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Initial Value Approach to a Class of Reaction-Diffusion Systems

New sets of transformations that convert an original two-point boundary value problem into an equivalent initial value problem have been proposed and illustrated in the solution of the diffusion-reaction problem for a monodispersed catalyst pellet. The use of the transformations reduces the computational effort considerably. The method is especially useful in the analysis of more complex cases, such as bidispersed catalyst pellets, catalysts undergoing decay, and gas-solid noncatalytic reactions where the use of the conventional numerical techniques is quite involved and cumbersome. The method is applied to some known and to some yet-unresolved cases and the new results obtained are discussed.

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SCOPE

The literature is replete with solutions to a variety of reaction-diffusion problems (Aris, 1975; Carberry, 1976). Typically, in these problems one obtains a second-order differential equation with boundary conditions specified at two different locations leading to a boundary value problem. The solution to boundary value problems, specially nonlinear, is considerably involved and great attention has been devoted in the past to reduce the attendant numerical complexities (Kubicek and Hlavacek, 1970; 1971 a,b,c; Hanna, 1980; Michelsen and Villadsen, 1978; Finlayson, 1974; Jayaraman et al., 1982). Approximate methods leading to simple algebraic expressions for effectiveness factors have also been proposed in the literature (Churchill, 1977; Wedel and Luss, 1980; Sundaram, 1981; Gottifredi et al., 1980 a,b). While reliable methods of solution such as that of Weisz and Hicks (1962) exist for monoporous systems, their use in more complex cases such as for systems with mass transfer limitations, bidispersed catalysts, catalysts undergoing decay, or gas-solid noncatalytic systems, is fairly involved and cumbersome. General numerical methods that avoid trial and error to obtain solutions to similar complex cases have been proposed by Wendt et al. (1979), Hahn and Wendt (1982), and Hahn and Shadman (1983).

In most practical cases one has to deal with multicomponent reacting and diffusing species which lead to more than one nonlinear equation. Depending on the nature of coupling involved among the phenomenological equations describing the system, suitable methods that avoid trial and error have been devised. Thus when the coupling occurs in the rate terms, the general method proposed by Wendt et al. (1979), Hahn and Wendt (1982), and Hahn and Shadman (1983) can be employed. A suitable variant of these methods may be necessary when the governing equation involves additional coupling such as at the boundary conditions.

In the present work we propose new sets of transformations for several different rate forms, the use of which leads to an equivalent initial value problem. This makes it possible to gain computational advantage over the existing methods. In the first phase of this work, the intention being to develop and test these transformations, their use has been restricted to simple monodispersed catalyst pellets. Some known systems (rate forms) are therefore first studied and the results obtained are compared with the earlier (known) results. Some new rate forms have also been analyzed.

Subsequently the method is extended to the case where interphase diffusion is present and then to the case where all the three resistances—flow, interphase and intraphase—are present. Finally, the applicability of the method is demonstrated for more complex situations such as those encountered in bidispersed catalysts with Langmuir-Hinshelwood (L-H) kinetics, not analyzed before. The results obtained throw significant light on the behavior of such systems.

CONCLUSIONS AND SIGNIFICANCE

A vast body of literature exists on diffusion-reaction in a catalyst pellet. In spite of this, there is need for newer and simpler methods of solution, particularly applicable to more realistic situations than considered so far, such as reaction with complex kinetics in a biporous catalyst matrix. A few such situations have been considered in the present anlalysis, after confirming the validity of the proposed method of solution by first applying it to established situations. The method developed

and the significance of the results obtained are outlined below for the different situations examined.

(1) New sets of transformations that convert an original two-point boundary value problem to an equivalent initial value problem have been proposed. Four different rate forms have been analyzed by using these transformations and the results presented in the form of the usual effectiveness factor vs. Thiele modulus curves. For the simple Langmuir-Hinshelwood (L-H) and bimolecular L-H rate forms, the results agree with the established results, thus proving the validity of the method.

(2) The proposed transformations can also be used for the case with interphase resistance. This is illustrated by considering a general *n* th order reaction. Finally a more general application of the method is illustrated by considering the case of a CSTR where, in addition to the flow resistance, the interphase and intraphase resistances are also accounted for.

(3) Two other rate forms, *viz.*, (i) $r = kC_AC_B/(1 + K_AC_A + K_BC_B)$ and (ii) autocatalytic $r = kC_AC_B$, not studied hitherto, have also been analyzed using appropriate transformations. In the first case, it is shown that increasing the value of the adsorption coefficient K'_B generally improves the effectiveness of the system. Also, there exists a critical value of the parameter ν_1 on either side of which the effectiveness factor of the system always increases. In the case of autocatalysis, it is shown that an effectiveness factor exceeding unity can be obtained for certain input concentrations; however, no multiplicity is seen to exist.

(4) The application of this method to bidispersed catalysts for a representative case of L-H kinetics clearly shows that the cumbersome computations required in the conventional method can be considerably reduced. A particularly important result of this work is that a variant of the proposed method leads to a very compact representation of the variation of η with the parameters of the system. This has not been possible so far. The analysis has brought out another significant result that falsification of the reaction kinetics occurs in the bidispersed catalyst. For a given kinetic law, certain new features, which are not present in monopore systems, become evident in bidispersed pellets. In view of the considerable use of bidispersed pellets in industrial systems, the present result has great pragmatic significance.

(5) The only limitation of this method is that for some situations it can lead to a set of nonautonomous differential equations. While this is of no consequence for purposes of computation, methods such as linear stability analysis cannot be invoked to obtain *a priori* information on the stability of systems.

INTRODUCTION

Chemically reacting systems, in particular those involving heterogeneous catalysis, have been investigated both from theoretical and experimental points of view (Aris, 1975; Carberry, 1976). The class of problems referred to as the reaction-diffusion problems have been solved for a number of situations and their results have useful implications in the design of fixed-bed reactors. The typical formulation of any of these problems leads to a differential equation of the type

$$\nabla^2 a = \bar{r} \tag{1}$$

where a is the dimensionless concentration of the reactant species and $\bar{r}$ the dimensionless reaction rate. The boundary conditions to this conservation equation describing the happenings in a single particle are invariably specified at two different locations. Typically, therefore, one is confronted with a boundary value problem. In the case where the reaction rate linearly depends on the concentration of species, this equation can be solved to obtain analytical results. On the other hand, in the more frequent case of nonlinear reaction rates, recourse to numerical methods becomes necessary.

Over the past few years, considerable attention has been focused on developing numerical methods to obtain solutions to these problems. Despite these efforts the search for easier numerical methods continues. [For the more recent attempts, see Hanna (1980), Ibanez (1979), Wendt et al. (1979), Hahn and Wendt (1982), Hahn and Shadman (1983), and Jayaraman et al. (1982).] The object of this paper is to propose a simple method for obtaining solutions to a number of situations and to present some significant conclusions from the results for specific cases.

More specifically, we present in this work a set of transformations for different forms of the reaction rate that converts the original two-point boundary value problem into an equivalent initial value problem. The initial value formulation can be solved more easily without any numerical complexities, such as trial and error required in the original two-point boundary value representation. The first intention in this work being to develop and test these transformations, to start with, their use is restricted to known cases for simple monopore systems; the results are compared with the available solutions. A few unresolved cases are then considered and the results obtained are discussed. The method is subsequently extended to include cases where interphase resistance or all the three—flow, interphase and intraphase—resistances are present. Finally the applicability of the method to more complex cases such as bidispersed catalysts is considered for a representative Langmuir-Hinshelwood kinetic form. The analysis for the last case provides some new and significant results which are discussed.

PROBLEM FORMULATION AND ANALYSIS: APPLICATION TO MONOPORE SYSTEMS

The transformations are devised for five different types of rate forms: (1) the simple Langmuir-Hinshelwood (L-H) rate law; (2) the L-H rate form of arbitrary order; (3) the bimolecular L-H rate form; (4) the autocatalytic rate form; and (5) the general *n*th order case with external mass transfer.

These rate forms are frequently used to describe the reaction rate for a number of systems. The set of proposed transformations for these different cases is presented in Table 1 and general guidelines for obtaining these transformations for different rate forms is summarized in Appendix I.

The use of these transformations in the present section is demonstrated for the case of a simple monodispersed pellet both in the absence and presence of interphase transport resistance. The analysis is then extended to a well-mixed CSTR system where all the three—flow, interphase and intraphase—resistances are accounted for. The set of transformations can also be used for more complex situations such as bidispersed pellets, or for a catalyst undergoing decay or for a gas-solid noncatalytic system; a representative case of bidispersed catalyst for L-H kinetics is considered to illustrate the method.

Particle Problem with No Interphase Gradient

Simple L-H kinetics, $r = kC_A/(1 + K_AC_A)$. The typical conservation equation for the species A for this case can be represented along with the boundary conditions as

$$\nabla^2 a = \frac{\phi^2 a}{1 + K'_A a};\ a(1) = 1;\ \left.\frac{da}{dx}\right|_{x=0} = 0 \tag{2}$$

where

$$\phi = R\sqrt{k/D_{eA}} \text{ and } K'_A = K_AC_{As}$$

The problem has already been solved by Krasuk and Smith (1965) who have presented their results in terms of effectiveness factor plots. We shall now apply the transformation corresponding to this case in Table 1 to convert this into an equivalent initial value problem and generate results in terms of the effectiveness factor plot.

The use of the transformations converts Eq. 2 into

$$\frac{dw}{d\tau} = \frac{1}{K_A'}\left[\frac{\theta}{w} - 1 - K_A'w\right] \tag{3}$$

$$\frac{d\theta}{d\tau} = \frac{1}{K_A'}\left[\frac{2\theta}{w} + \frac{\theta e^{\tau}[1 + K_A'(1 + Z_0)]K_A'}{[e^{\tau}[1 + K_A'(1 + Z_0)] - 1} - 2\theta K_A'\right] \tag{4}$$

where

$$w = \theta = 0 \text{ at } \tau = 0 \tag{5}$$

The set of Eqs. 3–5, however, has a singularity at $\tau = 0$, and θ/w at $\tau \to 0$ can be evaluated by successive application of *L'*Hospital's rule, to obtain a value 3 for the case of a sphere and 1 for the case of a slab. The Runge-Kutta method can now be employed to obtain the solution to this problem. It is interesting to note that the newly-defined independent variable τ appears also on the rh's of these equations; however, it presents no difficulty in the numerical integration. The general procedure for obtaining the effectiveness factor is described in Appendix II and for this particular case the effectiveness factor can be estimated as

$$\eta = \frac{3w}{\theta}.$$

The results generated for four different values of K_A' are shown in Figure 1 as η-ϕ curves. The results of Krasuk and Smith are also displayed in the figure for the sake of comparison.

The L-H form, $r = kC_A/(1 + K_AC_A)^n$. Certain catalytic reactions e.g., carbon monoxide oxidation on supported platinum catalyst, display a self-inhibited rate form represented by $r = kC_A/[1 + K_AC_A]^2$ (Cavandish and Oh, 1979; Pereira and Varma, 1978). Extensive studies have been made of the self-inhibited rate, or bimolecular Langmuir-Hinshelwood rate, particularly, with regard to effectiveness factors (Pereira and Varma, 1978; Becker and Wei, 1975; El Nashaie and Mahfouz, 1978). Becker and Wei (1975) first reported the existence of three solutions for the catalyst pellet. Later, Pereira and Varma (1978) and El Nashaie and Mahfouz (1978) independently established the existence of up to five steady states under certain conditions. It is not the objective here to reproduce all these results; however, the simplified method proposed here will be illustrated for a few cases.

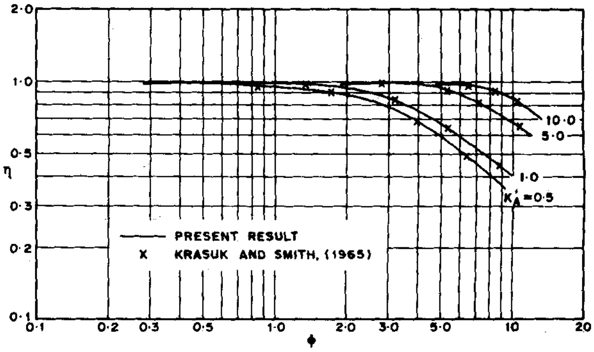


Figure 1. Influence of adsorption constant on effectiveness factor—Thiele modulus curve.

The conservation equation along with the boundary condition for the above case can be written as

$$\nabla^2 a = \frac{\phi^2 a}{(1 + K_A'a)^n};\ a(1) = 1;\ \left.\frac{da}{dx}\right|_{x=0} = 0 \tag{6}$$

After using the set of transformations corresponding to this case in Table 1, the following equations are obtained:

$$\frac{dw}{d\tau} = \frac{[1 + K_A'(1 + Z_0)]^{n-1}}{(n-1)K_A'} \times \left[\frac{\theta}{w} - 1 - \frac{(2-n)K_A'w}{[1 + K_A'(1 + Z_0)]^{n-1}(1 + \tau)}\right]$$

$$\frac{d\theta}{d\tau} = \frac{[1 + K_A'(1 + Z_0)]^{n-1}}{(n-1)K_A'} \times \left[\frac{2\theta}{w} + \frac{\theta K_A'(1 + \tau)^{2-n/n-1}[1 + K_A'(1 + Z_0)]^{2-n}}{(1 + \tau)^{1/(n-1)}[1 + K_A'(1 + Z_0)] - 1} - \frac{2\theta K_A'}{(1 + \tau)[1 + K_A'(1 + Z_0)]^{n-1}}\right] \tag{8}$$

$$\theta = 0,\ w = 0 \text{ at } \tau = 0 \tag{9}$$

The set of Eqs. 7–9 has been integrated to obtain the $\eta - \phi$ curve using the general procedure in the Appendix II. The typical cases of $K_A' = 8$ and 15 for $n = 2$ have been shown in Figure 2. It is seen from the figure that for $K_A' = 8$ the effectiveness factor exceeds unity but no multiplicity is evident. The analysis of Pereira and Varma (1978) indicates the multiplicity would exist for values of $K_A' > 12.2$. To check this point the results for the case $K_A' = 15$ have

TABLE 1. TRANSFORMATIONS FOR SEVERAL FORMS OF RATE EQUATIONS

S. No. *1*	Rate Form 2	Dimensionless Form of Rate in Eq. 1 3	Transformations Z 4	 w 5	 θ 6	 τ 7
1	$\frac{kC_A}{1 + K_AC_A}$	$\frac{\phi^2 a}{1 + K_A'a}$	$a = 1 + Z$	$\frac{x\frac{dZ}{dx}}{1 + K_A'(1 + Z)}$	$\frac{\phi^2 x^2(1 + Z)}{[1 + K_A'(1 + Z)]^2}$	$\ln\frac{1 + K_A'(1 + Z)}{1 + K_A'(1 + Z_0)}$
2	$\frac{kC_A}{(1 + K_AC_A)^n}$	$\frac{\phi^2 a}{(1 + K_A'a)^n}$	$a = 1 + Z$	$\frac{x\frac{dZ}{dx}}{[1 + K_A'(1 + Z)]^{2-n}}$	$\frac{\phi^2x^2(1 + Z)}{(1 + K_A'(1 + Z)]^2}$	$\left[\frac{1 + K_A'(1 + Z)}{1 + K_A'(1 + Z_0)}\right]^{n-1} - 1$
3	$\frac{kC_AC_B}{1 + K_AC_A + K_BC_B}$	$\frac{\phi^2a[v_{1a} - q_1]}{(1 - K_Bq_1)(1 + pa)}$	$\frac{a}{q} = 1 + Z$	$\frac{x\frac{dZ}{dx}}{(1 - K_B'q_1)(1 + pq(1 + Z))}$	$\frac{\phi^2x^2(1 + Z)}{(1 - K_B'q_1)^2(1 + pq(1 + Z))^2}$	$\ln\frac{1 + pq(1 + Z)}{1 + pq(1 + Z_0)}$
4	kC_AC_B	$\phi^2a(a + (1 - q(1 + \nu_1)))$	$\frac{a}{q} = 1 + Z$	$\frac{x\frac{dZ}{dx}}{1 + Z}$	$\phi^2x^2(q\nu_1(1 + Z) + 1 - q(1 + \nu_1))$	$\ln\frac{1 + Z}{1 + Z_0}$
5	kC_A^n	ϕ^2a^n	$a = K_1(1 + Z)$	$\frac{x\frac{dZ}{dx}}{1 + Z}$	$\phi^2K_1^{n-1}(1 + Z)^{n-1}x^2$	$\ln\frac{1 + z}{1 + Z_0}$

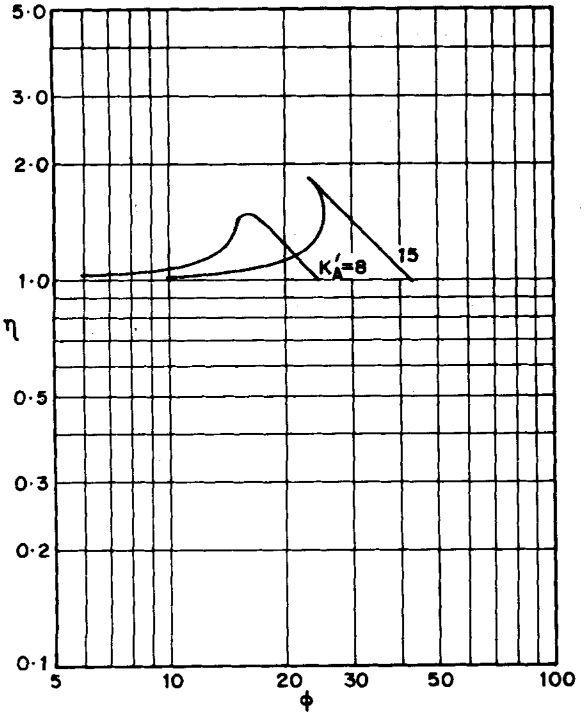


Figure 2. Influence of adsorption constant on effectiveness factor—Thiele modulus curve.

also been displayed in the figure showing the validity of the proposed method.

The L-H rate form, $r = kC_AC_B/(1 + K_AC_A + K_BC_B)$. Let us consider a reaction scheme of the type $A + \nu B \rightarrow$ products with a rate form $r = kC_AC_B/(1 + K_AC_A + K_BC_B)$. Catalytic reaction rate models based on multistep rate control frequently give rise to a rate form of this type, the essential features of which have been commented upon by Carberry (1976). This form is frequently invoked to explain the kinetic features of the alkylating reactions (Beranek and Kraus, 1978). While the analysis of catalyst pellet for similar rate forms has been reported earlier (Knudsen et al., 1966; Roberts and Satterfield, 1966; Hartman et al., 1967), this particular rate form does not seem to have been analyzed.

The conservation equation along with the boundary conditions for the species A and B can be written as

$$\nabla^2 a = \frac{\phi^2 ab}{1 + K'_Aa + K'_Bb};\ a(1) = q;\ \left.\frac{da}{dx}\right|_{x=0} = 0 \tag{10}$$

$$\nabla^2 b = \frac{D_{eA}}{D_{eB}}\,\nu\,\frac{\phi^2 ab}{1 + K'_Aa + K'_Bb};$$
$$b(1) = 1 - q;\ \left.\frac{db}{dx}\right|_{x=0} = 0 \tag{11}$$

Equations 10 and 11 can be combined to eliminate b; Eq. 10 then can be written as

$$\nabla^2 a = \frac{\phi^2 a[\nu_1 a - a_1]}{(1 - K'_Bq_1)(1 + pa)} \tag{12}$$

where

$$P = \frac{K'_A + K'_B\nu_1}{1 - K'_Bq_1};\ q = \frac{C_{As}}{C_T};\ \nu_1 = \frac{D_{eA}}{D_{eB}}\,\nu$$
$$q_1 = q(1 + \nu_1) - 1;\ \phi^2 = R^2\frac{k}{D_{eA}};\ K'_A = K_AC_T;$$
$$K'_B = K_BC_T \text{ and } C_T = C_{As} + C_{Bs} \tag{13}$$

Applying the transformation corresponding to this case presented in Table 1, we can rewrite Eq. 12 as

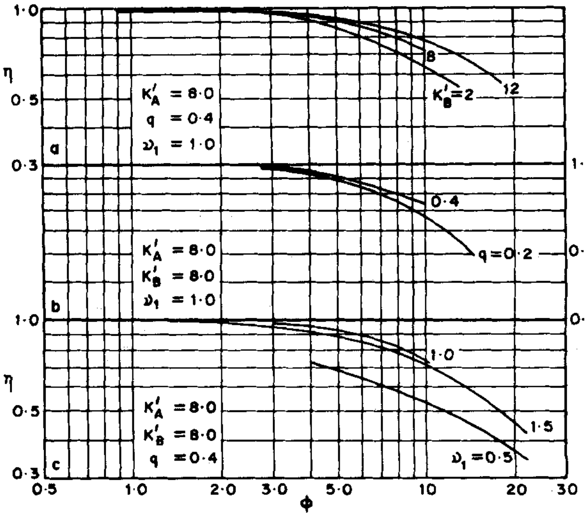


Figure 3. Influence of: (a) adsorption constant of second component; (b) input feed composition; and (c) stoichiometric coefficient on effectiveness factor—Thiele modulus curve for fixed values of other parametrs.

$$\frac{dw}{d\tau} = \frac{1}{pq(1 - K'_Bq_1)}\left[\left\{\frac{\nu_1}{p}[e^\tau(1 + pq(1 + Z_0)) - 1] - q_1\right\}\frac{\theta}{w} - 1 - pq(1 - K'_Bq_1)w\right] \tag{14}$$

$$\frac{d\theta}{d\tau} = \frac{2\theta}{w}\frac{1}{pq(1 - K'_Bq_1)} + \frac{\theta e^\tau[1 + pq(1 + Z_0)]}{[e^\tau[1 + pq(1 + Z_0)] - 1]} - 2\theta \tag{15}$$

$$w = \theta = 0 \text{ at } \tau = 0 \tag{16}$$

Using the procedure described in Appendix II the effectiveness factor is obtained as

$$\eta = \frac{3w}{(1 - q)\theta}$$

Figure 3a shows the influence of the variation of K'_B for fixed values of the other parameters. Increasing the values of K'_B is seen in general to improve the overall effectiveness of the particle. Figure 3b shows the influence of variation of the input feed composition. Decreasing the concentration of A in the feed results in a decrease in the effectiveness factor of the system. The variation with respect to the stoichiometric coefficient or the ratio of diffusivities of the species B and A, however, shows some interesting behavior. For a fixed set of other parameter values, there exists a critical value of ν_1 below which or above which the effectiveness factor always decreases (Figure 3c).

Autocatalysis, $r = kC_AC_B$. Let us consider a reaction scheme of the type $A + \nu B \rightarrow B + B$. The conservation equations for species A and B along with the boundary conditions are

$$\nabla^2 a = \phi^2 ab;\ a(1) = q;\ \left.\frac{da}{dx}\right|_{x=0} = 0 \tag{17}$$

$$\nabla^2 b = \nu_1\phi^2 ab;\ b(1) = (1 - q);\ \left.\frac{db}{dx}\right|_{x=0} = 0 \tag{18}$$

Expressing the concentration b in terms of the concentration a by using Eqs. 17 and 18 and using the transformations corresponding to this case presented in Table 1 we obtain (for slab geometry)

$$\frac{dw}{d\tau} = 1 - w + \frac{\theta}{w} \tag{19}$$

$$\frac{d\theta}{d\tau} = \frac{2\theta}{w} + \frac{\theta q\nu_1(1 + Z_0)e^\tau}{[q\nu_1(1 + Z_0)e^\tau + 1 - q(1 + \tau)]} \tag{20}$$

The solution to these equations has been obtained in terms of the $\eta - \phi$ curves (η being equal to $3w/(1 - q)\theta$) for varying values of the input concentration of A and are presented in Figure 4. It is

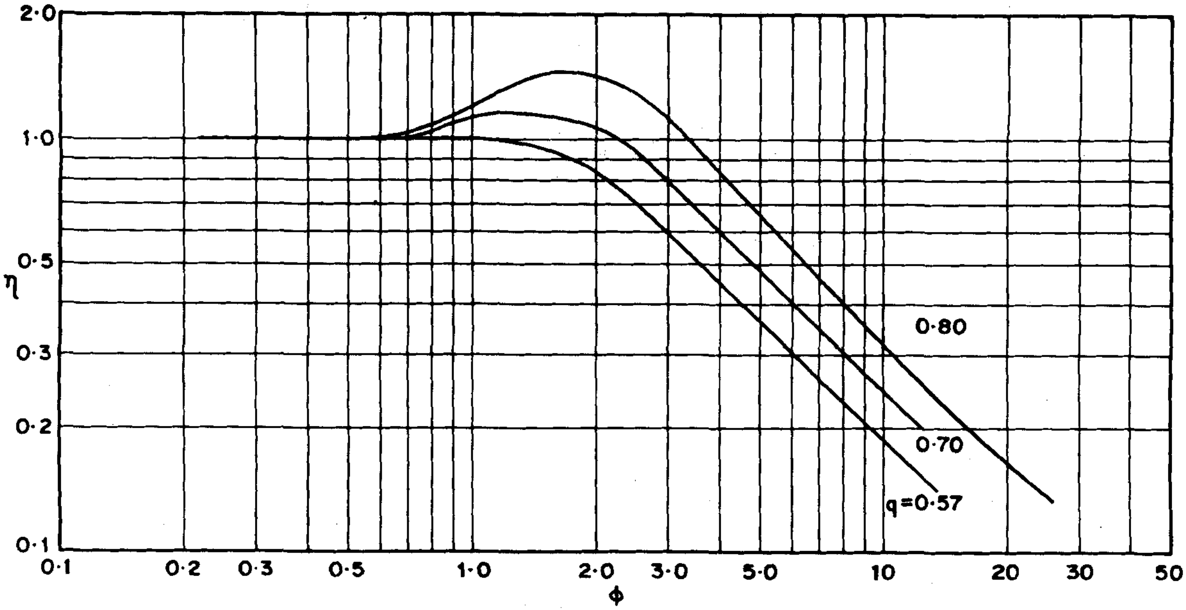


Figure 4. Influence of input feed composition on effectiveness factor—Thiele modulus curve.

clearly seen from the figure that for certain sets of parameter values the effectiveness factor exceeds unity; however, no instance of multiplicity could be generated.

Analysis of Systems with Interphase Resistance

In the analysis of systems presented above it was assumed that the interphase resistance was absent. It is possible to relax this assumption and provide a more complete analysis of the systems with both interphase and intraphase gradients. To illustrate this let us consider a case of a general nth order reaction. The conservation equation for the reactant species A along with the boundary conditions can be written as

$$\nabla^2 a = \phi^2 a^n; \left.\frac{da}{dx}\right|_{x=1} = Bi(1-a); \left.\frac{da}{dx}\right|_{x=0} = 0 \qquad (21)$$

Defining the transformation

$$a_1 = \frac{1}{1 - \frac{1}{Bi}\left.\frac{da}{dx}\right|_{x=1}} = \frac{a}{K_1} \qquad (22)$$

it is possible to rewrite Eq. 21 as

$$a_1 = \phi^2 K_1^{n-1} a_1^n; a_1(1) = 1; \left.\frac{da_1}{dx}\right|_{x=0} = 0 \qquad (23)$$

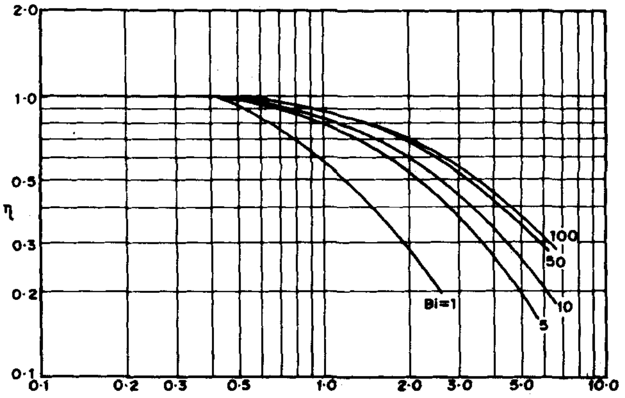


Figure 5. Influence of Biot number of effectiveness factor—Thiele modulus curve.

One can use the transformation in Table 1 defined for the general nth order case, and convert Eq. 23 into an equivalent initial value problem as

$$\frac{dw}{d\tau} = \frac{\theta}{w} - w - 1 \qquad (24)$$

$$\frac{d\theta}{d\tau} = \frac{2\theta}{w} + (n-1)\theta \qquad (25)$$

$$w = \theta = 0, \tau = 0 \qquad (26)$$

The set of Eqs. 24–26 is integrated using a slight modification of the procedure described in Appendix II to calculate the $\eta - \phi$ curve. The effectiveness factor is obtained as $\eta = 3\,K_1^2 w/\theta$.

The results obtained using this method are presented in Figure 5 for case $n = 2$. The simple exercise illustrates the application of the method to systems with interphase resistance. No information on effectiveness factor variations with Biot number for a general nth order exist. While the direct comparison of the effectiveness factors for various values of Biot number with the literature values is not possible, the obtained values are compared with those for a first-order reactions (Kulkarni and Karanth, 1978) and seem to fall in the right range.

Application to Systems with Combined Influence of Flow, Interphase and Intraparticle Resistances

Let us now consider the case of a CSTR containing the catalyst in the presence of interphase and intraparticle resistances. The conservation equations for the system can be formulated as

$$F(a_f - 1) = VK_g a_v(1 - a_s) \qquad (27)$$

$$a_s = \phi^2 f(a_s); \left.\frac{da_s}{dx}\right|_{x=1} = Bi(1 - a_s); \left.\frac{da_s}{dx}\right|_{x=0} = 0 \qquad (28)$$

It is possible to write

$$k_g a_v(1 - a_s) = \eta r \qquad (29)$$

where r represents the rate corresponding to the surface conditions of the particle. The value of η for several different rate forms can be obtained using the method presented in earlier sections. For a typical rate form of the type $f(a_s) = a_s/(1 + K_A' a_s)^2$ Eq. 27 can be written as

$$\frac{\alpha_1}{\eta}(1 - a_s) = \frac{a_s}{(1 + K_A' a_s)^2} \qquad (30)$$

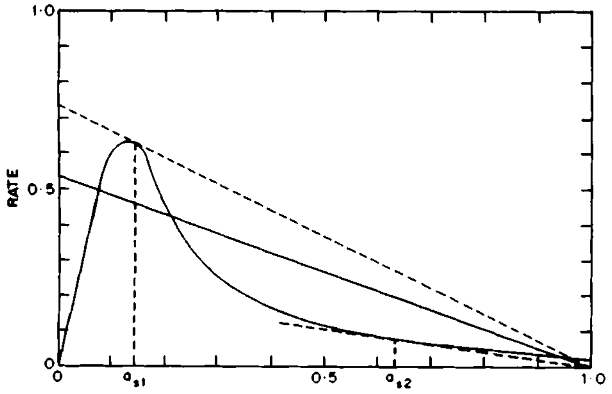


Figure 6. Variation of rate with concentration (Eq. 30).

A simple graphical procedure of plotting the lh's and rh's against the concentration can then be used to locate the roots of Eq. 30. The rh's of Eq. 30 represents the rate function and shows a maximum, while the lh's is a straight line with a slope of $(-\alpha_1/\eta)$. Qualitative plots of these functions are shown in Figure 6. It is seen that the straight line (lh's of Eq. 30) touches the rate curve at two points. Invoking the equality of the slopes for the rate function (rh's) and the straight line (lh's) at these points gives the necessary condition for the existence of multiple roots and can be easily obtained as $K_A' > 8$. The sufficiency condition for the existence of multiplicity is that the slope $(-\alpha_1/\eta)$ should lie between $(\alpha_1/\eta)^+$ and $(\alpha_1/\eta)_-$ where

$$\left(\frac{\alpha_1}{\eta}\right)^+ = \frac{a_{s1}}{(1 + K_A' a_{s1})^2}\frac{1}{1 - a_{s1}} \tag{31}$$

$$\left(\frac{\alpha_1}{\eta}\right)_- = \frac{a_{s2}}{(1 + K_A' a_{s2})^2}\frac{1}{1 - a_{s2}} \tag{32}$$

and a_{s1} and a_{s2} are the two values of a_s where the straight line touches the rate curve, for a given flow condition in the reactor. Equations 31 and 32 suggest that the effectiveness of the particle decides the value of the slope (α_1/η) and therefore the region of multiplicity. It is possible to have a system where the particle problem gives rise to three different values of η. Depending on the initial conditions, the particle effectiveness will approach either the higher (say η_1) or the lower (say η_2) value. Since all particles are subjected to the same environment and initial condition, the same value of η (either η_1 or η_2) exists in all the particles. Corresponding to these two values of η two different regions of (α_1/η) can exist for the reactor problem. It is also possible for the two regions to overlap and merge into a single extended region of multiplicity. It, therefore, seems from the analysis that the presence of interphase and intraphase gradients leads to further extension of the region of multiplicity. From a knowledge of $\eta - \phi - B_i$ variation, it is thus possible to obtain information about reactor behavior.

APPLICATION TO BIDISPERSED CATALYSTS: CASE OF L-H KINETICS

The present section is concerned with problems which typically involve nonlinearity in the source term and coupled boundary conditions. Such a physical situation is encountered in gas-solid catalytic reactions in pellets with bimolal pore structure. In gas-solid noncatalytic reactions this situation arises when particle-pellet (grain) models are used to describe the behavior. Besides, in many biochemical systems involving encapsulated enzymes, such a situation is fairly common.

The problem thus appears to be fairly general and we present below the methodology for solving such problems by considering a specific example: calculation of the effectiveness factors for a catalyst pellet with bimodal pore distribution when a reaction with simple (L-H) kinetics is occurring. While analyses for linear kinetics (Ors and Dogu, 1979) and general nth order nonlinear kinetics (Kulkarni et al., 1981; Jayaraman et al., 1982) in a micropore system are available, no information on L-H type of kinetics (which is more rational for catalytic systems) exists.

The conservation equations in dimensionless form can be written as:

$$\nabla_x^2 C_i = \frac{\phi^2 C_i}{(1 + K_A' C_i)};\ C_i(1) = C_a;\ \left.\frac{dC_i}{dx}\right|_{x=0} = 0 \tag{33}$$

$$\nabla_y^2 C_a = \alpha \left.\frac{dC_i}{dx}\right|_{x=1};\ C_a(1) = 1;\ \left.\frac{dC_a}{dy}\right|_{y=1} = 0 \tag{34}$$

The set of Eqs. 33–34 are nonlinear in the source term and involve the coupled boundary conditions. The conventional method of solution requires trial and error on both eqs. 33 and 34 such that the boundary conditions are satisfied. Generally a large amount of computer time is required to obtain the desired solution.

In the present work we avoid the trial and error completely by converting the boundary value problem into an equivalent initial value problem by using suitable transformations. The equivalent initial value problem is then solved to obtain $dC_i/dx|_{x=1}$ required in Eq. 34 which is subsequently integrated using the Weisz-Hicks (1962) method. While in principle this methodology can be used to eliminate total trial and error, it is beset with certain problems. Thus it is difficult to obtain η–ϕ variations for a given value of K_A' and α and the whole set of numerical data needs to be interpolated to obtain any meaningful information. In the present work we have avoided this by employing an alternative procedure.

Using a slight modification in the transformations corresponding to this rate form in Table 1 (where K_A' is replaced by $K_A' C_a$), Eq. 33 can be converted into an equivalent initial value problem. The transformed equations are similar in form to Eqs. 3–5 with the only difference that K_A' is replaced by $K_A' C_a$. These equations are now integrated to obtain the flux $dC_i/dx|_{x=1}$ for different values of K_A' and ϕ. The representative calculations for $K_A' = 50$, 75 and 100 and $\phi = 5$, 10, 13 and 16 are analyzed further.

It is apparent from these calculations that a definite relationship exists between $dC_i/dx|_{x=1}$ and C_a, and to elucidate this relationship further they are plotted on a log-log scale in Figures 7a,b,c where parallel lines for different values of K_A' and ϕ indicate that the slope of these lines is (almost) independent of the parameters K_A' and ϕ. The intercept, however, depends on the values of K_A' and ϕ. The intercept, is, therefore, plotted for different values of K_A' where again a straight line as shown in Figure 8 results. The intercept of this figure clearly shows a dependence on ϕ, Figure 9. Utilizing the linear relationships shown in Figures 7 to 9, the flux at the pore mouth of a micropore can then be related (by regression analysis) to the corresponding macropore concentrations C_a through the parameters K_A' and ϕ as follows:

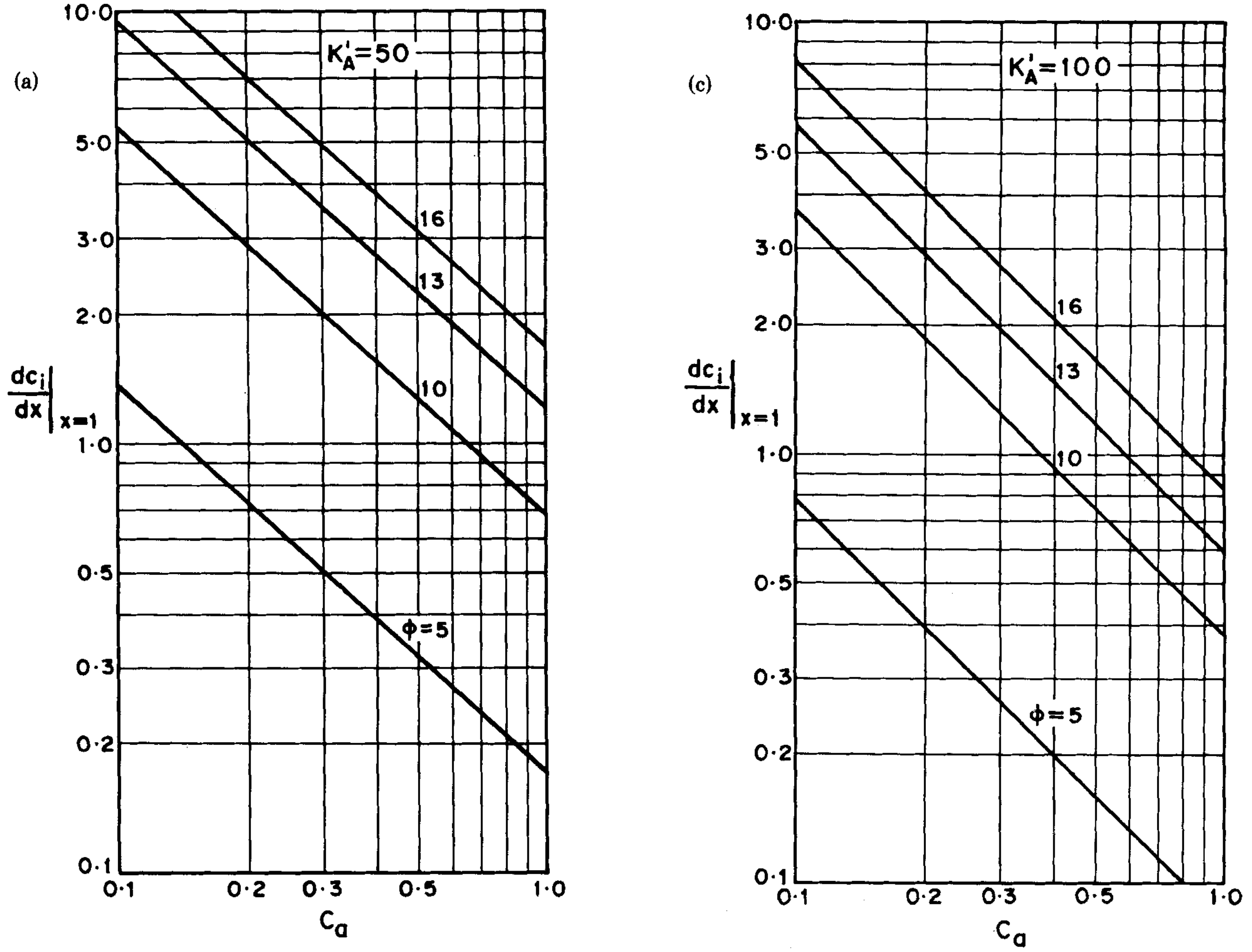
$$\left.\frac{dC_i}{dx}\right|_{x=1} = K_A^{-1}\phi^{1.5}C_a^{-1} \tag{35}$$

It is interesting to note that the negative slope of the curves in Figure 8 is almost always unity. It is apparent, therefore, that the original L-H kinetics now tends to behave as negative first-order kinetics. A falsification of reaction kinetics (or order), therefore, occurs in the system with bimodal pore distribution. Earlier Jayaraman et al. (1982) had observed a similar falsification when a zero-order reaction is carried out in a micro-macropore system. The falsification of the reaction order which is induced by the bipore distribution, therefore, gives rise to certain additional features of the system. Thus in the present case the simple L-H kinetics tends to exhibit multiplicity behavior corresponding to that of negative first-order kinetics.

Equation 35 can now be substituted in Eq. 34 to obtain

$$\nabla_y^2 C_a = \phi_m^2 C_a^{-1} \tag{36}$$

where ϕ_m represents the modified Thiele modulus defined as equal to $(K_A^{-1}\phi^{1.5}\alpha)$. Equation 36 can be converted into two first-order equations using the transformations corresponding to this case in Table 1. The transformed equations are similar to Eqs. 24–26 with $n = 1$.



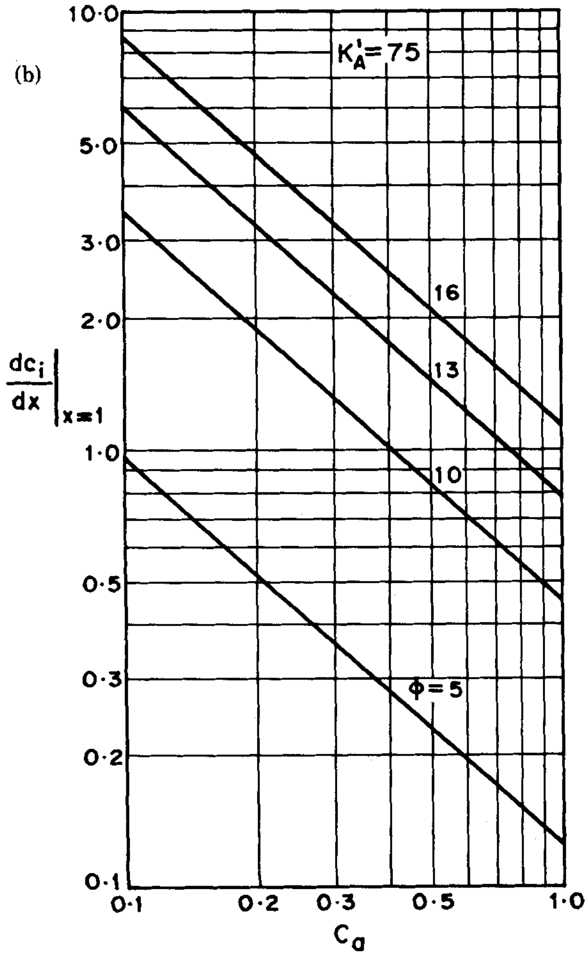


Figure 7. (a) Variation of flux at the surface of micropore with macropore concentration at the surface of micropore at $K_A' = 50$. (b) Variation of flux at the surface of micropore with macropore concentration at the surface of micropore at $K_A' = 75$. (c) Variation of flux at the surface of micropore A with macropore concentration at the surface of micropore at $K_A' = 100$.

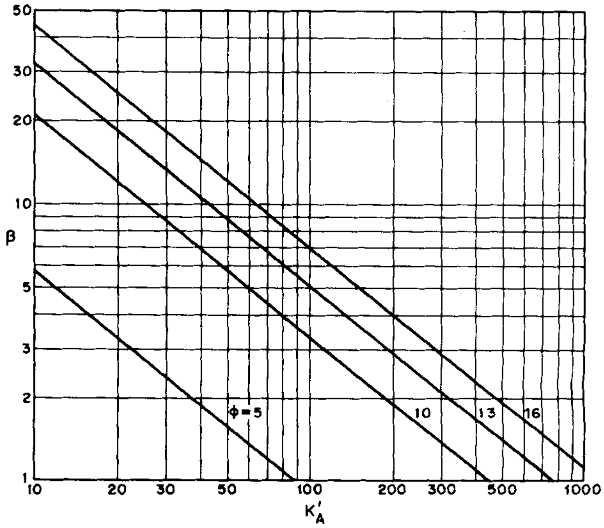


Figure 8. Variation of intercept in Figure 7a,b,c with K_A' at constant value of φ.

These equations have been solved to obtain variations of w and θ and τ with the inset in Figure 10 shows the results as a phase-plane plot. This figure clearly shows the critical point to be a stable focus with a range of θ (and hence ϕ_m) values for which multiplicity is possible. The corresponding $\eta - \phi_m$ curves can also be obtained

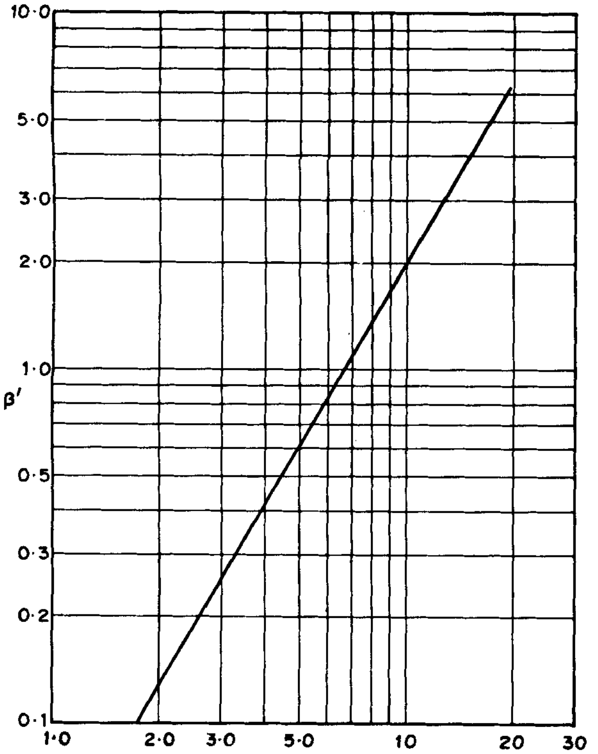


Figure 9. Variation of intercept in Figure 8 with φ.

from this figure using the relation $\eta = 3w/\theta$ and are shown in Figure 10. The striking advantage of Figure 10 is that the whole parameter space for K, ϕ and α is condensed into a single curve leading to a very compact representation of the variation of effectiveness factor with the parameters of the system.

The results in Figure 10 have been obtained by making use of the relationship for $dC_i/dx|_{x=1}$ given by Eq. 35. It would be remembered that this relationship was obtained using a graphical procedure that is inherently liable to error. This is especially important since it is used in the macropore equation for subsequent integration. To show its validity, the macropore Equation (Eq. 34) has been integrated using the Weisz-Hicks (1962) method. The effectiveness factor is now calculated as

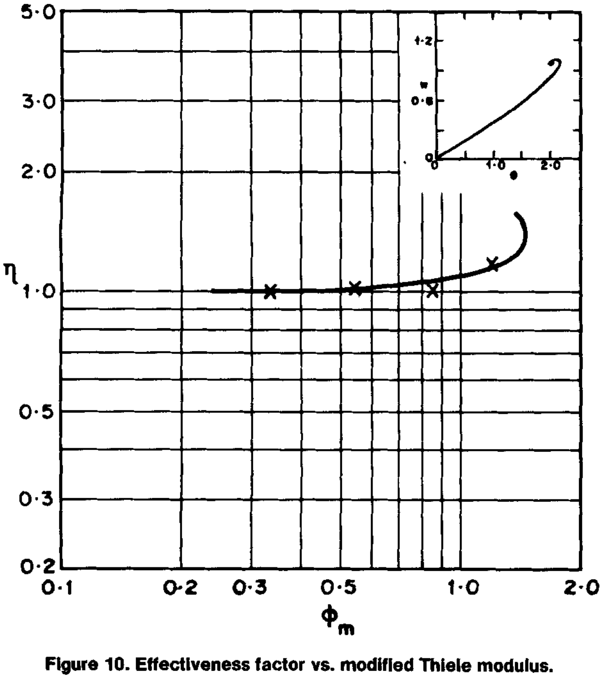


Figure 10. Effectiveness factor vs. modified Thiele modulus.

$$\eta = \frac{9(1 + K_A')}{\phi^2\alpha} \times \frac{dC_a}{dy}\bigg|_{y=1}$$

The values of η thus obtained are also marked in Figure 10 as crosses. In view of the close agreement between the η values obtained using the rigorous numerical method and Eq. 35 it is apparent that the simple method suggested can be conveniently used.

APPENDIX I: GENERAL METHOD FOR OBTAINING TRANSFORMATIONS *W*, *θ* AND *τ* FOR DIFFERENT RATE FORMS

The transformations w, θ and τ that convert the original two point boundary value problem into an equivalent initial value problem have been listed in Table 1 for several rate forms. These transformations have been arrived at by a combination of the feel for the rate form and by following certain logic. No general method to construct these transformations from fundamental principles can, therefore, be given. However, to assist in formulating these transformations for rate forms other than those reported here, some general guidelines can be given. Let us consider a general equation

$$\nabla_x^2 Z = \phi^2 f(1 + Z);\ Z(1) = 0;\ \frac{dZ}{dx}\bigg|(0) = 0 \qquad [1]$$

$$Z(0) = Z_0$$

in the transformed variable Z (usually defined as $C/C_s = 1 + Z$). To take care of the second derivative in Eq. 1, one of the transformation variables, say w, should contain a first-order derivative term. The quantity w is, therefore, defined as

$$w = \frac{x\dfrac{dZ}{dx}}{f_1(1 + Z)} \qquad [2]$$

where $f_1(1 + Z)$ is some suitably chosen function of $(1 + Z)$. With this definition of $w, \partial w/\partial\tau$ is obtained as

$$\frac{\partial w}{\partial \tau} = \frac{\partial w}{\partial x}\frac{\partial x}{\partial Z}\frac{\partial Z}{\partial \tau} \qquad [3]$$

where Z is assumed to be some function of τ to be defined. The first term $\partial w/\partial x$ in Eq. 3 can be obtained by differentiating the assumed functional relation for w (given by Eq. 2]. The functional form of Eq. 3 would, therefore, be

$$f_2\frac{d^2Z}{dx^2}\frac{dx}{dZ}\frac{dZ}{d\tau} + f_3\frac{dZ}{d\tau} + f_4\frac{dZ}{dx}\frac{dZ}{d\tau} \qquad [4]$$

where f_2, f_3 and f_4 are suitable functions of $(1 + Z)$ and can be obtained, once the functional form of f_1 in the definition of w is decided. Now the definition of θ is chosen such that the first term in Eq. 4 gives rise to a function of the form $(\theta/w - \text{const.})$. The definition of τ is chosen such that the second term in Eq. 4 is rendered constant. Once the definitions of w, θ and τ are fixed, it is usually possible to express the third term in terms of w and θ.

The θ transformation can also be differentiated to obtain $\partial\theta/\partial\tau = \partial\theta/\partial x\ \partial x/\partial Z\ \partial Z/\partial\tau$. Our experience suggests that minor modifications in the functional form for f_1 [f_1 is involved in the definition of w and this function depends on the type of rate form to be analyzed] usually lead to the desirable forms for the transformations.

APPENDIX II: GENERAL PROCEDURE FOR OBTAINING EFFECTIVENESS FACTOR

1. Assume values for the parameters (K_A^1, K_B^1, ν_1 and q).
2. Assume value for Z_0.

3. Calculate τ_s.
4. Integrate differential equal for case understudy, e.g., Eqs. 3 and 4 for case I.
5. Calculate ϕ^2 from the definition of θ.
6. Calculate η from appropriate definition involving w and θ.
7. Repeat for different values of Z_0 (step 2).
8. Repeat for different values of parameters in step 1.

NOTATION

a = dimensionless concentration of species A
a_1 = transformed concentration variable defined by Eq. 22
a_s = dimensionless concentration of species A at the catalyst surface
a_v = gas-solid interficial area
b = dimensionless concentration of species B
B_i = Biot number defined as k_gR/D_{eA}
C_a = dimensionless concentration in the macropore
C_A = concentration of species A
C_{AF} = concentration of species A in the inlet stream
C_{As} = concentration of species A at the surface of catalyst
C_B = concentration of species B
C_{Bs} = concentration of species B at the surface of catalyst
C_i = dimensionless concentration in the micropore
C_T = total concentration in the gas-phase
D_a = diffusivity in the macropore
D_{eA} = diffusivity of species A
D_{eB} = diffusivity of species B
F = flow rate
$f(a)$ = rate function defined by Eq. 28
k = rate constant
K_1 = parameter defined in Eq. 22
K_A = adsorption equilibrium constant of species A
K_B = adsorption equilibrium constant of species B
K_A' = dimensionless adsorption equilibrium constant for species A
a_f = dimensionless inlet concentration
K_B' = dimensionless adsorption equilibrium constant for species B
k_g = mass transfer coefficient
n = order of reaction
p = parameter defined by Eq. 13
q = parameter defined by Eq. 13
q_1 = parameter defined by Eq. 13
r = general term for rate
R = radius of the particle
$\bar{r}$ = dimensionless rate
r_i = radius of the micropore
V = volume of the reactor
w = transformation as defined in Table 1
x = general notation used to define dimensionless distance parameter
y = dimensionless distance specifically used in the macropore
Z = transformed concentration
Z_0 = value of Z at the centre of the pellet

Greek Letters

α = parameter defined as $3(1-\epsilon)D_i/D_a/R^2/r_i^2$
α_1 = parameter defined as k_ga_v/k
β = intercept in Figure 8
β' = intercept in Figure 9
η = effectiveness factor
ϵ = porosity of the pellet
τ = parameter defined in Table 1
ν = stoichiometric coefficient
ν_1 = parameter defined as $D_{eA}/D_{eB}\nu$
ϕ = general parameter used to define Thiele modulus
ϕ_m = modified Thiele modulus defined as $K_A'\phi^{1.5}\,\alpha$
∇^2 = Laplacian operator
θ = parameter defined in Table 1

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Mass Transfer with Chemical Reaction in Liquid Foam Reactors

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Mass transfer studies were conducted in a stable liquid foam reactor under various operating conditions to evaluate gas holdup, effective interfacial area, liquid-phase mass transfer coefficient and a modified interfacial mass transfer coefficient to include the surface-active agents employed. Gas holdup and effective interfacial area were evaluated experimentally. The interfacial mass transfer coefficient was evaluated semitheoretically, by considering the interfacial region as a separate phase and using the experimental data developed for mass transfer accompanied by a fast first-order chemical reaction. The liquid-phase mass transfer coefficient was also evaluated semitheoretically, using Danckwert's theory for the liquid phase and the experimental data on mass transfer accompanied by a slow pseudofirst-order chemical reaction.

An experimental unit was set up to provide a stable flowing foam column, simulating the foam reactor. Mass transfer rates were studied for superfacial gas velocities in the range from 1.5×10^{-2} m/s to 5×10^{-2} m/s, giving gas residence times in the range from 20 to 55 seconds. A cationic and nonionic surface-active agent and three different wire mesh sizes, giving bubble size distributions in the range from 2.2 to 5.4 mm Sauter mean diameters, were employed.

It is observed that gas holdup is insensitive to the type of surface-active agent; it is however, dependent on wire mesh size and gas velocity. The bubble diameter and, hence, the interfacial area are found to be insensitive to gas velocity in the range studied; they are, however, strong functions of wire mesh size. The liquid-phase mass transfer coefficient increases with increase in gas velocity. The surface-active agent introduces additional resistance to mass transfer in both reaction cases, this being the controlling one in the case of the fast reaction. A comparison with conventional packed bed contactors indicates the mass transfer rates to be about 8 times lower for the foam reactor, for the fast reaction case; for slow reactions, the foam reactor has mass transfer rates approximately 2–4 times higher than those for conventional packed bed contactors.

SCOPE

The foam bed reactor is rather new. It offers a very high gas-liquid interfacial area per unit volume of the bed, a large contact time, a fairly low-pressure drop—all these characteristics are very desirable for treatment of large quantities of lean gases, as in the case of contaminant separation from toxic gas streams.

Gas holdup, interfacial area, and mass transfer coefficients are the main parameters determining the mass transfer rates in gas-liquid absorbers and reactors. In foam reactors, usually surface-active materials are present. The presence of surface-active materials, however, could reduce mass transfer rates significantly, by introducing an interfacial resistance and by altering the hydrodynamics.

The literature available on the application of foam as a medium for gas absorption and reactions is scarce. In the studies reported, no attempts were made to evaluate the mass transfer parameters encountered under various operating conditions in foam bed reactors. The objective of the present work is to evaluate gas holdup, interfacial area, liquid-phase mass transfer coefficient and the interfacial resistance due to surfactant in the form of a modified interfacial mass transfer coefficient, in foam reactors under various operating conditions.

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