

where

$$Q = \frac{\phi_{11}}{\phi_{21}} = \frac{\phi_{10}}{\phi_{20}},\quad D_{AB} = \frac{D_{eA}}{D_{eB}},\quad C_{AB} = \frac{C_{Ao}}{C_{Bo}}$$

$$A_1 = \frac{1}{[1 + 1/(\phi_{11}\,\xi_c)]/\xi_c - 1 + 1/N_{ShA}}$$

$$A_2 = A_1 \left(1 + \frac{1}{\xi_c\,\phi_{11}}\right) \Big/ \xi_c$$

$$A_3 = \frac{1 - Q(b_1/a)\, D_{AB}\, C_{AB} (A_2 - A_1/\xi_c)}{[1 + 1/(\xi_c\,\phi_{21})]/\xi_c - 1 + 1/N_{ShB}}$$

$$A_4 = \frac{\dfrac{1}{\xi_c}\left[1 + \dfrac{1}{\xi_c\,\phi_{21}}\right] - Q D_{AB}\, C_{AB} \left(A_2 - \dfrac{A_1}{\xi_c}\right)\left(1 - \dfrac{1}{N_{ShB}}\right)}{\dfrac{1}{\xi_c}\left(1 + \dfrac{1}{\xi_c\,\phi_{21}}\right) - 1 + \dfrac{1}{N_{ShB}}}$$

$$A_5 = 1 + \phi_{21}\, \xi_c - \xi_c^2\, \phi_{21} \left(1 - \frac{1}{N_{ShB}}\right)$$

EFFECTIVENESS FACTOR FOR SIMULTANEOUS SOLID-FLUID REACTIONS

In order to conveniently evaluate the effect of diffusion on solid-fluid reactions, the effectiveness factor has been introduced (2, 3, 6). The effectiveness factor η_i for simultaneous reactions may be defined as

$$\eta_i = \frac{\text{actual reaction rate of component } i}{\begin{array}{c}\text{reaction rate of component } i \text{ obtainable when} \\ \text{the surface of reaction is at the same concen-} \\ \text{trations and temperatures of the bulk phase}\end{array}}$$

Unlike the effectiveness factor used in catalytic reactions, which is based on the gas concentration and temperature at the surface of the catalysts, the effectiveness factor for solid-fluid reactions is based on the concentration and temperature in the bulk fluid phase which do not change during the reaction.

In this paper, only the isothermal cases are presented. The nonisothermal cases are intended to be treated in another paper.

The effectiveness factors for the first-order reactions are shown below:

Independent reactions. [Equations (1), (2)]

$$\eta_A = \frac{4\pi r_c^2\, a\, k_{11}\, C_{So}\, C_{AC}}{4\pi r_c^2\, a\, k_{11}\, C_{So}\, C_{Ao}} = \frac{C_{AC}}{C_{Ao}}$$

$$= \frac{1}{1 + \xi_c^2\, \phi_{11} \left(\dfrac{1}{N_{ShA}} + \dfrac{1}{\xi_c} - 1\right)} \tag{30}$$

$$\eta_B = \frac{4\pi r_c^2\, b\, k_{21}\, C_{So}\, C_{BC}}{4\pi r_c^2\, b\, k_{21}\, C_{So}\, C_{Bo}} = \frac{C_{BC}}{C_{Bo}}$$

$$= \frac{1}{1 + \xi_c^2\, \phi_{21} \left(\dfrac{1}{N_{ShB}} + \dfrac{1}{\xi_c} - 1\right)} \tag{31}$$

Parallel reactions. [Equations (7), (8)]

$$\eta_A = \frac{4\pi r_c^2 C_{So} (a_1\, k_{11} + a_2\, k_{21}) C_{AC}}{4\pi r_c^2 C_{So} (a_1\, k_{11} + a_2\, k_{21}) C_{Ao}}$$

$$= \frac{1}{1 + \xi_c^2\ (\phi_{11} + \phi_{21}) \left(\dfrac{1}{\xi_c} + \dfrac{1}{N_{ShA}} - 1\right)} \tag{32}$$

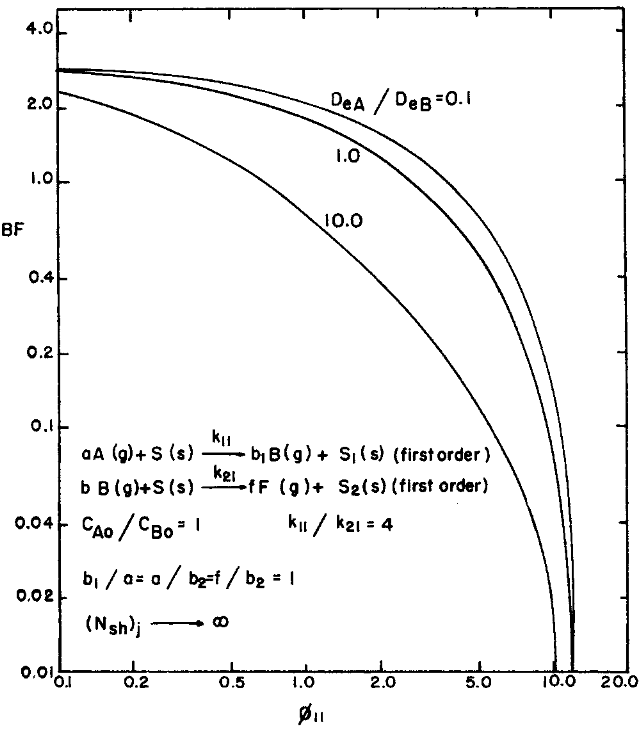

Fig. 4. The selectivity as a function of Thiele modulus at $\xi_c = 0.5$ for consecutive first-order reactions (constant particle diameter).

TABLE 1. SUMMARY OF CONDITIONS UNDER WHICH THE SELECTIVITY IS HIGH

Order of reaction Desired	Un-desired	Independent reactions	Parallel reactions	Consecutive reactions
First	First	*Small ϕ_{11} when $Q > 1$ Large ϕ_{11} when $Q < 1$	Large $\left(\dfrac{bk_{11}}{fk_{21}}\right)$	*Small ϕ_{11} and small (D_{eA}/D_{eB})
Zero	First	*Large ϕ_{10} and large (D_{eA}/D_{eB})	*Large ϕ_{10} and small (D_{eA}/D_{eB})	*Small ϕ_{10} and small (D_{eA}/D_{eB})
First	Zero	*Small ϕ_{11} Selectivity is independent of (D_{eA}/D_{eB})	*Small ϕ_{11} and small (D_{eA}/D_{eB})	*Small ϕ_{11} Selectivity is independent of (D_{eA}/D_{eB})
Zero	Zero	Large $\left(\dfrac{ak_{10}}{bk_{20}}\right)$	Large $\left(\dfrac{bk_{10}}{fk_{20}}\right)$	Large $\left(\dfrac{k_{10}}{k_{20}} - 1\right) \Big/ \left(\dfrac{f}{b_2}\right)$

* The parameters selected are: $C_{Ao}/C_{Bo} = 1$, k_{11}/k_{21}, $k_{11}\, C_{Bo}/k_{20}$ and $k_{10}/k_{21}\, C_{Ao} = 4$; $(N_{Sh})_j \to \infty$, the ratio of stoichiometric coefficients $= 1$.

$$\eta_B = \frac{4\pi r_c^2 b k_{11}\, C_{So}\, C_{AC}}{4\pi r_c^2 b k_{11}\, C_{So}\, C_{Ao}} = \frac{C_{AC}}{C_{Ao}} = \eta_A \qquad (33)$$

$$\eta_F = \frac{4\pi r_c^2\, f k_{21}\, C_{So}\, C_{AC}}{4\pi r_c^2\, f k_{21}\, C_{So}\, C_{Ao}} = \frac{C_{AC}}{C_{Ao}} = \eta_A \qquad (34)$$

Consecutive reactions. [Equations (12), (13)]

$$\eta_A = \frac{4\pi r_c^2 a_1 k_{11}\, C_{So}\, C_{AC}}{4\pi r_c^2 a_1 k_{11}\, C_{So}\, C_{Ao}} = \frac{C_{AC}}{C_{Ao}}$$

$$= \frac{1}{1 + \xi_c^2\, \phi_{11} \left(\dfrac{1}{\xi_c} + \dfrac{1}{N_{ShA}} - 1 \right)} \qquad (35)$$

$$\eta_B = \frac{4\pi r_c^2\, C_{So}(-b_1\, k_{11}\, C_{AC} + b_2\, k_{21}\, C_{BC})}{4\pi r_c^2\, C_{So}(-b_1\, k_{11}\, C_{Ao} + b_2\, k_{21}\, C_{Bo})}$$

$$= \frac{-\dfrac{C_{AC}}{C_{Ao}} + \dfrac{b_2}{b_1}\, \dfrac{k_{21}}{k_{11}}\, \dfrac{C_{Bo}}{C_{Ao}}\, \dfrac{C_{BC}}{C_{Bo}}}{-1 + \dfrac{b_2}{b_1}\, \dfrac{k_{21}}{k_{11}}\, \dfrac{C_{Bo}}{C_{Ao}}} \qquad (36)$$

$$\eta_F = \frac{4\pi r_c^2 f\, C_{So}\, k_{21}\, C_{BC}}{4\pi r_c^2 f\, C_{So}\, k_{21}\, C_{Bo}} = \frac{C_{BC}}{C_{Bo}}$$

$$= \frac{\dfrac{1}{\xi_c^2\, \phi_{21}} - \dfrac{b_1}{a}\, \dfrac{D_{eA}}{D_{eB}}\, \dfrac{\phi_{11}}{\phi_{21}}\, \dfrac{C_{Ao}}{C_{Bo}}\, \dfrac{C_{AC}}{C_{Ao}}}{\dfrac{1}{\xi_c^2\, \phi_{21}} + \dfrac{1}{N_{ShB}} - 1 + \dfrac{1}{\xi_c}} \qquad (37)$$

SELECTIVITIES FOR PARTICLES WITH REDUCING SIZE

In the previous derivation of selectivity, the external particle diameter was considered to remain unchanged during the reaction. In some cases, the diameter of the particle decreases without formation of the ash layer as the reaction progresses. Under this condition, the mass transfer coefficient across the fluid film k_{mi} is a function of particle diameter, and the derivation becomes complicated.

For a single particle at a particle Reynolds number below 200, the following correlation is available (*1*):

$$N_{Sh} = 1.0 + 0.276\, (N_{Re})^{1/2}\, (N_{Sc})^{1/3}$$

When Reynolds number is very low, N_{Sh} is approximately equal to unity, that is, $k_{mi} = D_{fi}/r_c$, where D_{fi} is a constant and may be approximated by the molecular diffusivity.

The selectivities for particles with reducing size under this condition for different types of simultaneous reactions are defined similarly as follows. For independent reactions S_{AB}

$$= \frac{k_{mA}(C_{Ao} - C_{As})}{k_{mB}(C_{Bo} - C_{Bs})} = \frac{D_{fA}(C_{Ao} - C_{As})}{D_{fB}(C_{Bo} - C_{Bs})} = \frac{a r_{1j}}{b r_{2j}} \Bigg|_{\substack{\text{reaction}\\ \text{surface}}}$$

and for parallel and consecutive reactions

$$S_{BF} = \frac{k_{mB}(C_{Bo} - C_{BS})}{k_{mF}(C_{Fo} - C_{FS})} \left\{ \begin{array}{ll} = \dfrac{b r_{1j}}{f r_{2j}} & \text{(parallel)} \\ = \dfrac{-b_1 r_{1j} + b_2 r_{2j}}{-f r_{2j}} \Bigg|_{\substack{\text{reaction}\\ \text{surface}}} & \text{(consecutive)} \end{array} \right.$$

Selectivities of the particles with reducing diameter may be obtained for the three types of reactions from those of the constant particle diameter cases by setting $(N_{Sh})_j = 1$ and by replacing the effective diffusivity D_{ei} with the molecular diffusivity D_{fi}.

DISCUSSION

As in catalytic reacting systems (*5*), the product selectivity of noncatalytic solid-fluid reacting systems is often more important than the rate of reaction itself. For example, in gasification of carbonaceous matter with steam to produce synthesis gas, hydrogen produced in the reaction will subsequently react with carbon to produce methane. If the purpose of the gasification is to produce hydrogen, carbon monoxide in the product gas must be subsequently shifted to produce hydrogen rich gas. It will be desirable then to keep the methane producing reaction as little as possible.

Therefore, some criteria for obtaining a higher selectivity of one reaction over the other reaction are needed to achieve an effective performance of noncatalytic solid-fluid reaction.

The conditions under which the selectivity will become high for $(N_{Sh})_j \to \infty$ are summarized in Table 1. The selectivities are symmetrical with respect to $\xi_c = 0.5$, that is, at $X = 0.875$. It can be shown that $\partial S_{BF}/\partial \xi_c = 0$ at

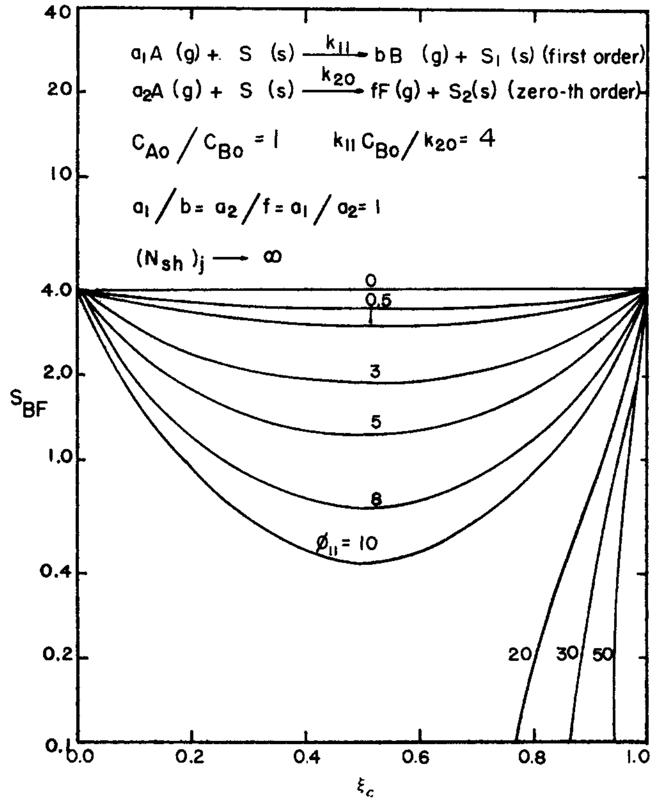

Fig. 5. The selectivity of parallel reactions as a function of dimensionless reacting radius (constant particle size).

$\xi_c = 0.5$. The same trend can also be seen in the effectiveness factors for solid-gas reactions (3). The concentration profiles for the particles with constant diameter are also symmetrical with respect to $\xi_c = 0.5$.

Figure 1 shows the selectivities of the first order independent reactions as a function of the Thiele modulus at $\xi_c = 0.5$. It indicates that for $Q > 1$, a smaller ϕ_{11} promotes higher selectivities, but for $Q < 1$, a larger ϕ_{11} gives better selectivities, where $Q = \phi_{11}/\phi_{21}$.

In terms of particle sizes, this implies that when $Q > 1$, smaller particles offer better selectivities, while when $Q < 1$, larger particles should be used to obtain better product gas distribution.

Figure 2 shows the selectivities of the independent reactions when the desired reaction is zero order and the undesired reaction is first order. Figure 3 shows the selectivities when the desired reaction is first order and the undesired reaction is zero order. It is seen from the figures that a larger ϕ_{10} gives a higher selectivity in the former case. The selectivities in this case are affected by the ratio of D_{eA}/D_{eB}, while for the latter case the selectivities are higher for smaller ϕ_{11} and are not affected by the ratio D_{eA}/D_{eB}.

Figure 4 shows the selectivities of the first order consecutive reactions, indicating smaller ϕ_{11} and smaller D_{eA}/D_{eB} are better for high selectivities.

The rate of zero order reaction being independent of the reactant concentration will approach zero when the reactant concentration at the reacting surface becomes zero. The conversion at which the reaction dies out is a function of ξ_c, the Thiele modulus, and the Sherwood's number and can be obtained from concentration profiles as follows.

For constant particle diameter:

Independent reactions:

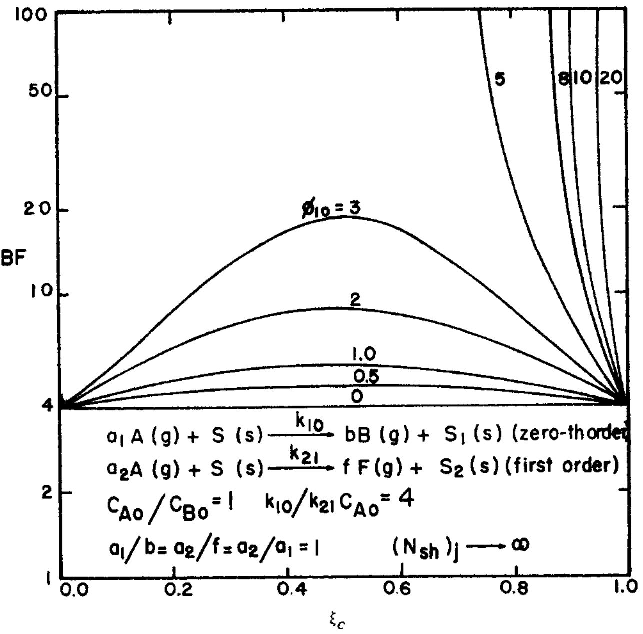

Fig. 6. The selectivity of parallel reactions as a function of dimensionless reacting radius (constant particle diameter).

$$\xi_c = \frac{1 + \sqrt{1 - \dfrac{4[1 - (1/N_{Shj})]}{\phi_{i0}}}}{2\left(1 - \dfrac{1}{N_{Shj}}\right)} \tag{38}$$

$i = 1$, $j = A$ when $C_{AC} = 0$

$i = 2$, $j = B$ when $C_{BC} = 0$

Parallel reactions:

$$\xi_c = \frac{1 + \sqrt{1 - \dfrac{4\left(1 - \dfrac{1}{N_{ShA}}\right)}{\phi_{i0} + \phi_{j0}}}}{2\left(1 - \dfrac{1}{N_{ShA}}\right)} \tag{39}$$

Desired reaction is first order, undesired reaction is zero order. (k_{11}, k_{20})

$$\phi_{i0} = \phi_{20}, \quad \phi_{j0} = 0 \tag{39a}$$

Desired reaction is zero order, undesired reaction is first order reaction. (k_{10}, k_{21})

$$\phi_{i0} = \phi_{10}, \quad \phi_{j0} = 0 \tag{39b}$$

Both zero order reactions

$$\phi_{i0} = \phi_{10}, \quad \phi_{j0} = \phi_{20} \tag{39c}$$

Consecutive reactions:

Desired reaction is first order, undesired is zero order. (k_{11}, k_{20})

$$\begin{gathered}\left[1 - \xi_c\,\phi_{20} + \xi_c^2\,\phi_{20}\left(1 - \frac{1}{N_{ShB}}\right)\right] \\ \left[\xi_c + \frac{1}{\phi_{11}} - \xi_c^2 + \frac{\xi_c^2}{N_{ShA}}\right] + \left(\frac{b_1}{a}\right) \\ \left(\frac{D_{eA}}{D_{eB}}\right)\left(\frac{C_{Ao}}{C_{Bo}}\right)\left[\xi_c + \frac{\xi_c^2}{N_{ShB}} - \xi_c^2\right] = 0 \\ \text{when } C_{BC} = 0\end{gathered} \tag{40}$$

Desired reaction is zero order, undesired is first order. (k_{10}, k_{21})

$$\xi_c = \frac{1 + \sqrt{1 - \dfrac{4\left(1 - \dfrac{1}{N_{ShA}}\right)}{\phi_{10}}}}{2\left(1 - \dfrac{1}{N_{ShA}}\right)} \quad \text{when } C_{AC} = 0 \tag{41}$$

Both zero order. (k_{10}, k_{20})

$$\xi_c = \frac{1 + \sqrt{1 - \dfrac{4\left(1 - \dfrac{1}{N_{ShA}}\right)}{\phi_{10}}}}{2\left(1 - \dfrac{1}{N_{ShA}}\right)} \quad \text{when } C_{AC} = 0 \tag{42a}$$

$$\xi_c = \frac{1 + \sqrt{1 - \dfrac{4\left(1 - \dfrac{1}{N_{ShB}}\right)}{\phi_{20}\left[1 - \left(\dfrac{b_1}{a}\right)\left(\dfrac{D_{eA}}{D_{eB}}\right)\left(\dfrac{\phi_{10}}{\phi_{20}}\right)\left(\dfrac{C_{Ao}}{C_{Bo}}\right)\right]}}}{2\left(1 - \dfrac{1}{N_{ShB}}\right)}$$

$$\text{when } C_{BC} = 0 \tag{42b}$$

For parallel reactions when one of the reactions is a zero order, the reaction will become extinct as concentration of fluid reactant becomes zero at the reacting surface. When this happens, the selectivities will approach zero or infinity, depending on which of the two reactions is the zero order. When fluid film diffusion is unimportant, that is $N_{Shj} \to \infty$, Equations (39) and (39*a*) reduce to

$$\xi_c = \frac{1 + \sqrt{1 - \dfrac{4}{\phi_{20}}}}{2} \quad S_{BF} \to 0 \tag{43a}$$

and Equations (39) and (39*b*) reduce to

$$\xi_c = \frac{1 + \sqrt{1 - \dfrac{4}{\phi_{10}}}}{2} \quad S_{BF} \to \infty \tag{43b}$$

Figure 5 shows the selectivities of a constant diameter particle undergoing parallel reactions (first order with respect to the desired reaction and zero order with respect to the undesired reaction) as a function of solid reactant conversion. It is seen that smaller ϕ_{11} gives a higher selectivity for this case. Also, when C_{AC} approaches zero, the selectivity becomes zero. Figure 6 shows the selectivities for the case in which the desired reaction is zero order and the undesired reaction is first order. In this case a large ϕ_{10} gives higher selectivities. Also, when C_{AC} approaches zero, the selectivity becomes infinity. Since for first order reactions, the rate depends on the concentration while for the zero order reaction it is independent of the concentration, a reduction in concentration of the reactant will decrease the rate of the first order reaction but does not change the rate of the zero order reaction.

For consecutive reactions, the selectivity will change the sign when diffusion flux of B reverses its direction. When the consumption of B is greater than the production of B, the concentration of B will fall until it becomes smaller than C_{Bo}, at which point the diffusion of B will change its direction. This point corresponds to $C_{BC}/C_{Bo} = 1$ and $(\partial C_B/\partial r)_R = 0$.

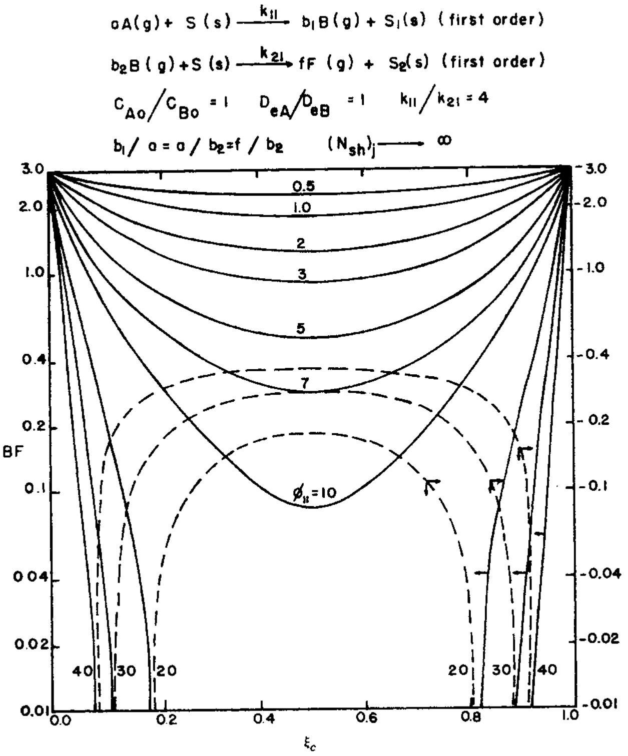

Fig. 7. The selectivity of consecutive reactions as a function of dimensionless reaction radius (constant particle diameter).

The points at which the selectivity reverses its sign are as follows: $(N_{Shj} \to \infty)$

For constant particle diameter:

Desired reaction is first order and undesired reaction is zero order

$$\xi_c = \frac{1 \pm \sqrt{1 - 4(AD_1CQ - 1)/\phi_{11}}}{2} \tag{44}$$

Desired reaction is zero order and undesired reaction is first order

$$AD_1CQ = 1 \tag{45}$$

Both desired and undesired reactions are first order

$$\xi_c = \frac{1 \pm \sqrt{1 - 4(AD_1CQ - 1)/\phi_{11}}}{2} \tag{46}$$

where

$$A = \frac{b_1}{a}, \quad D_1 = \frac{D_{eA}}{D_{eB}}, \quad C = \frac{C_{Ao}}{C_{Bo}}, \quad Q = \frac{\phi_{1i}}{\phi_{2i}}$$

$$i = 0 \text{ for zero order}$$
$$= 1 \text{ for first order}$$

Figure 7 shows the selectivities of the first order consecutive reactions as a function of solid reactant conversion for constant diameter particle. It indicates that a smaller Thiele modulus is better for high selectivity. In this figure, the dotted lines represent negative selectivities. This implies that the rate of consumption of B is greater than the rate of production of B.

The effectiveness factors for isothermal simultaneous reactions are very similar to those for single reaction except for the consecutive reactions as shown in the previous section. For independent reactions and parallel reactions, the effects of diffusion are very much like those of a single

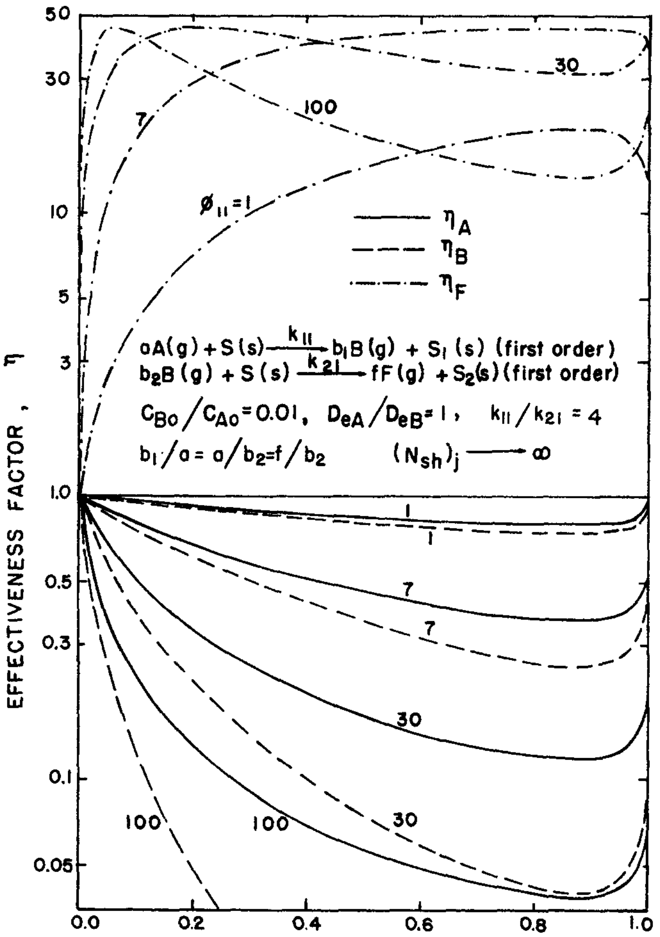

Fig. 8. Effectiveness factors for isothermal consecutive reactions.

reaction (3). η_i is nearly independent of the solid reactant conversion and approaches unity as $\phi_{i1} \to 0$, where the chemical reaction becomes the rate controlling step. η_i is small when ϕ_{i1} is large, meaning fluid diffusion through inert solid product layer is the rate controlling step. Furthermore, the effectiveness factor is symmetrical at $\xi_c = 0.5$, exhibiting the possibility of geometrical instability to occur for conversions larger than 87.5% (3). However, for consecutive reactions, the diffusion of component B will reverse its direction when C_{BC}/C_{Bo} becomes unity, and consequently the effectiveness factor η_B will become negative for $C_{BC}/C_{Bo} < 1$. The condition under which the diffusion reverses its direction is given by Equation (46) for $(N_{Shj}) \to \infty$. Since the effectiveness factor for component F depends only on the concentration ratio C_{BC}/C_{Bo}, η_F is larger than unity when η_B is a positive and less than unity when η_B is a negative. Figure 8 indicates the relations of η_A, η_B, and η_F with respect to solid conversion X for various ϕ_{11}.

CONCLUSION

The selectivities of the noncatalytic solid-fluid reactions are obtained for three types of simultaneous reactions based on unreacted core shrinking model with constant particle diameter. The criteria for obtaining a higher selectivity are examined.

The selectivities depend on the type of reaction and the order of reactions. For consecutive reactions, small ϕ_{11} and small D_{eA}/D_{eB} will ensure higher selectivities. For independent and parallel reactions, large ϕ_{10} is better when the desired reactions is a zero order; small ϕ_{11} is better when the desired reaction is a first order.

When the first reaction and the second reaction are both zero order, the selectivities for all three types of reactions depend on the ratio of the reaction rate constants and the stoichiometric coefficients. For parallel reactions, not only the zero order but for any order of reactions, as long as they are of the same order, the selectivities will become only the function of rate constants and stoichiometric coefficients.

The effectiveness factors for the first order independent and parallel reactions are shown to be similar to those for single reactions. However, for consecutive reactions, the effectiveness factor for component B as well as the selectivity may become negative when the diffusion reverses its direction.

ACKNOWLEDGMENT

The authors wish to express their gratitude to the Office of Coal Research, U.S. Department of the Interior, Washington, D. C., for their financial support.

NOTATION

a, b, e, f = stoichiometric coefficients of components A, B, E, and F, respectively

C_i, C_{io}, C_{is} = concentration of component i, io refers to the bulk phase, is refers to the outer surface of the particle, $i = A, B, E$, and F, mole/L^3

C_{So} = initial concentration of solid reactant, mole/L^3

D_{ei} = effective diffusivity of component i in ash layer $i = A, B$, and F, L^2/θ

D_{fi} = molecular diffusivity of component i, $i = A, B, E$ and F, L^2/θ

k_{ij} = reaction rate constant for the i^{th} reaction, the order of reaction being j^{th} order (based on reaction surface area), $\dfrac{L^{3(j+1)-2}}{\theta(\text{mole})^j}$

k_{mi} = mass transfer coefficient for component i across the fluid film, $i = A, B, E$, and F, L/θ

$N_{Sh\,j}$ = Sherwood's number for component j $(= k_{mj}R/D_{ej})$, $j = A, B, E$, and F

Q = ratio of Thiele modulus $(= \phi_{1j}/\phi_{2j})$

r_c = distance from the center of the particle to reaction surface, L

r_{ij} = rate of reaction for the i^{th} reaction with j^{th} order, mole/$L^2\theta$

R = outer radius of the solid particle, L

S_{ij} = selectivity for component i over j, $i = A$ or B, $j = B$ or F

X = fractional conversion of solid reactant

ϵ = voidage of the ash layer

ϕ_{ij} = Thiele modulus for i^{th} reaction with j^{th} order of reaction

ξ_c = dimensionless reacting radius $(= r_c/R)$

η_i = effectiveness factor for component i, $i = A, B, F$

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Manuscript received November 8, 1968; revision received March 10, 1969; paper accepted March 12, 1969. Paper presented at AIChE New Orleans meeting.