Simultaneous Nonisothermal Noncatalytic Solid-Gas Reactions

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The kinetics of simultaneous, noncatalytic solid-gas reaction systems has been analyzed in terms of the selectivity and effectiveness factor, based on the unreacted core shrinking model. The reaction systems discussed include the first-order independent, parallel, and consecutive reactions with the simultaneous influences of heat and mass transfer. The effects of various chemical and transport properties on the stability, selectivity, and effectiveness factor of the system are discussed. The pseudosteady state approximation is employed to reduce the mathematical difficulties.

Noncatalytic solid-fluid reactions, which include solid-liquid and solid-gas systems, are of great industrial importance and their examples are readily found in many chemical and metallurgical industries. A large number of examples involving a single-fluid reactant have been discussed (*1, 4* to *12, 14* to *16, 18, 21* to *23*). However in many industrial operations, more than one reaction can take place simultaneously, either because the feed contains multiple-fluid reactants or because the products are reactive with the solid. One of the examples for the simultaneous solid-gas reaction is the fluorination of uranium compounds.

The treatment involving simultaneous multiple reactions is much more complicated than that for a single reaction due to the interaction among the rates of chemical reactions and the rate of mass and energy transport. The simultaneous isothermal reactions were discussed in a previous paper (*20*) in which the heat effect was not considered.

Since solid-gas reactions are either exothermic or endothermic, an appreciable temperature gradient could exist within the particle. The analysis of the behavior of such a system becomes very complicated, since now not only the reactant concentration but also the rate constants, which are generally exponentially dependent on temperature, will be a function of the position within the particle.

This paper is concerned with the solutions of nonlinear equations relating simultaneous mass and heat transfer in an unreacted core shrinking particle under the pseudo-steady state approximation. Specifically, the selectivity and effectiveness factor in relation to the particle and fluid properties and reaction conditions are developed.

MATHEMATICAL MODEL FOR THE NONISOTHERMAL SIMULTANEOUS SOLID-GAS REACTIONS

A surface reaction of solid-gas systems can be viewed as consisting of the following steps: diffusion of the fluid reactants across the fluid film surrounding the solid and then through the porous solid layer; adsorption of the fluid reactants at the solid reactant surface; reaction with the solid surface; and desorption and diffusion of the fluid products away from the reaction surface through the porous solid and finally across the fluid film. Since these steps occur in series, if any one step is much slower than all the others, that step alone will be the rate controlling. However, the solid-fluid reactions are in general influenced simultaneously by more than one step; the single-step rate-controlling processes are the limiting cases.

Owing to the complexity of the problems involved, a rigorous treatment seems unattainable even for the solid with the simplest geometry. Besides, in practice many problems exist such as changing size and shape of the solid during reaction and the formation of a product layer around the solid reactant which may crack or ablate. Also there is a problem of mass and energy transfer to and from the solid across the surrounding fluid. Therefore it is imperative that a relatively simple mathematical model be employed for the noncatalytic nonisothermal simultaneous reactions between solids and gases.

The unreacted-core-shrinking model (*18, 22*) for describing a noncatalytic heterogeneous gas-solid reaction system is applicable if the solid reactant is impervious to the gas reactant and the reactions start from the outer surface of the solid particle. The reaction surface moves toward the interior of the solid, leaving behind a layer of solid product and/or inert solid (ash layer). During the process, the moving reaction surface forms an unreacted core which shrinks in radius with time. It is further assumed that the particle retains its original size and shape without deformation of the inert layer which has formed.

In simultaneous reactions, since more than two components are involved, it is convenient to define an effective diffusivity D_{ei} for component i in a mixture. The flux of i component is (*2*)

$$N_i = - CD_{ei} \nabla x_i + x_i \sum_{j=1}^{n} N_j \tag{1}$$

For the case with equimolar counterdiffusion, we have $\sum_{j=1}^{n} N_j = 0$. For systems containing a large amount of inert gas, that is, with very dilute reactant gas concentration, the second term on the right-hand side of Equation (1) is negligibly small compared to the first term. Under such situations Equation (1) reduces to

$$N_i = - CD_{ei} \nabla x_i \tag{2}$$

The mass balance for a species i in the ash layer for the multicomponent system is given by

$$\epsilon \frac{\partial C_i}{\partial t} = - (\nabla \cdot N_i) \tag{3}$$

From Equations (2) and (3), the material balance equation for component i takes the form

$$\epsilon \frac{\partial C_i}{\partial t} = \nabla \cdot (CD_{ei} \nabla x_i) \tag{4}$$

For a spherical particle in r direction of transfer only, Equation (4) becomes

$$\epsilon \frac{\partial C_i}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left(C D_{ei} r^2 \frac{\partial x_i}{\partial r} \right) \tag{5}$$

The total concentration C is proportional to $1/T$ if the ideal gas law holds and the total pressure is constant. Since the effective diffusivity D_{ei} is considered to be proportional to $T^{1.5 \sim 2}$ in the molecular diffusion regime, and to $T^{0.5}$ in Knudsen diffusion regime, for convenience D_{ei} is taken to be proportional to $T^{1.0}$ for the overall diffusion regime. Thus the product CD_{ei} is independent of temperature, and Equation (5) becomes

$$\epsilon \frac{\partial C_i}{\partial t} = \frac{C D_{ei}}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial x_i}{\partial r} \right) \tag{6}$$

Now, consider the following three types of simultaneous reactions:

I. Independent reactions

$$\begin{aligned} aA(g) + S(s) &\xrightarrow{k_1} eE(g) + S_1(s) \\ bB(g) + S(s) &\xrightarrow{k_2} fF(g) + S_2(s) \end{aligned} \tag{7}$$

II. Parallel reactions

$$\begin{aligned} a_1A(g) + S(s) &\xrightarrow{k_1} bB(g) + S_1(s) \\ a_2A(g) + S(s) &\xrightarrow{k_2} fF(g) + S_2(s) \end{aligned} \tag{8}$$

III. Consecutive reactions

$$\begin{aligned} aA(g) + S(s) &\xrightarrow{k_1} b_1B(g) + S_1(s) \\ b_2B(g) + S(s) &\xrightarrow{k_2} fF(g) + S_2(s) \end{aligned} \tag{9}$$

The material balance equations in the ash layer for these systems are given by Equation (6) with $\epsilon \frac{\partial C_i}{\partial t} = 0$ under pseudosteady state. The dimensionless forms of the mass and heat balance and their boundary conditions can be expressed as

Mass balance:

$$\frac{d^2\omega_i}{d\xi^2} + \frac{2}{\xi} \frac{d\omega_i}{d\xi} = 0 \quad \xi_c < \xi < 1 \tag{10}$$

Boundary condition at $\xi = 1$:

$$\left. \frac{d\omega_i}{d\xi} \right|_{\xi=1} = N_{Shi} \left(1 - \omega_{is} \right) \tag{11}$$

Boundary condition at $\xi = \xi_c$ is dependent on the type of reactions.

For independent reactions

$$\left. \begin{aligned} \left. \frac{d\omega_A}{d\xi} \right|_{\xi=\xi_c} &= \phi_1 \left(\frac{\omega_{AC}}{U_c} \right) \exp \left[\frac{E_1}{\mathcal{R}T_0} \left(1 - \frac{1}{U_c} \right) \right] \\ \left. \frac{d\omega_B}{d\xi} \right|_{\xi=\xi_c} &= \phi_2 \left(\frac{\omega_{BC}}{U_c} \right) \exp \left[\frac{E_2}{\mathcal{R}T_0} \left(1 - \frac{1}{U_c} \right) \right] \end{aligned} \right\} \tag{12}$$

For parallel reactions

$$\left. \frac{d\omega_A}{d\xi} \right|_{\xi=\xi_c} = \left(\frac{\omega_{AC}}{U_c} \right) \left\{ \phi_1 \exp \left[\frac{E_1}{\mathcal{R}T_0} \left(1 - \frac{1}{U_c} \right) \right] \right.$$

$$\left. + \phi_2 \exp \left[\frac{E_1}{\mathcal{R}T_0} \left(\frac{E_2}{E_1} \right) \left(1 - \frac{1}{U_c} \right) \right] \right\}$$

$$\left. \frac{d\omega_B}{d\xi} \right|_{\xi=\xi_c} = - \left(\frac{b}{a_1} \right) \phi_1 \left(\frac{\omega_{AC}}{U_c} \right) \left(\frac{x_{A0}}{x_{B0}} \right)$$

$$\left[\frac{D_{eA(T_0)}}{D_{eB(T_0)}} \right] \exp \left[\frac{E_1}{\mathcal{R}T_0} \left(1 - \frac{1}{U_c} \right) \right] \tag{13}$$

$$\left. \frac{d\omega_F}{d\xi} \right|_{\xi=\xi_c} = - \left(\frac{f}{a_2} \right) \phi_2 \left(\frac{\omega_{AC}}{U_c} \right) \left[\frac{D_{eA(T_0)}}{D_{eF(T_0)}} \right]$$

$$\left(\frac{x_{A0}}{x_{F0}} \right) \exp \left[\frac{E_2}{\mathcal{R}T_0} \left(1 - \frac{1}{U_c} \right) \right]$$

For consecutive reactions

$$\left. \frac{d\omega_A}{d\xi} \right|_{\xi=\xi_c} = \phi_1 \left(\frac{\omega_{AC}}{U_c} \right) \exp \left[\frac{E_1}{\mathcal{R}T_0} \left(1 - \frac{1}{U_c} \right) \right]$$

$$\left. \frac{d\omega_B}{d\xi} \right|_{\xi=\xi_c} = - \phi_1 \left(\frac{b_1}{a} \right) \left(\frac{\omega_{AC}}{U_c} \right) \left(\frac{x_{A0}}{x_{B0}} \right)$$

$$\left[\frac{D_{eA(T_0)}}{D_{eB(T_0)}} \right] \exp \left[\frac{E_1}{\mathcal{R}T_0} \left(1 - \frac{1}{U_c} \right) \right] \tag{14}$$

$$+ \phi_2 \left(\frac{\omega_{BC}}{U_c} \right) \exp \left[\frac{E_1}{\mathcal{R}T_0} \left(\frac{E_2}{E_1} \right) \left(1 - \frac{1}{U_c} \right) \right]$$

$$\left. \frac{d\omega_F}{d\xi} \right|_{\xi=\xi_c} = - \phi_2 \left(\frac{f}{b_2} \right) \left(\frac{\omega_{BC}}{U_c} \right) \left(\frac{x_{B0}}{x_{F0}} \right)$$

$$\left[\frac{D_{eB(T_0)}}{D_{eF(T_0)}} \right] \exp \left[\frac{E_1}{\mathcal{R}T_0} \left(\frac{E_2}{E_1} \right) \left(1 - \frac{1}{U_c} \right) \right]$$

Notice that in the previous equations the relations $(CD_{ei})_{T_c} = (CD_{ei})_{T_0}$ and $(C)_{T_c}/(C)_{T_0} = T_0/T_c$ are used.

Heat balance:

$$\frac{d^2U}{d\xi^2} + \frac{2}{\xi} \frac{dU}{d\xi} = 0 \quad \xi_c < \xi < 1 \tag{15}$$

Boundary condition at $\xi = 1$:

$$\left. - \frac{dU}{d\xi} \right|_{\xi=1} = (N_{Nu})_P \left(U_s - 1 \right) \tag{16}$$

Boundary condition at $\xi = \xi_c$ is dependent on the type of reactions.

For independent reactions

$$\left. - \left(\frac{\mathcal{R}T_0}{E_1} \right) \left(\frac{dU}{d\xi} \right) \right|_{\xi=\xi_c} = \phi_1\beta_1 \left(\frac{\omega_{AC}}{U_c} \right)$$

$$\exp \left[\frac{E_1}{\mathcal{R}T_0} \left(1 - \frac{1}{U_c} \right) \right] + \phi_2\beta_2 \left(\frac{\omega_{BC}}{U_c} \right) \left(\frac{E_2}{E_1} \right)$$

$$\exp \left[\frac{E_2}{\mathcal{R}T_0} \left(1 - \frac{1}{U_c} \right) \right] \tag{17}$$

For parallel reactions

$$\left. - \left(\frac{\mathcal{R}T_0}{E_1} \right) \left(\frac{dU}{d\xi} \right) \right|_{\xi=\xi_c} = \left(\frac{\omega_{AC}}{U_c} \right)$$

$$\left\{ \phi_1\beta_1 \exp \left[\frac{E_1}{\mathcal{R}T_0} \left(1 - \frac{1}{U_c} \right) \right] \right.$$

$$+ \phi_2\beta_2 \left(\frac{E_2}{E_1}\right) \exp\left[\frac{E_1}{\mathcal{R}T_0}\left(\frac{E_2}{E_1}\right)\left(1-\frac{1}{U_c}\right)\right]\Bigg\} \qquad (18)$$

For consecutive reactions

$$-\left(\frac{\mathcal{R}T_0}{E_1}\right)\left(\frac{dU}{d\xi}\right)\Bigg|_{\xi=\xi_c} = \phi_1\beta_1\left(\frac{\omega_{AC}}{U_c}\right) \exp\left[\frac{E_1}{\mathcal{R}T_0}\left(1-\frac{1}{U_c}\right)\right] + \phi_2\beta_2\left(\frac{E_2}{E_1}\right)\left(\frac{\omega_{BC}}{U_c}\right) \exp\left[\frac{E_2}{\mathcal{R}T_0}\left(1-\frac{1}{U_c}\right)\right] \qquad (19)$$

In order to obtain the concentration and temperature profiles, the material and heat balance equations are solved simultaneously under pseudosteady state approximation. The solutions for the three types of reactions are shown as

I. Independent reactions

$$\omega_i = \frac{1+\xi_c^2\left(\frac{\phi_j}{U_c}\right)\left(\frac{1}{\xi_c}-\frac{1}{\xi}\right)\exp\left[\frac{E_j}{\mathcal{R}T_0}\left(1-\frac{1}{U_c}\right)\right]}{1+\xi_c^2\left(\frac{\phi_j}{U_c}\right)\left(\frac{1}{N_{Shi}}+\frac{1}{\xi_c}-1\right)\exp\left[\frac{E_j}{\mathcal{R}T_0}\left(1-\frac{1}{U_c}\right)\right]} \qquad (20)$$

where

$i = A$ when $j = 1$

$i = B$ when $j = 2$

$$U = \frac{\frac{1}{\xi_c}+\frac{U_c}{(N_{Nu})_P}-U_c-\frac{1-U_c}{\xi}}{\frac{1}{\xi_c}+\frac{1}{(N_{Nu})_P}-1} \qquad (21)$$

Where for fixed ξ_c, U_c is the root of the following equation:

$$\frac{\frac{\mathcal{R}T_0}{E_1}(U_c-1)}{\xi_c+\frac{\xi_c^2}{(N_{Nu})_P}-\xi_c^2} = \frac{\beta_1}{\left(\frac{U_c}{\phi_1}\right)\exp\left[\frac{E_1}{\mathcal{R}T_0}\left(\frac{1}{U_c}-1\right)\right]+\xi_c^2\left(\frac{1}{N_{ShA}}-1+\frac{1}{\xi_c}\right)} + \frac{\beta_2\left(\frac{E_2}{E_1}\right)}{\left(\frac{U_c}{\phi_2}\right)\exp\left[\frac{E_1}{\mathcal{R}T_0}\left(\frac{E_2}{E_1}\right)\left(\frac{1}{U_c}-1\right)\right]+\xi_c^2\left(\frac{1}{N_{ShB}}-1+\frac{1}{\xi_c}\right)} \qquad (22)$$

II. Parallel reactions

$$\omega_A = \frac{1+\xi_c^2\left\{\left(\frac{\phi_1}{U_c}\right)\exp\left[\frac{E_1}{\mathcal{R}T_0}\left(1-\frac{1}{U_c}\right)\right]+\left(\frac{\phi_2}{U_c}\right)\exp\left[\frac{E_1}{\mathcal{R}T_0}\left(\frac{E_2}{E_1}\right)\left(1-\frac{1}{U_c}\right)\right]\right\}\left(\frac{1}{\xi_c}-\frac{1}{\xi}\right)}{1+\xi_c^2\left\{\left(\frac{\phi_1}{U_c}\right)\exp\left[\frac{E_1}{\mathcal{R}T_0}\left(1-\frac{1}{U_c}\right)\right]+\left(\frac{\phi_2}{U_c}\right)\exp\left[\frac{E_1}{\mathcal{R}T_0}\left(\frac{E_2}{E_1}\right)\left(1-\frac{1}{U_c}\right)\right]\right\}\left(\frac{1}{\xi_c}+\frac{1}{N_{ShA}}-1\right)} \qquad (23)$$

U is the same as in Equation (21) but U_c is the root of the following equation:

$$\frac{\frac{\mathcal{R}T_0}{E_1}(U_c-1)}{\xi_c^2\left(\frac{1}{\xi_c}+\frac{1}{(N_{Nu})_P}-1\right)} = \frac{\beta_1\phi_1\exp\left[\frac{E_1}{\mathcal{R}T_0}\left(1-\frac{1}{U_c}\right)\right]+\beta_2\phi_2\exp\left[\frac{E_1}{\mathcal{R}T_0}\left(\frac{E_2}{E_1}\right)\left(1-\frac{1}{U_c}\right)\right]}{1+\xi_c^2\left\{\left(\frac{\phi_1}{U_c}\right)\exp\left[\frac{E_1}{\mathcal{R}T_0}\left(1-\frac{1}{U_c}\right)\right]+\left(\frac{\phi_2}{U_c}\right)\exp\left[\frac{E_1}{\mathcal{R}T_0}\left(\frac{E_2}{E_1}\right)\left(1-\frac{1}{U_c}\right)\right]\right\}\left(\frac{1}{N_{ShA}}+\frac{1}{\xi_c}-1\right)} \qquad (24)$$

III. Consecutive reactions

$$\omega_A = \frac{1 + \xi_c^2 \left(\frac{\phi_1}{U_c}\right) \exp\left[\frac{E_1}{\mathcal{R}T_0}\left(1 - \frac{1}{U_c}\right)\right]\left(\frac{1}{\xi_c} - \frac{1}{\xi}\right)}{1 + \xi_c^2 \left(\frac{\phi_1}{U_c}\right) \exp\left[\frac{E_1}{\mathcal{R}T_0}\left(1 - \frac{1}{U_c}\right)\right]\left(\frac{1}{N_{ShA}} + \frac{1}{\xi_c} - 1\right)} \tag{25}$$

$$\omega_B = \frac{1 + \xi_c^2 \left(\frac{\phi_2}{U_c}\right) \exp\left[\nu\left(\frac{E_2}{E_1}\right)\right]\left(\frac{1}{\xi_c} - \frac{1}{\xi}\right) + \left[\frac{b_1 C_{A0}\phi_1 D_{eA(T_0)}}{a\, C_{B0} U_c D_{eB(T_0)}}\right]\left(\frac{1}{N_{ShB}} - 1 + \frac{1}{\xi}\right)\xi_c^2 \exp(\nu)\,\omega_A}{1 + \xi_c^2 \left(\frac{\phi_2}{U_c}\right)\left(\frac{1}{N_{ShB}} - 1 + \frac{1}{\xi_c}\right)\exp\left[\nu\left(\frac{E_2}{E_1}\right)\right]} \tag{26}$$

where

$$\nu = \frac{E_1}{\mathcal{R}T_0}\left(1 - \frac{1}{U_c}\right)$$

Temperature profile U is the same as in Equation (21) but U_c is the root of the following equation:

$$\frac{\frac{\mathcal{R}T_0}{E_1}(U_c - 1)}{\xi_c^2\left(\frac{1}{\xi_c} + \frac{1}{(N_{Nu})_P} - 1\right)} = \beta_1\phi_1\left(\frac{\omega_{AC}}{U_c}\right)\exp\left[\frac{E_1}{\mathcal{R}T_0}\left(1 - \frac{1}{U_c}\right)\right] + \beta_2\phi_2\left(\frac{E_2}{E_1}\right)\left(\frac{\omega_{BC}}{U_c}\right)\exp\left[\frac{E_1}{\mathcal{R}T_0}\left(\frac{E_2}{E_1}\right)\left(1 - \frac{1}{U_c}\right)\right] \tag{27}$$

where

$$\omega_{AC} = \frac{1}{1 + \xi_c^2\left(\frac{\phi_1}{U_c}\right)\exp\left[\frac{E_1}{\mathcal{R}T_0}\left(1 - \frac{1}{U_c}\right)\right]\left(\frac{1}{N_{ShA}} + \frac{1}{\xi_c} - 1\right)} \tag{28}$$

$$\omega_{BC} = \frac{1 + \left(\frac{b_1}{a}\right)\left(\frac{C_{A0}}{C_{B0}}\right)\left(\frac{\phi_1}{U_c}\right)\left[\frac{D_{eA(T_0)}}{D_{eB(T_0)}}\right]\left(\frac{1}{N_{ShB}} + \frac{1}{\xi_c} - 1\right)\xi_c^2 \exp\left[\frac{E_1}{\mathcal{R}T_0}\left(1 - \frac{1}{U_c}\right)\right]\omega_{AC}}{1 + \xi_c^2\left(\frac{\phi_2}{U_c}\right)\exp\left[\frac{E_1}{\mathcal{R}T_0}\left(\frac{E_2}{E_1}\right)\left(1 - \frac{1}{U_c}\right)\right]\left(\frac{1}{N_{ShB}} - 1 + \frac{1}{\xi_c}\right)} \tag{29}$$

The left- and right-hand sides of Equations (22), (24), and (27) represent dimensionless heat loss and heat generation per unit area of reaction surface, respectively.

SELECTIVITY AND EFFECTIVENESS FACTOR OF THE NONISOTHERMAL SOLID-GAS REACTIONS

The selectivity defined here is the same as that for the isothermal case (*20*), and is the ratio of the flux of the desired product to that of the undesired product at the surface of solid particle, or the ratio of the reaction rate of the desired product to that of the undesired product at the reaction surface.

$$S_{iq} = \left.\frac{CD_{ei}\left(\frac{\partial x_i}{\partial r}\right)}{CD_{eq}\left(\frac{\partial x_q}{\partial r}\right)}\right|_{\text{surface of solid particle}}$$

$$= \frac{\text{reaction rate of component } i \text{ at reacting surface } r_c}{\text{reaction rate of component } q \text{ at reacting surface } r_c} \tag{30}$$

where species i is desired and q is undesired product.

For independent reactions

$$S_{AB} = \left(\frac{a}{b}\right)\left(\frac{k_1^0}{k_2^0}\right)\left(\frac{C_{A0}}{C_{B0}}\right)\exp\left[\frac{E_1}{\mathcal{R}T_0}\left(\frac{E_2}{E_1} - 1\right)\right] \left\{\frac{\exp\left[\frac{E_1}{\mathcal{R}T_0}\left(\frac{E_2}{E_1}\right)\left(\frac{1}{U_c} - 1\right)\right] + \xi_c^2\left(\frac{\phi_2}{U_c}\right)\left(\frac{1}{N_{ShB}} - 1 + \frac{1}{\xi_c}\right)}{\exp\left[\frac{E_1}{\mathcal{R}T_0}\left(\frac{1}{U_c} - 1\right)\right] + \xi_c^2\left(\frac{\phi_1}{U_c}\right)\left(\frac{1}{N_{ShA}} - 1 + \frac{1}{\xi_c}\right)}\right\} \tag{31}$$

For parallel reactions

$$S_{BF} = \left(\frac{b}{f}\right)\left(\frac{k_1^0}{k_2^0}\right)\exp\left[\frac{E_1}{\mathcal{R}T_0}\frac{1}{U_c}\left(\frac{E_2}{E_1} - 1\right)\right] \tag{32}$$

For consecutive reactions

$$S_{BF} = \left(\frac{b_1}{f}\right)\left(\frac{k_1{}^0}{k_2{}^0}\right)\left(\frac{C_{A0}}{C_{B0}}\right)$$

$$\left(\frac{\omega_{AC}}{\omega_{BC}}\right) \exp\left[\frac{E_1}{\mathcal{R}T_0}\frac{1}{U_c}\left(\frac{E_2}{E_1} - 1\right)\right] - \frac{b_2}{f} \qquad (33)$$

where ω_{AC} and ω_{BC} are given by Equations (28) and (29), respectively.

Similar to the effectiveness factor for the single reaction (7, 8, 18), the effectiveness factor for component i is defined here as

$$\eta_i = \frac{\text{actual reaction rate of component } i}{\text{reaction rate of component } i \text{ obtainable at the fluid concentration and temperature of the bulk phase}} \qquad (34)$$

Independent reactions

$$\eta_A = \frac{1}{U_c \exp\left[\frac{E_1}{\mathcal{R}T_0}\left(\frac{1}{U_c} - 1\right)\right] + \xi_c{}^2\,\phi_1\left(\frac{1}{N_{ShA}} + \frac{1}{\xi_c} - 1\right)} \qquad (35)$$

$$\eta_B = \frac{1}{U_c \exp\left[\frac{E_1}{\mathcal{R}T_0}\left(\frac{E_2}{E_1}\right)\left(\frac{1}{U_c} - 1\right)\right] + \xi_c{}^2\,\phi_2\left(\frac{1}{N_{ShB}} + \frac{1}{\xi_c} - 1\right)} \qquad (36)$$

Parallel reactions

$$\eta_A = \frac{\exp\left[\frac{E_1}{\mathcal{R}T_0}\left(\frac{E_2}{E_1}\right)\left(1 - \frac{1}{U_c}\right)\right] + \left(\frac{a_1}{a_2}\right)\left(\frac{k_1{}^0}{k_2{}^0}\right)\exp\left[\frac{E_1}{\mathcal{R}T_0}\left(\frac{E_2}{E_1} - \frac{1}{U_c}\right)\right]}{\left\{1 + \left(\frac{a_1}{a_2}\right)\left(\frac{k_1{}^0}{k_2{}^0}\right)\exp\left[\frac{E_1}{\mathcal{R}T_0}\left(\frac{E_2}{E_1} - 1\right)\right]\right\}\left\{U_c + \xi_c{}^2\left[\phi_1 \exp(\nu) + \phi_2 \exp\left(\nu \quad \frac{E_2}{E_1}\right)\right]\left(\frac{1}{N_{ShA}} + \frac{1}{\xi_c} - 1\right)\right\}} \qquad (37)$$

where

$$\nu = \frac{E_1}{\mathcal{R}T_0}\left(1 - \frac{1}{U_c}\right)$$

$$\eta_B = \frac{\exp\left[\frac{E_1}{\mathcal{R}T_0}\left(1 - \frac{1}{U_c}\right)\right]}{U_c + \xi_c{}^2\left\{\phi_1 \exp\left[\frac{E_1}{\mathcal{R}T_0}\left(1 - \frac{1}{U_c}\right)\right] + \phi_2 \exp\left[\frac{E_1}{\mathcal{R}T_0}\left(\frac{E_2}{E_1}\right)\left(1 - \frac{1}{U_c}\right)\right]\right\}\left(\frac{1}{\xi_c} + \frac{1}{N_{ShA}} - 1\right)} \qquad (38)$$

$$\eta_F = \frac{\exp\left[\frac{E_1}{\mathcal{R}T_0}\left(\frac{E_2}{E_1}\right)\left(1 - \frac{1}{U_c}\right)\right]}{U_c + \xi_c{}^2\left\{\phi_1 \exp\left[\frac{E_1}{\mathcal{R}T_0}\left(1 - \frac{1}{U_c}\right)\right] + \phi_2 \exp\left[\frac{E_1}{\mathcal{R}T_0}\left(\frac{E_2}{E_1}\right)\left(1 - \frac{1}{U_c}\right)\right]\right\}\left(\frac{1}{\xi_c} + \frac{1}{N_{ShA}} - 1\right)} \qquad (39)$$

Consecutive reactions

$$\eta_A = \frac{1}{U_c \exp\left[\frac{E_1}{\mathcal{R}T_0}\left(\frac{1}{U_c} - 1\right)\right] + \xi_c{}^2\,\phi_1\left(\frac{1}{N_{ShA}} + \frac{1}{\xi_c} - 1\right)} \qquad (40)$$

$$\eta_B = \frac{-\left(\frac{\omega_{AC}}{U_c}\right)\exp\left[\frac{E_1}{\mathcal{R}T_0}\left(1 - \frac{1}{U_c}\right)\right] + \left(\frac{b_2}{b_1}\right)\left(\frac{k_2{}^0}{k_1{}^0}\right)\left(\frac{C_{B0}}{C_{A0}}\right)\left(\frac{\omega_{BC}}{U_c}\right)\exp\left[\frac{E_1}{\mathcal{R}T_0}\left(1 - \frac{E_2}{E_1}\frac{1}{U_c}\right)\right]}{-1 + \left(\frac{b_2}{b_1}\right)\left(\frac{k_2{}^0}{k_1{}^0}\right)\left(\frac{C_{B0}}{C_{A0}}\right)\exp\left[\frac{E_1}{\mathcal{R}T_0}\left(1 - \frac{E_2}{E_1}\right)\right]} \qquad (41)$$

$$\eta_F = \left(\frac{\omega_{BC}}{U_c}\right) \exp\left[\frac{E_1}{\mathcal{R}T_0}\left(\frac{E_2}{E_1}\right)\left(1 - \frac{1}{U_c}\right)\right] \quad (42)$$

where ω_{AC} and ω_{BC} are given by Equations (28) and (29).

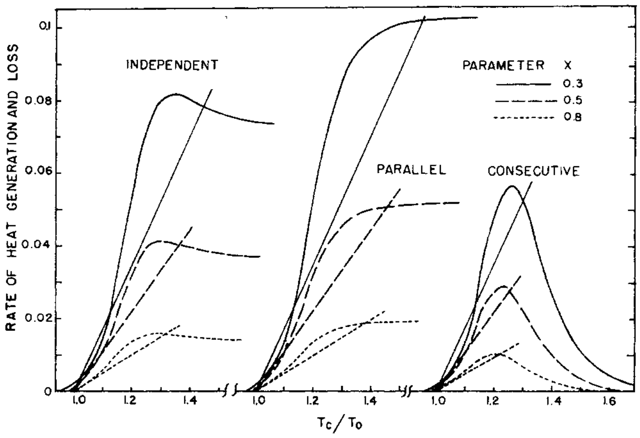
DISCUSSION

The problem of heterogeneous solid-fluid chemical reactions accompanying a moving boundary of reaction surface has been treated by means of the pseudosteady state approximation to reduce the mathematical difficulties in solving the differential equations. This approximation for material balance is a good one for most of the solid-gas reaction systems except for those with extremely high pressure and very low solid reactant concentration (*3, 13, 18*). For heat balance Wen (*18*) discussed the accuracy of the pseudosteady state approximation, indicating that it may not be a good one for solid-gas reaction systems under certain conditions, such as during the shifting of rate-controlling regimes and during the initial period of reaction when heat capacity of the solid and temperature gradient in the particles are large. However, even for the heat balance, pseudosteady state approximation is still a valuable and valid assumption for most cases. This is because the temperature gradient between reaction surface and the ambient condition is rather small when chemical reaction is the rate-controlling step; and the temperature at the reacting surface is nearly a constant when diffusion is the rate-controlling step. Under these conditions, accumulation term in heat balance equation becomes negligibly small. The discussion on steady state and unsteady state solutions for solid-gas reaction is presented elsewhere (*19*).

The parameters appearing in the selectivity and effectiveness factor expressions are $\mathcal{R}T_0/E_1$, E_2/E_1, k_2^0/k_1^0, C_{B0}/C_{A0}, $(N_{Nu})_P$, N_{Shi}, D_{eB}/D_{eA}, $(\Delta H_2)/(\Delta H_1)$, ϕ_1, β_1, and the stoichiometric coefficient ratios. To find the effect of the individual parameters on the effectiveness factor and selectivity is time-consuming and unnecessary. In this paper the appropriate values for the important parameters are selected and their effects discussed.

The values of U_c solved from Equations (22), (24), and (27) at a fixed value of ξ_c are the dimensionless temperatures of reaction surface at which the rate of heat generation equals that of heat loss. The radiational heat loss from the surface of the particle, which is proportional to the fourth power of particle surface temperature, makes it impossible to obtain an analytical solution. Therefore an overall heat transfer coefficient h_p is used which combines both the convective and linearized radiative heat transfer contributions.

Figure 1 shows the relationship between the net heat generation and heat loss curves for independent, parallel, and consecutive reactions, respectively. The ordinate of Figure 1 represents the dimensionless heat generation and heat loss per particle for the three types of reactions considered. The shapes of the heat generation curves depend on the type of reactions and the values of the parameters. The values of parameters selected are shown on the figure with the stoichiometric coefficient ratios of unity. The positive value of β_1 and the negative value of $(\Delta H_2)/(\Delta H_1)$ mean that the first reaction is exothermic, while the second is endothermic. The selected values of E_2/E_1 and k_2^0/k_1^0 are such that the rate of the first reaction is four times faster than that of the second reaction at all times. Under such conditions, the heat released from the first reaction is more than the heat absorbed by the second reaction for the cases of independent and parallel reactions. For consecutive reactions, however, the net heat generation reaches a maximum and then approaches zero as T_c/T_0 becomes higher, apparently due to the competing processes of the production of product gas B by the first reaction and the consumption of this gas as a reactant in the second reaction.



$\mathcal{R}T_0/E_1 = 0.04$, $E_2/E_1 = 1.0$, $k_2^0/k_1^0 = 0.25$, $D_{eB}/D_{eA} = 1.0$, $C_{B0}/C_{A0} = 1.0$, $N_{Shi} \longrightarrow 100$
$(\Delta H_2)/(\Delta H_1) = -0.5$, $(N_{Nu})_p \longrightarrow 10$, $\phi_{1(T_0)} = 0.139$, $\beta_1 = 0.02$

Fig. 1. Relation of heat generation and heat loss during course of reactions for three types of simultaneous reactions.

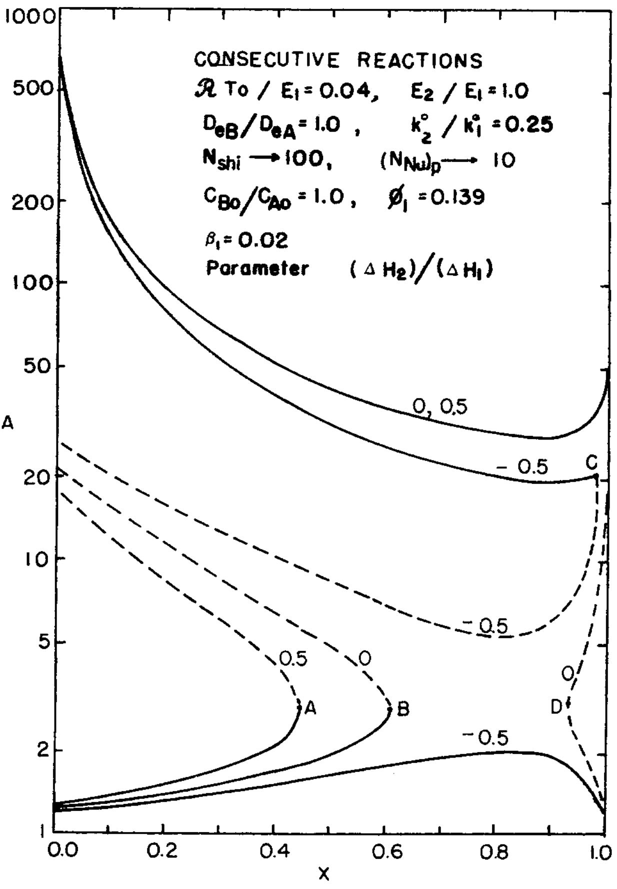


Fig. 2. Effect of $(\Delta H_2)/(\Delta H_1)$ on η_A for consecutive reactions.

Figure 2 indicates the effect of $(\Delta H_2)/(\Delta H_1)$ on η_A for consecutive reactions with other parameters kept the same as in Figure 1. Ignition (*8*) occurs at points *A* and *B* when $(\Delta H_2)/(\Delta H_1)$ are 0.5 and 0, respectively. Since β_1 is positive, the first reaction is exothermic; the values of $(\Delta H_2)/(\Delta H_1)$ of 0.5, 0, and -0.5 then indicate the second reaction to be exothermic, isothermal, and endothermic, respectively. The increasing endothermicity in that order increases the possibility for extinction to occur, as evidenced by point *C* when $(\Delta H_2)/(\Delta H_1) = -0.5$.

Figure 3 shows the effect of $\mathcal{R}T_0/E_1$ in η_A for independent reactions, with $(\Delta H_2)/(\Delta H_1) = -0.5$. Other parameters are kept the same as in Figure 2. For $\mathcal{R}T_0/E_1 = 0.038$, three stable regions, including one metastable, exist (*8*) before solid conversion of 95% is reached where an extinction point exists. If the initial rate is in diffusion-controlling region, it would shift to chemical reaction-controlling region at this extinction point, while chemical reaction would control through the entire range of conversion when the initial rate is in chemical reaction-controlled regime. As the value of $\mathcal{R}T_0/E_1$ is increased to 0.04, the extinction point shifts toward complete conversion. For higher values of $\mathcal{R}T_0/E_1$, only the diffusion-controlling region exists and the effectiveness factors become very low as conversion increases.

Figures 4 to 8 show the effects of β_1 on the effectiveness factor and selectivity. As can be seen from the definition, β_j is determined by two properties of solid, D_{ei} and k_e, and by chemical reaction parameters E_j, C_{i0}, and ΔH_j. The magnitude of β_1 encountered in various reaction systems has been discussed by Weisz and Hicks (*17*), where T_0 was used instead of $E_j/\mathcal{R}$. In this paper the values of β_1 are selected as 0.02, 0.015, 0.01, 0.005, and 0, where $\beta_1 = 0$ at a finite value of $(\Delta H_2)/(\Delta H_1)$ corresponds to isothermal situation. The values of β_2 depend on β_1, $(\Delta H_2)/(\Delta H_1)$, E_2/E_1, D_{eB}/D_{eA} (in parallel reactions $D_{eA}/D_{eA} = 1$). Because the value of $(\Delta H_2)/(\Delta H_1)$ selected for these figures is -0.5, β_2 is negative for all positive values of β_1, meaning that the second reactions are endothermic.

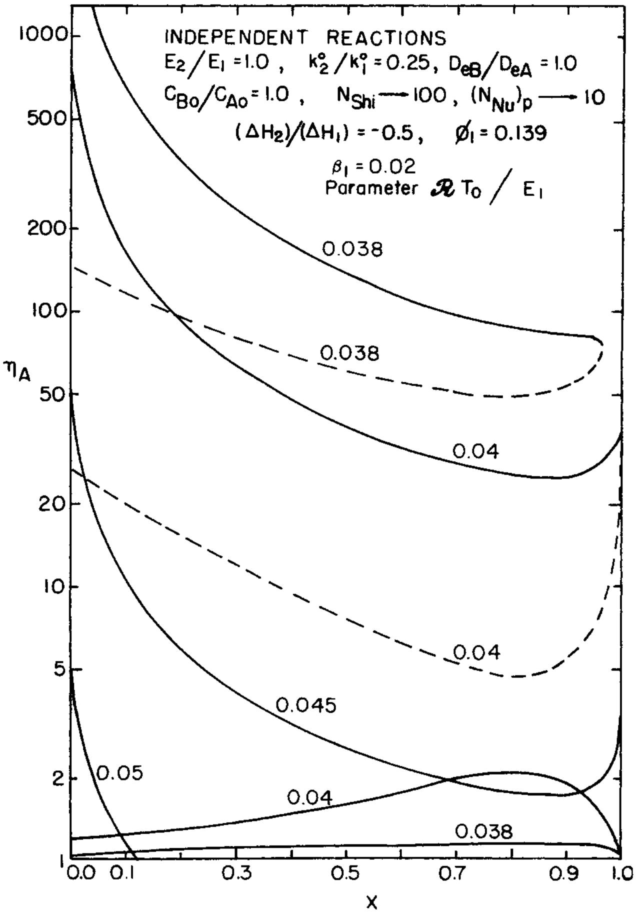


Fig. 3. Effect of $\mathcal{R}\,T_0/E_1$ on η_A for independent reactions.

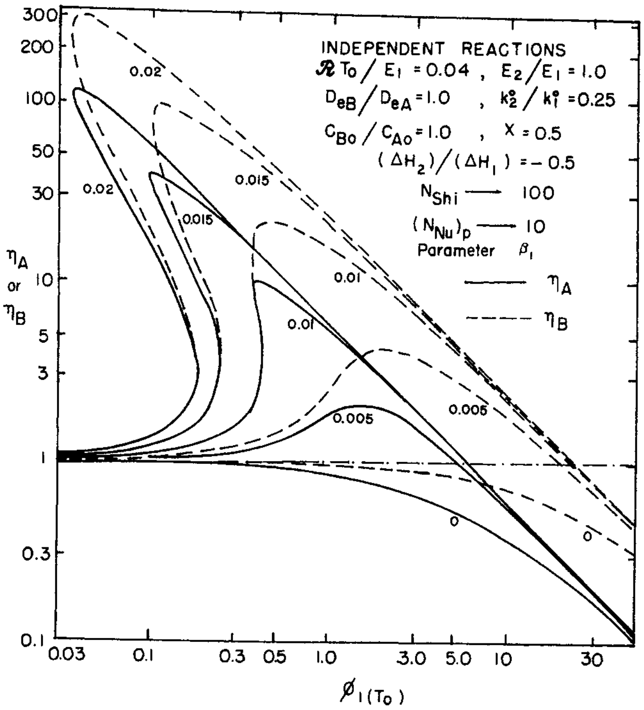


Fig. 4. Effect of β_1 on η_A and η_B for independent reactions.

Figures 4 and 5 show the effect of β_1 on η_A and η_B and selectivity, respectively, for independent reactions under the same conditions at $X = 0.5$. The parameters other than β_1 and ϕ_1 are the same as in Figure 1. From the selectivity equation for independent reactions, it can be shown that when ϕ_1 is very low, that is, when chemical reaction is controlling, the selectivity reduces to

$$S_{AB} = \frac{aC_{A0}k_{1(T_c)}}{bC_{B0}k_{2(T_c)}}$$

which is equal to 4 in this case. On the other hand when ϕ_1 is very high, namely, the rate is diffusion controlled, the selectivity becomes

$$S_{AB} = \frac{C_{A0}D_{eA(T_0)}\left(\dfrac{1}{N_{ShB}} + \dfrac{1}{\xi_c} - 1\right)}{C_{B0}D_{eB(T_0)}\left(\dfrac{1}{N_{ShA}} + \dfrac{1}{\xi_c} - 1\right)}$$

which is 1 in this case. These limiting values are seen clearly in Figure 5. It can also be seen that at the same controlling region and the same ϕ_1, higher value of β_1 gives higher effectiveness factors and lower selectivity.

Figures 6 and 7 for consecutive reactions correspond, respectively, to Figures 4 and 5, except that now $C_{B0}/C_{A0} = 0.01$. At some stage during the reaction, the desired product *B* may be consumed by the second reaction at a rate faster than it is produced by the first reaction, causing gas *B* to diffuse in an undesirable inward direction and hence negative selectivity (*20*). This situation can be prevented by keeping the bulk phase concentration of *B*, C_{B0} very low. This explains why $C_{B0}/C_{A0} = 0.01$ is

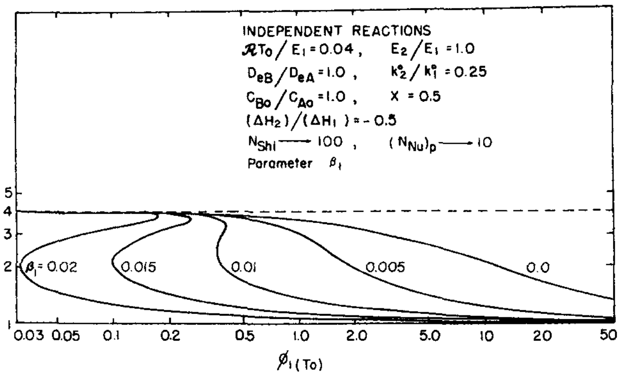


Fig. 5. Effect of β_1 on selectivity for independent reactions.

chosen for the consecutive reactions. From the selectivity equation for consecutive reactions, it can be shown that when ϕ_1 is very small, S_{BF} approaches

$$\frac{b_1 C_{A0} k_{1(T_c)}}{f\, C_{B0} k_{2(T_c)}} - \frac{b_2}{f}$$

which is equal to 399 in this case. On the other hand, when ϕ_1 is very large, S_{BF} approaches

$$\frac{\left(\frac{b_1}{f}\right)\left(\frac{b_2}{a}\right)\left(\frac{C_{A0}}{C_{B0}}\right)\left(\frac{D_{eA(T_0)}}{D_{eB(T_0)}}\right)\left(\frac{1}{N_{ShB}} + \frac{1}{\xi_c} - 1\right)}{\frac{1}{N_{ShA}} + \frac{1}{\xi_c} - 1 + \left(\frac{1}{N_{ShB}} + \frac{1}{\xi_c} - 1\right)\left(\frac{b_1}{a}\right)\left(\frac{C_{A0}}{C_{B0}}\right)\left(\frac{D_{eA(T_0)}}{D_{eB(T_0)}}\right)} - \frac{b_2}{f}$$

which is equal to -0.0099 for the selected parameters. As can be seen from Figure 7, when ϕ_1 increases, S_{BF} becomes smaller and smaller and will become negative for high ϕ_1. Figures 6 and 7 also indicate that, as in the case of independent reactions, at the same value of ϕ_1, higher value of β_1 gives higher effectiveness factor and lower selectivity.

Figure 8 shows the effect of β_1 on effectiveness factor for parallel reactions. The parameters selected are the same as in Figure 4. The curves of η_A versus ϕ_1 plot resemble those for the independent and consecutive reactions. The selectivity for parallel reactions, in which the gaseous reactants in both the first and second reactions are of the same species, is dependent on the ratio of the reaction rate constants and the ratio of stoichiometric coefficients. The parameter values selected for Figure 8 are $E_2 = E_1$, $b/f = 1$ and $k_1^0/k_2^0 = 4$. Hence, the selectivity S_{BF} becomes constant and equals 4.

CONCLUSION

In the solid-gas reactions when the chemical reaction is accompanied by a heat effect, not only the concentration gradient, but also appreciable temperature gradient, can exist within the solid particle. Therefore the effect of heats of reaction on the reaction rate cannot be neglected.

The thermal instability and abrupt transition of the rate-controlling factor may all happen during the entire stage of reactions, depending on the parameters selected. Using the concept of effectiveness factor, these instabilities can easily be located, as in the case of single reaction (*8*).

The selectivity for different types of simultaneous reactions depend on the values of the parameters. In general, small β_1 gives high selectivity at a fixed value of ϕ_1. For independent reactions, when ϕ_1 is small, the selectivity

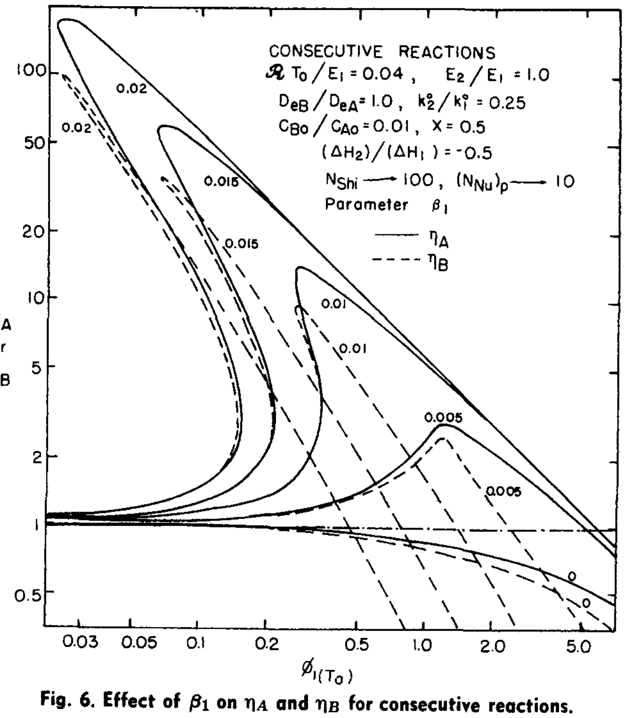


Fig. 6. Effect of β_1 on η_A and η_B for consecutive reactions.

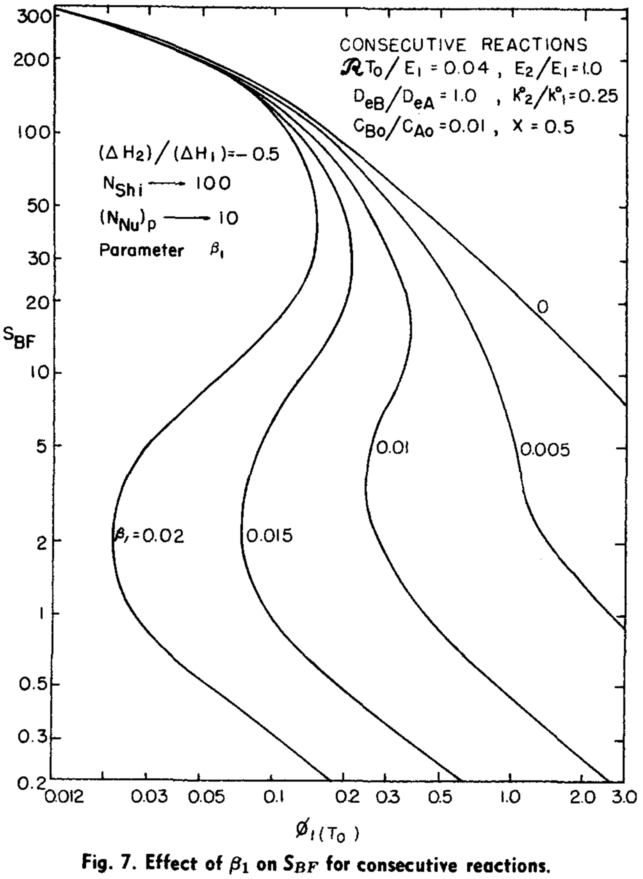


Fig. 7. Effect of β_1 on S_{BF} for consecutive reactions.

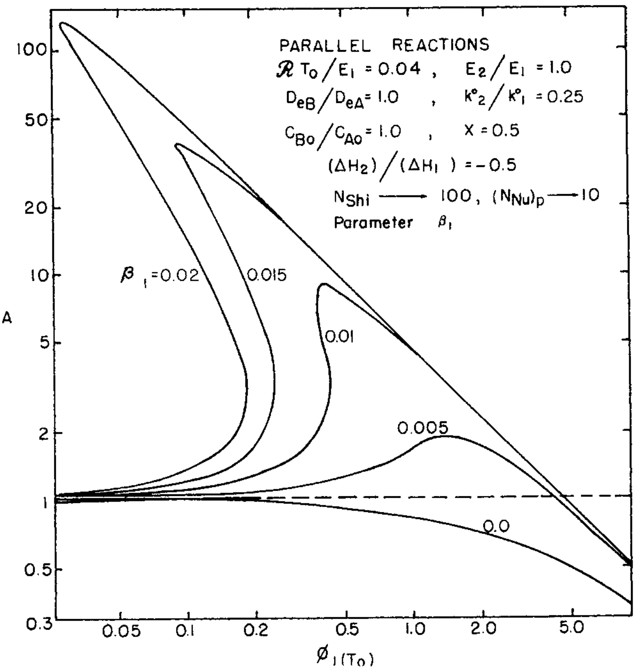


Fig. 8. Effect of β_1 on η_A for parallel reactions.

depends greatly on the ratio of the rate constants; for large ϕ_1 the selectivity depends considerably on the ratio of the effective diffusivities. For parallel reactions the selectivity depends only on the ratio of the rate constants at all values of ϕ_1 because both reactions 1 and 2 are of the first order with respect to the gaseous reactant A. For consecutive reactions, negative values of selectivity could result due to the reversal in the direction of diffusion of the desired product B. This phenomenon is particularly significant when ϕ_1 and C_{B0}/C_{A0} are both large.

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NOTATION

$a, a_1, a_2, b, b_1, b_2, e, f$ = stoichiometric coefficients for components A, B, E, and F, respectively
C = total concentration of gases, mole/L^3
C_i, C_{i0}, C_{is} = concentration of gas component i, where $i = A, B, E$, and F. 0 refers to the bulk phase, s refers to the outer surface of the particle, mole/L^3
C_{S0} = initial concentration of solid reactant, mole/L^3
D_{ei} = effective diffusivity of component, i, L^2/θ
E_j = activation energy of reaction rate constant for j^{th} reaction where $j = 1, 2$, H/mole
h_p = overall convective and linearized radiative heat transfer coefficient, $H/L^2\theta T$
ΔH_j = heat of reaction per mole of reactant for j^{th} reaction, H/mole
I_i = stoichiometric coefficient for component i
k_e = effective thermal conductivity of ash layer, $H/L\theta T$
k_{mi} = mass transfer coefficient for component i across gas film, L/θ
k_j^0 = frequency factor for j^{th} reaction based on surface area, L^4/mole θ
$k_{j(T_0)}$ = reaction rate constant for jth reaction at T_0 based on surface area, L^4/mole θ
N_i = molar flux for component i relative to fixed coordinates, mole/$L^2\theta$
$(N_{Nu})_P$ = modified Nussel number $(= Rh_p/k_e)$
N_{Shi} = Sherwood number for component i $(= k_{mi}R/D_{ei})$
r = distance from center of sphere, L
r_c = radius of unreacted core, L
R = particle radius, L
$\mathcal{R}$ = gas constant, H/mole T
S_{iq} = selectivity for component i over q
T, T_c, T_0, T_s = temperature 0 refers to bulk gas phase, c refers to unreacted core surface, s refers to outer surface of the particle T
U = T/T_0
U_c = T_c/T_0
U_s = T_s/T_0
x_i = mole fraction of component i, x_{i0} in bulk gas phase, x_{is} at outer surface of particle, x_{ic} at unreacted core surface
X = conversion of solid reactant S

Greek Letters

β_j = $C_{i0}D_{ei(T_0)}\ (-\Delta H_j)\mathcal{R}/k_eE_j$, where subscripts i and j denote gaseous reactant i of the j^{th} reaction
ϵ = porosity of ash layer
η_i = effectiveness factor for component i
ξ = r/R
ξ_c = r_c/R
ϕ_j = $I_iRk_{j(T_0)}C_{S0}/D_{ei(T_0)}$ modified Thiele modulus, where I_i is stoichiometric coefficient of gaseous reactant i, and subscripts i and j denote gaseous reactant i of the j^{th} reaction
ω_i = x_i/x_{i0}
ω_{ic} = x_{ic}/x_{i0}
ω_{is} = x_{is}/x_{i0}

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