STUDIES OF REACTION - DIFFUSION IN POROUS CATALYSTS

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BY

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Certified that the work incorporated in the thesis "Studies of Reaction-Diffusion in Porous Catalysts" submitted by Mrs. Asha S. Datar was carried out by the candidate under my supervision. Such material as has been obtained from other sources has been duly acknowledged in the thesis.

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GENERAL INTRODUCTION

GENERAL INTRODUCTION

Many industrial reactions are catalytic in nature and often the catalyst used is a solid. The catalysts are frequently formed by compaction of powder particles into pellets. If the particles of the powder are porous, compaction will create a bimodal pore distribution with micropores lying inside the porous particles and macropores between single or agglomerated particles. If however the powder particles are nonporous the pellet will have only macropores. In both the cases diffusion as well as chemical reaction are involved, and the relative importance of the rates of these would determine the design as well as the performance of the reactor.

Investigation of the problem of reaction and diffusion in chemically reacting systems started in the early 1930's. In 1939 Thiele analysed the interaction between reaction and diffusion in a porous catalyst by studying a simple first order reaction in regular geometries like slab, cylinder and sphere, and a parameter 'Thiele modulus' representing the relative rates of reaction and diffusion was introduced. The results were presented in the form of effectiveness factor versus Thiele modulus plots. The effectiveness factor is defined as the ratio of the actual reaction rate to its value when there is no diffusional limitation.

Essentially reaction-diffusion problems lead to a boundary value situation. The nonlinear nature of these equations may cause considerable complexities in obtaining solutions to these equations. The nonlinearity can arise due to several reasons: (i) nonlinear reaction rate term, (ii) derivative term, e.g. when volume change occurs, (iii) dependence of transport coefficients on variables such as temperature or concentration (which in this case are dependent on distance) or (iv) the boundary conditions. In such cases it is difficult to solve it analytically and numerical analysis has to be undertaken depending upon the nature of the problem. Considerable trial and error is required to solve these problems, specially when bimodal pore distribution is taken into consideration. It gives rise to two second order differential equations which are coupled at the boundary conditions. It is this coupling which creates problems that cannot be handled easily.

Several methods have been developed for the solution of nonlinear two point boundary value problems. In shooting methods (Coste et al, 1961) the equations were integrated by the marching technique. The guesses required for the initial values were improved during computation by appropriate interpolation formulae. A nonlinear equation was converted to a linear equation by linearisation of the nonlinear terms, and then difference schemes or marching techniques were used (Carberry and Wedel, 1963; Lee, 1968, 1966). Integration or marching techniques cause difficulty in studying the stability of the system. Quasi-linearisation techniques are effective even when a system has nonlinearity problems associated with the finite difference method,and stability difficulties are also taken care of.

Weisz and Hicks' (1962) studied a first order irreversible nonisothermal reaction in a catalyst pellet. A transformation was found which by an appropriate choice of value of the dependent variable at the outer boundary and of two other parameters enables one to find the value of the third parameter. The resulting equations were solved as initial value problems, thus avoiding trial and error. In this case it may not be possible to obtain solutions for fixed values of parameters.

Stewart and Villadsen (1969) used collocation procedure for calculation of effectiveness factors for a single reaction in particles of various shapes. Stewart (1978) derived invariant solutions for diffusion-reaction problems in permeable catalysts.

A method has been developed (Wedel and Luss, 1980) for computing the approximate value of the effectiveness factor for any rate expression for which a unique steady state exists.

It is seen that even though accurate numerical methods (Villadsen and Michelsen, 1978) have been developed for computing effectiveness factors, very few attempts have been made to obtain fast and sufficiently accurate approximations of the effectiveness factor. Considerable attention has been devoted to reduce the numerical complexities (Kubicek and Hlavacek, 1970, 1971 a, b, c; Hanna, 1980; Jayaraman et al, 1983; Wendt et al, 1978). Analytical expressions for effectiveness factors have been obtained by using the finite integral transform technique by Do and Bailey (1982). They have obtained asymptotic solutions for large and small values of Thiele modulus and Biot numbers by using perturbation techniques. A transform iterative technique has been used (Jerry, 1983) to obtain solutions to nonlinear concentration boundary value problems.

Effectiveness factors for a large variety of reaction rate forms including the commonly encountered Langmuir-Hinshelwood (L-H) type of kinetic expressions have been reported in the literature for different pellet configurations. A comprehensive account of the results can be found in authorative texts: Aris, 1975; Satterfield, 1970; Doraiswamy and Sharma, 1983 . Sundaram (1982) obtained expression for effectiveness factor for L-H type of kinetics. Analytical expressions for a single reaction with arbitrary kinetics and geometry have been developed by Gottifredi et al (1980 a, b).

The thesis is divided into three sections. Section I develops new sets of transformations that convert an original two point boundary value problem into an equivalent initial value problem. Chapter I introduces a method for obtaining the transformations for a specific rate form. In Chapter 2 use of the transformations has been illustrated for certain known cases of reaction-diffusion problems in monodispersed catalyst systems, to confirm the validity of the method, which has then been applied to some new cases. In addition to this, a case where external mass transfer resistance exists has been taken into account. Finally it has been extended to a case of CSTR where, in addition to flow resistance, interphase and intraphase resistances have also been taken care of. Chapter 3 analyses the more complex case of a bidispersed catalyst in which a simple L-H type of reaction is considered and it is shown that trial and error can be completely avoided.

Section II of the thesis has been devoted to the calculation of effectiveness factors for catalysts possessing bipore distribution. The analysis includes practical complications such as diffusivity variations within the pellet, nonisothermicity generated due to the reaction, and catalyst deactivation. The first chapter of this section, viz. Chapter 4 of the thesis, provides an introduction to bidispersed catalysts. Chapter 5 deals with the case of diffusivity variations. Several reactions of industrial importance are known to be carried out over catalysts (such as the synthetic zeolites) where variations in the transport properties cannot be ignored. The analysis assumes different forms of the variation of these transport properties, such as the diffusivities, and in general reports the influence of such variations on the effectiveness of the catalyst.

Chapter 6 deals with the case of bipore catalysts with nonisothermicity due to the generation of heat by the reaction. The results, again evaluated in terms of the effectiveness of the catalyst, indicate different regions in parameter space where nonunique situations can prevail.

Chapter 7 treats the case of catalyst deactivation. Both series and parallel types of catalyst deactivation are considered and the results are expressed in terms of effectiveness factors.

In all cases where due to the bipore nature of the catalyst, we end up with a set of coupled differential equations for the micro and the macroparticle regions, the use of conventional numerical methods becomes cumbersome requiring considerable trial and error. These problems can be solved by using the methods of weighted residuals.

Sections I and II in the thesis have been devoted to the solution of problems of practical interest that arise in bidispersed pellets. The reaction rate forms considered in these sections vary from simple first order reaction to nonlinear rate forms of the L-H type and in some of these situations multiplicity of events has been noted. Section III of the thesis deals with a situation where the reaction rate form is nonlinear and exhibits multiplicity of states under certain sets of conditions. The essential intention in this section has been to find whether some of these states can coexist and the eventuality of what happens when an infinitesimaly small disturbance persists in such a situation.

Chapter 8 (the only chapter of Section III) introduces the problem highlighting its essential role in explaining possible pattern formations, dissipative structures, etc. The necessary conditions for the occurrence of coexisting solutions in reaction-diffusion systems have been derived subsequently where a specific example of an autocatalytic reaction is discussed. Further the analysis of the practically more relevant case of bimolecular L-H kinetics and the conditions of coexistence of the two stable solutions have been considered. The case when the diffusion involved is nonisotropic is also analysed in this chapter.

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SECTION I

INITIAL VALUE APPROACH TO A CLASS OF REACTION-DIFFUSION PROBLEMS

CHAPTER-1

INTRODUCTION

CHAPTER 1

INTRODUCTION

Chemically reacting systems involving heterogeneous catalysis have been investigated both from the theoretical and experimental points of view (Satterfield, 1970; Aris, 1975; Carberry, 1976; Doraiswamy and Sharma, 1983). The class of problems referred to as reaction-diffusion problems have been solved for a number of situations and their results have useful implications in the design of reactors. The typical formulation of any of these problems leads to a differential equation of the type

$$\nabla_x^2 a = \bar{r} \tag{1.1}$$

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 is linearly dependent upon the concentration of species this equation can be solved to obtain analytical results. On the other hand, in most of the cases one obtains nonlinear differential equations. The nonlinearities in these equations can arise as described in the previous chapter (General Introduction). It is possible in a given situation to have some or all of these nonlinearities present simultaneously. No analytical solution can be found in such cases and recourse to numerical analysis becomes necessary.

Over the past few years considerable attention has been focussed on developing numerical methods to obtain solutions to these problems (Villadsen and Stewart, 1967; Kubicek and Hlavacek, 1970, 1971 a,b,c; Hanna, 1980; Villadsen and Michelsen, 1978; Finlayson, 1974; Suzuki, 1979; Jayaraman <u>et al</u>, 1983; Ibanez, 1979). General numerical methods that avoid trial and error to obtain solutions to similar complex cases have been proposed by Wendt <u>et al</u> (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 differential equation. Depending upon the coupling involved amongst the phenomenological equations describing the system, suitable methods that avoid trial and error have been devised. Thus when the coupling occurs in the rate (reaction) terms, the general method proposed by Wendt <u>et al</u> (1979), Hahn and Wendt (1982) and Hahn and Shadman (1981) can be employed, despite the stiffness of the system. The case of bidispersed catalyst also involves multiple species and in the simplest case involves the solution of two second order differential equations. The equations, besides being nonlinear, are coupled at the boundary conditions. It is this coupling of two concentrations at the boundaries that generates problems that cannot be handled easily and also differentiates the present case from the one involving only multiple species.

Approximate methods leading to simple algebraic expressions for the effectiveness factors have also been proposed in the literature (Churchill, 1977; Wedel and Luss, 1980; Sundaram, 1982; Gottifredi et al, 1980 a,b; Gonzo and Gottifredi, 1983). 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 non-catalytic systems, is fairly involved.

In this section we present a set of transformations for different forms of the reaction rate that convert 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 problem. 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 monoporous systems (Chapter 2) such as the simple Langmuir-Hinshelwood kinetics and bimolecular Langmuir-Hinshelwood kinetics and the results are compared with available solutions. A few unresolved cases such as the bimolecular Langmuir-Hinshelwood rate form of the type $r = kC_AC_B / (1+K_AC_A+K_BC_B)$ and the autocatalytic rate form are then considered and the results obtained are discussed.

The method is subsequently extended to include the cases where interphase resistance is present and then to the case where all the three- flow, interphase and intraphase-resistances - are present. Finally the applicability of the method to more complex cases is considered in Chapter 3, for a representative Langmuir-Hinshelwood kinetic form. The analysis for this case provides some new and significant results.

1.1 Method for Obtaining the Transformations w, θ and τ for Langmuir-Hinshelwood (L-H) Rate Form

The transformations w, θ and τ that convert the original two point boundary value problem into an equivalent initial value problem have been arrived at by a combination of intuition and 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, transformations for the case of simple Langmuir-Hinshelwood rate form are developed.

The conservation equations for L-H rate equation in dimensionless form are

$$\nabla_x^2 a = \frac{\phi^2 a}{(1 + K_A' a)} \qquad (1.2)$$

$$a = 1, \quad x = 1, \qquad da/dx = 0, \quad x = 0$$

where $a = \dfrac{C_A}{C_{AS}}$, $x = \dfrac{X}{r_i}$, $K_A' = K_A C_{AS}$

Substituting $a = 1 + Z$, the above equations are converted into

$$\nabla_x^2 Z = \frac{\phi^2 (1 + Z)}{(1 + K_A' (1+Z))} \qquad (1.3)$$

$$Z = 0, \quad x = 1; \quad dZ/dx = 0, \quad x = 0; \quad Z = Z_o, \ x = 0$$

To take care of the second derivative in equation 1.3 one of the transformation variables, say w, should contain a first order derivative term. The quantity w is therefore defined as

$$w = \frac{x \, (dZ/dx)}{1 + K_A' (1 + Z)} \qquad (1.4)$$

With this definition, w, (dw/dτ) is obtained as

$$\frac{dw}{d\tau} = \frac{\partial w}{\partial x}\frac{\partial x}{\partial Z}\frac{\partial Z}{\partial \tau} \qquad (1.5)$$

where Z is assumed to be some function of τ to be defined. The first term $\partial w/\partial x$ in equation 1.5 can be obtained by differentiating the assumed functional relation for w (given by 1.4). The functional form of equation 1.5 would therefore be

$$\frac{x}{1+K_A'(1+Z)}\frac{d^2Z}{dx^2}\frac{dx}{dZ}\frac{dZ}{d\tau} + \frac{1}{1+K_A'(1+Z)}\frac{dZ}{d\tau}$$

$$- x\frac{dZ}{dx}\frac{K'}{[1+K_A'(1+Z)]^2}\frac{dZ}{d\tau} \qquad (1.6)$$

Now

$$\frac{d^2Z}{dx^2} = \frac{\phi^2(1+Z)}{1+K_A'(1+Z)} - \frac{2w}{x^2}(1+K_A'(1+Z))$$

and

$$\frac{dx}{dZ} = \frac{x}{w(1+K_A'(1+Z))}$$

Equation 1.6 can thus be written as

$$\frac{x^2\phi^2(1+Z)}{w[1+K_A'(1+Z)]^3}\frac{dZ}{d\tau} - 2\frac{dZ}{d\tau} + \frac{1}{1+K_A'(1+Z)}\frac{dZ}{d\tau} - K'w\frac{dZ}{d\tau}$$

$$(1.7)$$

The definition of θ is chosen such that the first term in equation 1.6 (i.e. first two terms in equation 1.7) gives rise to a function of the form (θ/w - constant), and definition of τ is chosen such that the third term in equation 1.7 is rendered constant. Hence θ and τ will be

$$\theta = \frac{x^2 \phi^2 (1 + Z)}{\left[1 + K_A' \, (1 + Z)\right]^2} \qquad (1.8)$$

$$\tau = \ln \frac{1 + K_A' \, (1 + Z)}{1 + K_A' \, (1 + Z_o)} \qquad (1.9)$$

Once the definitions of w, θ and τ are fixed, θ can be differentiated to obtain

$$\frac{d\theta}{d\tau} = \frac{\partial \theta}{\partial x} \; \frac{\partial x}{\partial Z} \; \frac{\partial Z}{\partial \tau} \qquad (1.10)$$

Using these transformations w, θ, and the original equation 1.2 is converted into two first order differential equations as

$$\frac{dw}{d\tau} = \frac{1}{K_A} \left[\frac{\theta}{w} - 1 - K_A' \, w\right] \qquad (1.11)$$

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

(1.12)

CHAPTER-2

APPLICATION TO MONOPOROUS SYSTEMS

along with the boundary conditions

$$w = \theta = 0 \quad \text{at} \quad \tau = 0 \qquad (1.13)$$

Thus it is seen that the transformations convert the original two point boundary value problem into an equivalent initial value problem.

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CHAPTER 2

APPLICATION TO MONOPOROUS SYSTEMS

In the present chapter we shall demonstrate the use of the transformations generally discussed in Chapter 1 - for the case of a simple monodispersed pellet both in the absence and presence of interphase transport resistance.

2.1 The Particle Problem with no Interphase Gradient

The transformations for four different types of rate forms commonly used to describe the kinetics of reacting systems are developed in this section. The typical rate forms analysed are:

1. The simple L-H rate law

$$r = kC_A/(1 + K_AC_A)$$

2. L-H rate form of arbitrary order

$$r = kC_A/(1 + K_AC_A)^n$$

3. L-H rate form of the type

$$r = kC_AC_B/(1 + K_AC_A + K_BC_B)$$

4. The autocatalytic rate form

$$r = kC_AC_B$$

2.1.1 The simple Langmuir-Hinshelwood kinetics

$$r = kC_A/(1 + K_AC_A)$$

The conservation equations for species A for this case along with the boundary conditions can be written as

$$\frac{D_{eA}}{X^2} \frac{d}{dX} X^2 \frac{dC_A}{dX} = \frac{kC_A}{(1+K_A C_A)} \qquad (2.1)$$

$$C_A = C_{AS} , \quad X = 0, \quad \frac{dC_A}{dX} = 0 , \quad X = r_i \qquad (2.2)$$

The equations in dimensionless form become

$$\nabla_x^2 a = \frac{\phi^2 a}{(1 + K_A' a)} \qquad (2.3)$$

$$a = 1, \quad x = 1, \quad \frac{da}{dx} = 0, \quad x = 0 \qquad (2.4)$$

where $\phi = r_i \sqrt{k/D_{eA}}$ and $K_A' = K_A C_{AS}$

This problem has already been solved by Krasuk and Smith (1965) who have presented results in terms of the usual effectiveness factor vs. Thiele modulus plots.

Substituting

$$a = 1 + Z \qquad (2.5)$$

$$\nabla_x^2 Z = \frac{\phi^2 (1 + Z)}{(1 + K_A' (1 + Z))} \qquad (2.6)$$

$$Z = 0, \quad x = 1; \quad dZ/dx = 0, \quad x = 0; \quad Z = Z_o, \ x = 0 \qquad (2.7)$$

By using the following transformations,

$$w = \frac{x \frac{dZ}{dx}}{(1 + K_A'(1 + Z))}$$

$$\theta = \frac{\phi^2 x^2 (1 + Z)}{[1 + K_A' (1 + Z)]^2} \tag{2.8}$$

$$\tau = \ln \frac{1 + K_A' (1 + Z)}{1 + K_A' (1 + Z_o)}$$

the set of equations 2.6 - 2.7 is converted into

$$\frac{dw}{d\tau} = \frac{1}{K_A'} \left[\frac{\theta}{w} - 1 - K_A' w \right] \tag{2.9}$$

$$\frac{d\theta}{d\tau} = \frac{1}{K_A'} \left[\frac{2\theta}{w} + \frac{\theta\, e^{\tau} [1 + K_A' (1 + Z_o)] K_A'}{\left\{ e^{\tau} [1 + K_A' (1 + Z_o)] - 1 \right\}} - 2\theta K_A' \right] \tag{2.10}$$

where $w = \theta = 0$ at $\tau = 0$ (2.11)

The set of equations 2.9 - 2.11 however has a singularity at $\tau = 0$. The value of θ/w as $\tau \to 0$, by L'Hospital's rule becomes 3 for the case of sphere and 1 for the case of 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 rhs of these equations; however this presents no difficulty in the numerical integration. The results are generated in terms of effectiveness factor plots. The procedure for obtaining the effectiveness factor for this case is as follows:

1. Fix a value of the adsorption constant K_A' .
2. Assume a value of Z_o, i.e. the concentration at the centre of the pellet.
3. For the assumed value of Z_o in (2) obtain $\tau = \tau_s$, the value of τ at the surface condition, which is simply equal to $\ln\left[(1+K_A')/(1+K_A'(1+Z_o))\right]$ for this case.
4. Integrate the set of equations 2.9 - 2.11 from $\tau = 0$ to $\tau = \tau_s$ to obtain the values of θ and w at the surface.
5. Knowing the value of θ at the surface, obtain ϕ from the definition of θ as $\phi^2 = \theta_s\,(1+K_A')^2$.
6. Obtain the effectiveness factor for this value of ϕ and the fixed value of K_A' in (1) $\eta = 3w/\theta$.
7. Change the value of Z_o assumed in (2) to obtain $\eta - \phi$ curve for fixed value of K_A'.
8. Change the value of K_A' and repeat the procedure.

The results generated for four different values of K_A' are shown in Figure 2.1 as $\eta - \phi$ curves. The results of Krasuk and Smith (1965) are also displayed.

2.1.2 The Langmuir-Hinshelwood rate form of arbitrary order

$$r = \frac{kC_A}{(1+K_AC_A)^n}$$

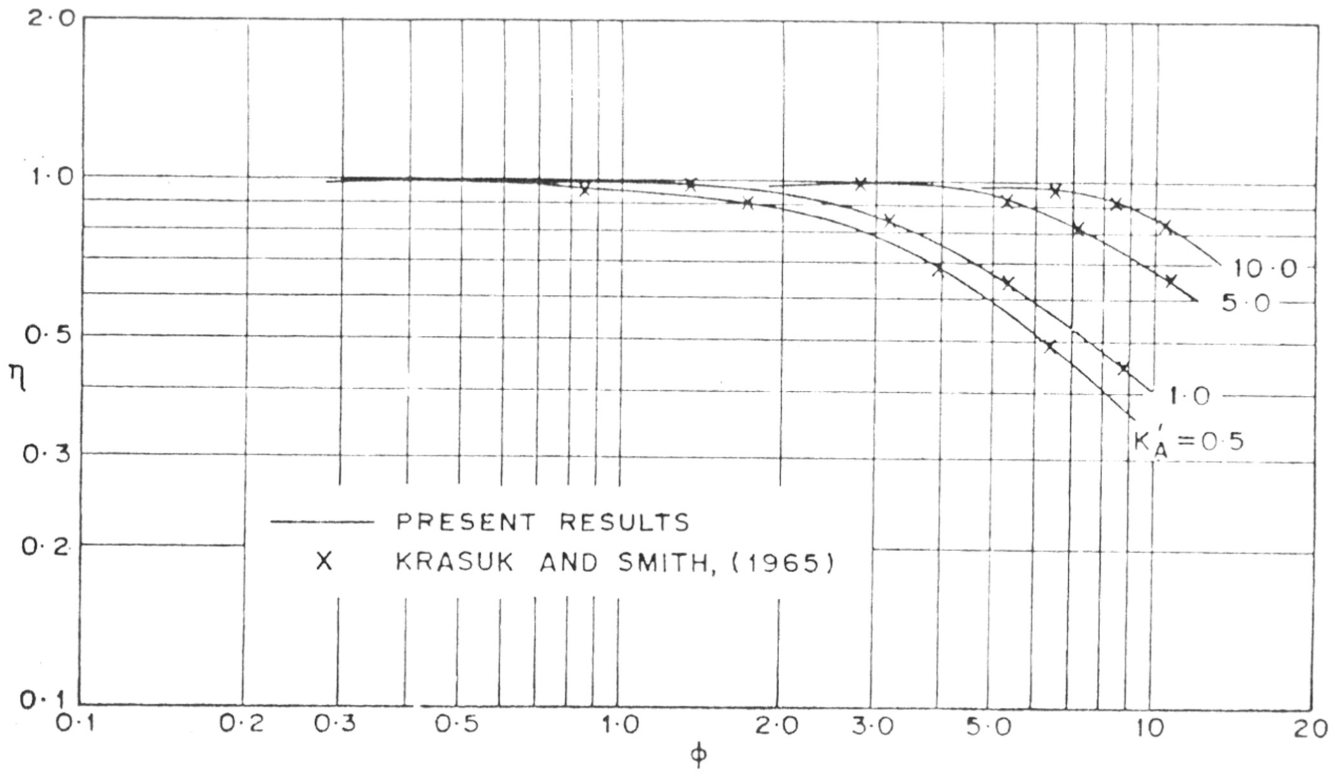


FIG. 2·1: INFLUENCE OF ADSORPTION CONSTANT ON EFFECTIVENESS FACTOR—THIELE MODULUS CURVE

Certain catalytic reactions, e.g. carbon monoxide over platinum and other noble metals in excess of oxygen, display a self-inhibited rate form represented by $r = kC_A/(1+K_AC_A)^2$ (Cavendish and Oh, 1979; Pereira and Varma, 1978). Several hydrocarbons such as ethylene and propylene, when oxidised over noble metals, also follow similar rate laws (Carberry, 1976). Extensive studies have been made of self-inhibited rate or bimolecular L-H rate form, particularly with regard to effectiveness factors (Pereira and Varma, 1978; Becker and Wei, 1976; El Nashaie and Mahfouz, 1978). Becker and Wei (1976) first reported the existence of three solutions for the catalyst pellet. Later Pereira and Varma (1978) showed that up to five distinct steady state solutions exist for the sphere under both the isothermal and nonisothermal conditions while only up to three solutions are obtained for the slab. The phenomenon of five steady states is shown to depend solely on the value of the adsorption rate constant. It is not our objective to reproduce all these results. However, the simplified method proposed here will be illustrated for a few cases.

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

$$\frac{D_{eA}}{X^2} \frac{d}{dX} \left[X^2 \frac{dC_A}{dX} \right] = \frac{kC_A}{(1 + K_AC_A)^n} \qquad (2.12)$$

$$C_A = C_{AS} \, , \quad X = r_i \quad , \quad dC_A/d_X = 0 \, , \quad X = 0 \qquad (2.13)$$

The dimensionless form of these equations can be written as

$$\nabla_x^2 a = \frac{\phi^2 a}{(1 + K_A' a)^n} \tag{2.14}$$

$$a = 1, \quad x = 1, \quad da/dx = 0, \quad x = 0 \tag{2.15}$$

Using

$$a = 1 + Z \tag{2.16}$$

equations 2.14 - 2.15 can be written in the following form

$$\nabla_x^2 Z = \frac{\phi\,(1 + Z)}{\left[1 + K_A'\,(1 + Z)\right]^n} \tag{2.17}$$

$$Z = 0, \ x = 1; \quad dZ/dx = 0, \ x = 0; \quad Z = Z_o, \ x = 0 \tag{2.18}$$

After incorporating the transformations

$$w = x\frac{dZ}{dx} \Big/ \left[1 + K_A'\,(1+Z)\right]^{2-n}$$

$$\theta = \frac{\phi^2 x^2\,(1+Z)}{\left[1 + K_A'(1+Z)\right]^2} \tag{2.19}$$

$$\tau = \left[\frac{1 + K_A'\,(1 + Z)}{1 + K_A'\,(1 + Z_o)}\right]^{n-1} - 1$$

the following equations are obtained:

$$\frac{dw}{d\tau} = \frac{\left[1+K_A'\ (1+Z_o)\right]^{n-1}}{(n-1)K_A'} \left[\frac{\theta}{w} - 1 - \frac{(2-n)K_A'\ w}{\left[1+K_A'(1+Z_o)\right]^{n-1}(1+\tau)}\right] \tag{2.20}$$

$$\frac{d\theta}{d\tau} = \frac{\left[1+K'\ (1+Z_o)\right]^{n-1}}{(n-1)\ K_A'} \left[\frac{2\theta}{w} + \frac{\theta K_A'(1+\tau)^{\frac{2-n}{n-1}}\left[1+K'(1+Z_o)\right]^{2-n}}{\left\{(1+\tau)^{1/(n-1)}\left[1+K_A'(1+Z_o)\right]-1\right\}} - \frac{2\ \theta\ K_A'}{(1+\tau)\left[1+K_A'\ (1+Z_o)\right]^{n-1}}\right] \tag{2.21}$$

$$\theta = w = 0 \quad \text{at} \quad \tau = 0 \tag{2.22}$$

The set of equations 2.20 - 2.22 has been integrated using the semi-implicit Runge-Kutta method to obtain the $\eta - \phi$ curve. The effectiveness factor η is calculated using the following procedure:

1. Fix a value of the adsorption constant K_A'.
2. Assume a value of Z_o, i.e. the concentrations at the centre of the pellet.
3. For the assumed value of Z_o in (2) obtain $\tau = \tau_s$ the value of at the surface, which is equal to $(1+K_A')/(1+K_A'(1+Z_o))^{n-1} - 1$ for this case.
4. Integrate equations 2.20 - 2.22 from $\tau = 0$ to $\tau = \tau_s$ to obtain the values of w and θ at the surface.
5. Knowing the value of θ at the surface, i.e. θ_s, obtain ϕ from the definition of θ as $\phi^2 = \theta_s (1+K_A')^2$.

6. Obtain the effectiveness factor for this value of ϕ and the fixed value of K_A' in (1) from $\eta = 3w/\theta$.
7. Change the values of Z_o assumed in (2) to obtain the $\eta - \phi$ curve for the fixed values of K_A' .
8. Change the value of K_A' and repeat the procedure.

Typical cases for $K_A' = 8$ and 15 for $n = 2$ have been shown in Figure 2.2. 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 that the multiplicity would exist for the values of $K_A' > 12.2$. To check this point the results for the case of $K_A' = 15$ have also been displayed in the figure showing the validity of the proposed method.

2.1.3 Langmuir-Hinshelwood rate form

$$r = \frac{k\, C_A\, C_B}{1+K_A C_A+K_B C_B}$$

Let us consider a reaction scheme of the type $A + B \longrightarrow$ Products, with the rate form $r = kC_AC_B/\left(1+K_AC_A+K_BC_B\right)$. Catalytic reaction rate models based on multi-step 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,

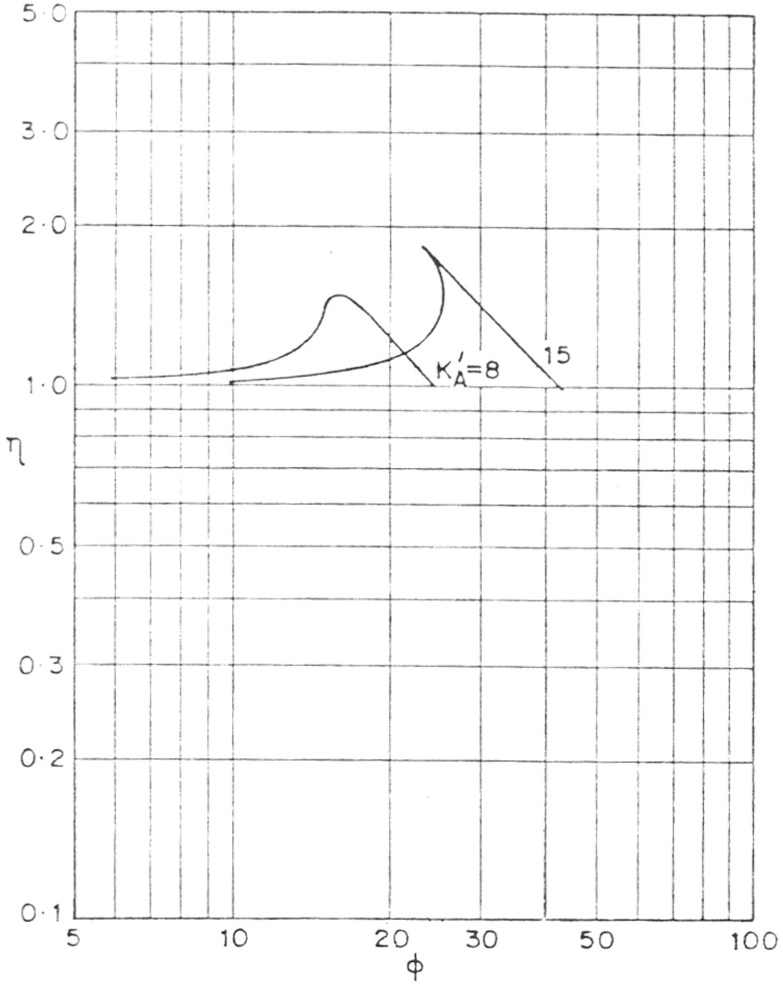


FIG. 2·2: INFLUENCE OF ADSORPTION CONSTANT ON EFFECTIVENESS FACTOR–THIELE MODULUS CURVE e.g. disproportion of 2-propyl-benzene over Al_2O_3-SiO_2 (Beraneck and Kraus, 1978). While the analysis of a catalyst pellet for similar rate forms, e.g. $r = kC_A/(1+K_AC_A+K_BC_B)$, has been reported earlier (Knudsen et al, 1966; Roberts and Satterfield, 1966; Hartman et al, 1967), this particular rate term does not seem to have been analysed.

The conservation equations along with the boundary conditions for the species A are

$$\frac{D_{eA}}{X^2}\frac{d}{dX}\left[X^2\frac{dC_A}{dX}\right] = \frac{kC_AC_B}{(1+K_AC_A+K_BC_B)} \qquad (2.23)$$

$$C_A = C_{AS}, \quad X = r_1, \quad dC_A/dX = 0, \quad X = 0 \qquad (2.24)$$

Similarly, for species B,

$$\frac{D_{eB}}{X^2}\frac{d}{dX}\left[X^2\frac{dC_B}{dX}\right] = \frac{\nu kC_AC_B}{(1+K_AC_A+K_BC_B)} \qquad (2.25)$$

$$C_B = C_{BS}, \quad X = r_1, \quad dC_B/dX = 0, \quad X = 0 \qquad (2.26)$$

In dimensionless form, the above equations can be written as

$$\nabla_x^2 a = \frac{\phi^2 a\, b}{1 + K_A' a + K_B' b} \qquad (2.27)$$

$$\nabla_x^2 b = \frac{D_{eA}}{D_{eB}} \nu \frac{\phi^2 a b}{1 + K_A' a + K_B' b} \qquad (2.28)$$

$$a = q, \quad b = 1-q, \quad x = 1, \quad da/dx = db/dx = 0, \quad x = 0 \qquad (2.29)$$

Here C_A and C_B are nondimensionlised with respect to C_T.

Equations 2.27 and 2.28 can be combined to eliminate b in terms of a; thus we get the following relation:

$$b = \nu_1 a - q_1 \qquad (2.30)$$

where $\nu_1 = \nu \frac{D_{eA}}{D_{eB}}, \quad q_1 = q\,(1+ \nu_1) - 1, \quad q = C_{AS}/CT$ (2.31)

Substituting 2.30 in 2.27 we get

$$\nabla_x^2 a = \frac{\phi^2 a \; \nu_1 a - q_1}{(1- K_B' q_1)(1 + p a)} \qquad (2.32)$$

Setting

$$a/q = (1 + Z) \qquad (2.33)$$

equation 2.32 can be written as

$$\nabla_x^2 Z = \frac{\phi^2 (1+Z) \left[\nu_1 q (1+Z) - q_1\right]}{(1-K_B' q_1)\,(1+ pq\,(1+Z))} \qquad (2.34)$$

where $$p = \frac{K_A' + K_B' \nu_1}{1 - K_B' q_1}, \quad \phi^2 = R^2 \quad \frac{k}{D_{eA}},$$

$$K_A' = K_A C_T, \quad K_B' = K_B C_T \quad \text{and} \quad C_T = C_{AS} + C_{BS}$$

Applying the transformations

$$w = \frac{x\,(dZ/dx)}{(1-K_B'\,q_1)\,(1+pq\,(1+Z))}$$

$$\theta = \frac{\phi^2 x^2\,(1+Z)}{(1-K_B'\,q_1)^2\,(1+pq(1+Z)^2} \tag{2.35}$$

$$\tau = \ln \frac{1 + pq\,(1+Z)}{1 + pq\,(1+Z_o)}$$

equation 2.32 can be recast as

$$\frac{dw}{d\tau} = \frac{1}{pq(1-K_B'q_1)} \left[\left\{ \frac{\nu_1}{p} \left[e^{\tau}(1+pq\,(1+Z_o)) - 1 \right] - q_1 \right\} \frac{\theta}{w} - \right.$$

$$\left. - 1 - pq\,(1 - K_B'\,q_1)\,w \right] \tag{2.36}$$

$$\frac{d\theta}{d\tau} = \frac{2\theta}{w} \, \frac{1}{pq\,(1-K_B'q_1)} + \frac{\theta\, e^{\tau} \left[1 + pq\,(1 + Z_o)\right]}{e^{\tau}\left[(1 + pq\,(1+Z_o))\right] - 1} - 2\theta \tag{2.37}$$

$$w = \theta = 0 \quad \text{at} \quad \tau = 0 \tag{2.38}$$

The effectiveness factor in this case is obtained by using the following procedure:

1. Fix values of K_A' , K_B' , q and ν_1 .
2. Assuming a value Z_o, i.e. concentration at the centre of the pellet, obtain $\tau = \tau_s$, the value of τ at the surface,

$$\tau_s = \ln \frac{1 + pq}{1+pq\ (1 + Z_o)} \ .$$

3. Integrate the set of equations 2.36 - 2.38 from $\tau = 0$ to $\tau = \tau_s$ to obtain the value of w and θ at the surface.
4. Obtain ϕ from θ at the surface as $\phi^2 = \theta_s\ (1 - K_B'\ q_1)^2\ (1 + pq)^2$.
5. Obtain the effectiveness factor corresponding to this value of ϕ and fixed values of other parameters in (1) q, $K_A' K_B'$ from $\eta = 3w/\ \theta(1-q)$.
6. Change the assumed value of Z_o in (2) to obtain $\eta - \phi$ curve for fixed values of parameters in (1).
7. Change the values of parameters one by one and repeat the procedure.

The results are presented as $\eta - \phi$ plots for the following sets of parameter values:

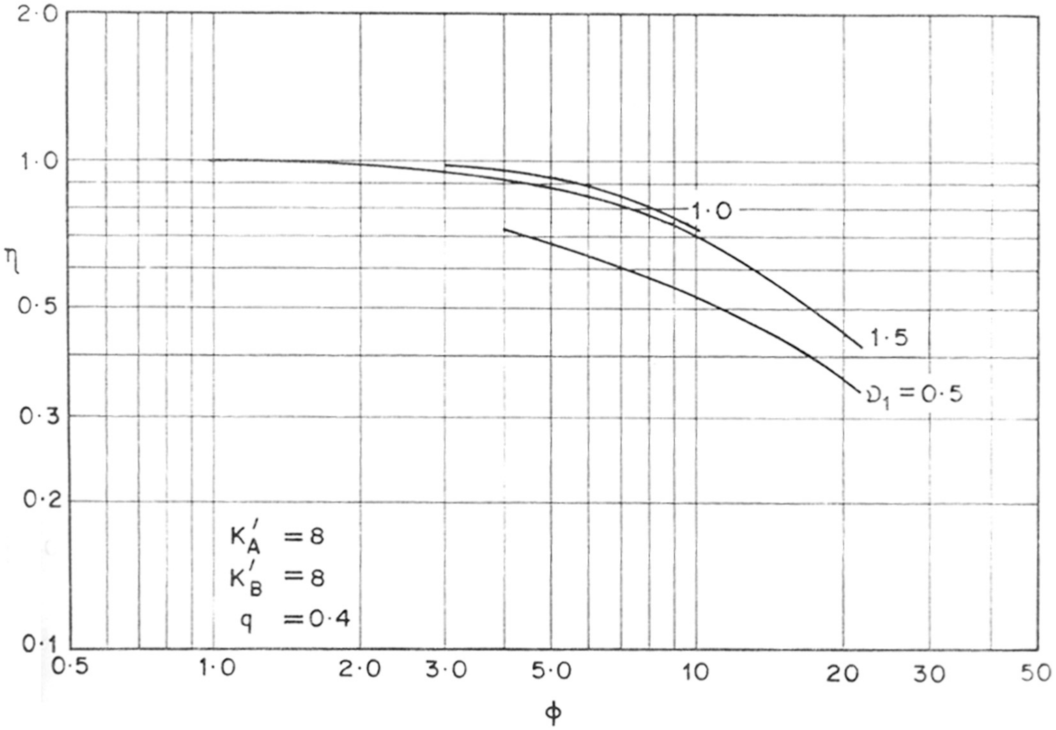
1. $K_A' = K_B' = 8$, $q = 0.4$, $\nu_1 = 1$
2. $K_A' = 8$, $K_B' = 2$, $q = 0.4$, $\nu_1 = 1$
3. $K_A' = 8$, $K_B' = 12$, $q = 0.4$, $\nu_1 = 1$
4. $K_A' = K_B' = 8$, $q = 0.4$, $\nu_1 = 0.5$
5. $K_A' = K_B' = 8$, $q = 0.4$, $\nu_1 = 1.5$
6. $K_A' = K_B' = 8$, $q = 0.2$, $\nu_1 = 1$

Figure 2.3 shows the influence of variation of K_B' for fixed values of other parameters. Increasing the value of K_B' is seen in general to improve the overall effectiveness of the particle. Figure 2.4 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 A and B, however, shows some interesting behaviour. For fixed values of other parameters, there exists a critical value of ν_1 on either side of which the effectiveness factor always decreases (Figure 2.5).

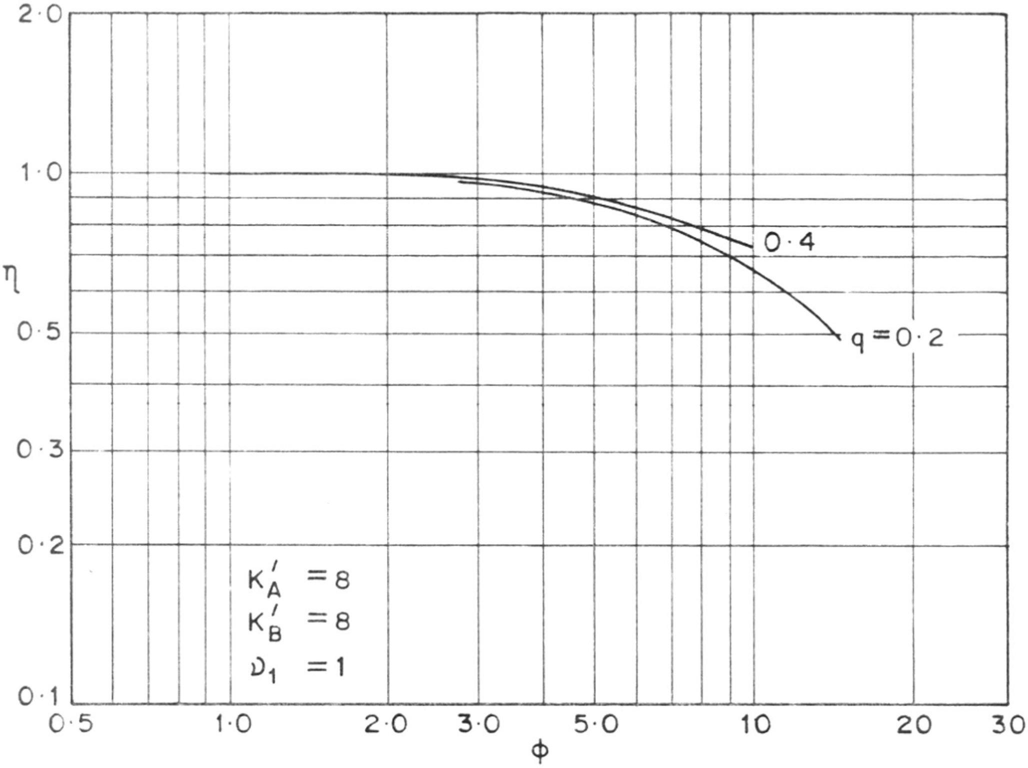
2.1.4 Autocatalysis

$$r = kC_AC_B$$

Let us consider a reaction scheme of the type $A + B \longrightarrow B + B$. The conservation equations for species A and B along with the boundary conditions can be written as



2·3: INFLUENCE OF STOICHIOMETRIC COEFFICIENT ON EFFECTIVENESS FACTOR–THIELE MODULUS CURVE



IG. 2·4: INFLUENCE OF INPUT FEED COMPOSITION ON EFFECTIVENESS FACTOR—THIELE MODULUS CURVE

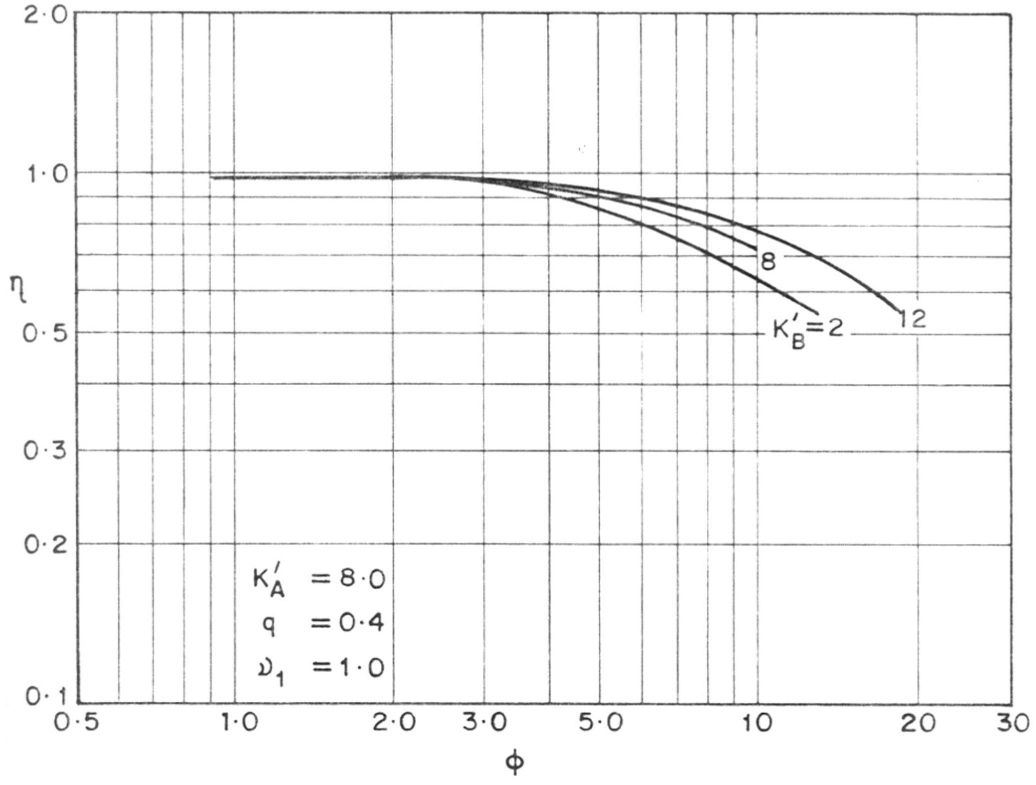


FIG. 2·5: INFLUENCE OF ADSORPTION CONSTANT OF SECOND COMPONENT ON EFFECTIVENESS FACTOR–THIELE MODULUS CURVE FOR FIXED VALUES OF OTHER PARAMETERS

$$D_{eA} \frac{d^2C_A}{dX^2} = kC_AC_B \tag{2.39}$$

$$C_A = C_{AS}, \quad X = r_1 , \quad dC_A/dX = 0, \quad X = 0 \tag{2.40}$$

$$D_{eB} \frac{d^2C_B}{dX^2} = \nu k \; C_AC_B \tag{2.41}$$

$$C_B = C_{BS}, \quad X = r_1 , \quad dC_B/dX = 0, \quad X = 0 \tag{2.42}$$

In dimensionless form these equations become

$$\frac{d^2a}{dx^2} = \phi^2 \; a \; b \tag{2.43}$$

$$\frac{d^2b}{dx^2} = \nu_1 \; \phi^2 \; a \; b \tag{2.44}$$

$$a = q \;, \quad b = 1 - q \;, \quad x = 1 \;, \quad da/dx = db/dx = 0, \quad x = 0 \tag{2.45}$$

Expressing the concentration b in terms of the concentration a by using 2.43 and 2.44, we get

$$b = \nu_1 \; a - 1 - q(1+ \nu_1) \tag{2.46}$$

Substituting this in equation 2.41, we get

$$\frac{d^2 \; a}{dx^{\;2}} = \phi^2 \; a \cdot \left\{ \nu_1 a + \; 1 - q \; (1+\nu_1) \right\} \tag{2.47}$$

where $$\phi^2 = R^2 \frac{kC_T}{D_{eA}}, \quad a = \frac{C_A}{C_T}, \quad q = \frac{C_{AS}}{C_T}$$

Using $a/q = (1+Z)$, equation 2.47 can be written as

$$\frac{d^2Z}{dx^2} = \phi^2 (1+Z) \left\{ q \nu_1 (1+Z) + (1-q(1+\nu_1)) \right\} \qquad (2.48)$$

By using the following transformations

$$w = \frac{Z\frac{dZ}{dx}}{1+Z}$$

$$\Theta = \phi^2 x^2 (q \quad {}_1 (1+Z) + 1 - q (1 + \quad {}_1) \qquad (2.49)$$

$$\tau = \ln \frac{1+Z}{1+Z_o}$$

we obtain (for slab geometry)

$$\frac{dw}{d\tau} = 1 - w + \frac{\Theta}{w} \qquad (2.50)$$

$$\frac{d\Theta}{d\tau} = \frac{2\Theta}{w} + \frac{\Theta q \nu_1 (1+Z_o) e^{\tau}}{\left[q \nu_1 (1+Z_o) e^{\tau} + (1-q(1+\nu_1)) \right]} \qquad (2.51)$$

$$w = \Theta = \tau = 0 \qquad (2.52)$$

The solution to these equations has been obtained in terms of the $\eta - \phi$ curve. The procedure for obtaining η is given below.

1. Fix the values of q and ν_1 .
2. Assume a value of Z_o, i.e. concentration at the centre of the pellet.
3. Obtain the value of at the surface, $\tau_s = \ln 1/(1+Z_o)$.
4. Integrate equations 2.50 - 2.52 from $\tau = 0$ to $\tau = \tau_s$ to obtain w and Θ at the surface.
5. From Θ at the surface calculate ϕ as

$$\phi^2 = \frac{\Theta_s}{[q\nu_1 + 1 - q(1+\nu_1)]} \quad .$$

6. From w and Θ at the surface calculate η for that particular value of ϕ as $\eta = 3w/[(1-q)\Theta]$.
7. Change the value of Z_o and repeat the procedure from (2) onwards to obtain the $\eta - \phi$ curve for fixed values of parameter in (1).
8. Change the values of parameters in (1) and repeat the whole procedure.

The $\eta - \phi$ curves obtained for varying values of input concentration of A are presented in Figure 2.6. It is clearly seen that for certain sets of parameter values the effectiveness factor exceeds unity. However, no multiplicity could be

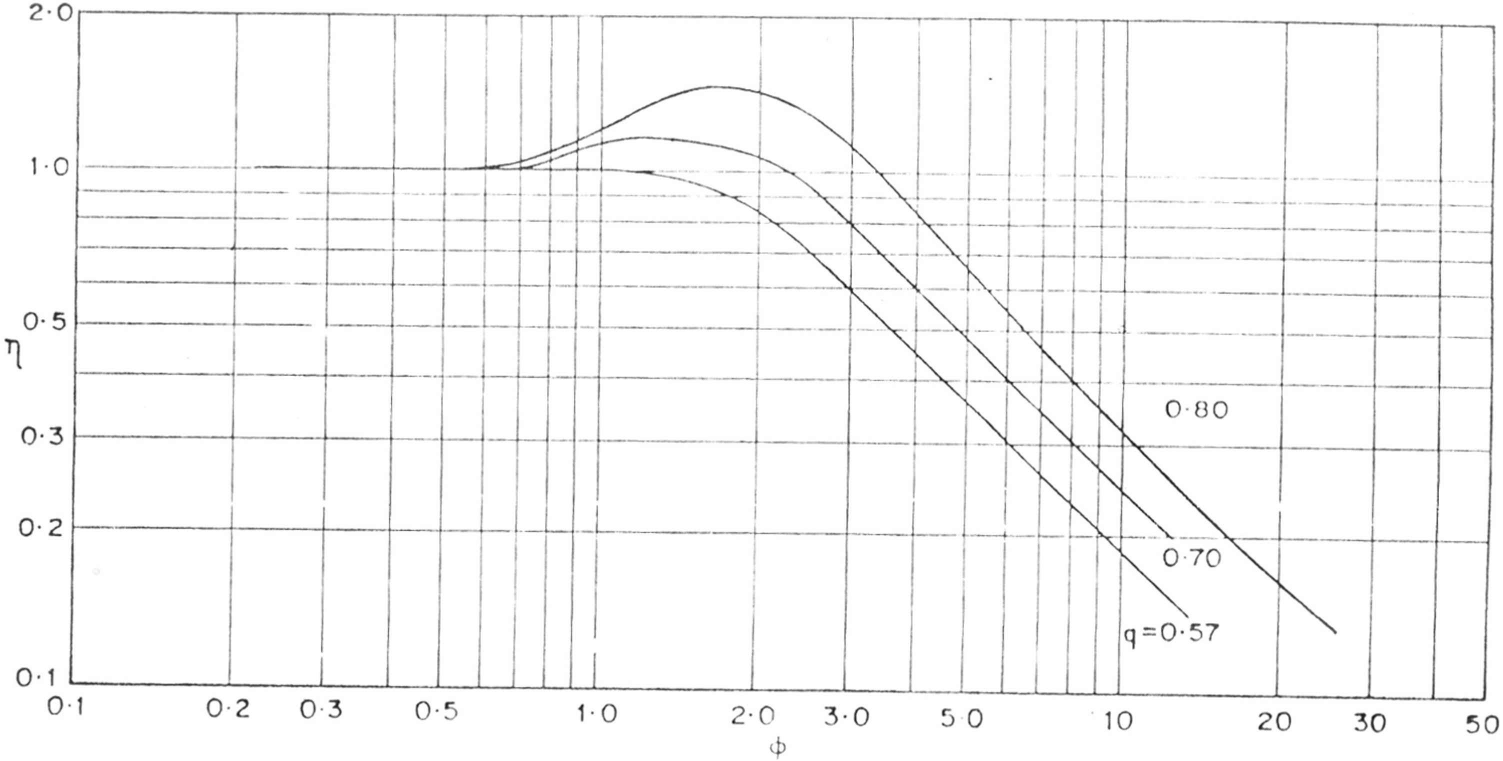


FIG. 2·6: INFLUENCE OF INPUT FEED COMPOSITION ON EFFECTIVENESS FACTOR – THIELE MODULUS CURVE generated. It is difficult to obtain a priori information on the stability and multiplicity of states in view of the nonautonomous nature of these equations.

2.2 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 the case of a general r^th^ order reaction. The conservation equation for the reactant species A along with the boundary conditions can be written as

$$\frac{D_{eA}}{X^2} \frac{d}{dX}\left[X^2 \frac{dC_A}{dx}\right] = kC_A^n \qquad (2.52)$$

$$X = r_i , \quad \frac{dC_A}{dX} = B_i(C_{AS} - C_A), \quad X = 0, \quad \frac{dC_A}{dX} = 0 \qquad (2.53)$$

The corresponding dimensionless equations are

$$\nabla_x^2 a = \phi^2 a^n \qquad (2.54)$$

$$\frac{da}{dx} = B_i(1-a), \quad x=1 , \quad \frac{da}{dx} = 0, \quad x = 0 \qquad (2.55)$$

Defining the transformation

$$a_1 = \frac{a}{1 - \frac{1}{B_i} \left.\frac{da}{dx}\right|_{x=1}} = \frac{a}{K_1} \qquad (2.56)$$

it is possible to rewrite the set of equations 2.54 - 2.55 as

$$\nabla_x^2 a_1 = \phi^2 K_1^{n-1} a_1^n \tag{2.57}$$

$$a_1 = 1, \quad x = 1 , \quad \frac{da_1}{dx} = 0 , \quad x = 0 \tag{2.58}$$

By using the transformation

$$a_1 = K_1 (1 + Z) \tag{2.59}$$

equation 2.57 can be written as

$$\nabla_x^2 Z = \phi^2 K_1 (1+Z) \tag{2.60}$$

Using the transformations

$$w = \frac{x (dZ/dx)}{1 + Z}$$

$$\theta = \phi^2 K_1^{n-1} (1+Z)^{n-1} x^2 \tag{2.61}$$

$$\tau = \ln \frac{1 + Z}{1 + Z_o}$$

the set of equations 2.57 - 2.58 are converted into an equivalent initial value problem as

$$\frac{dw}{d\tau} = \frac{\theta}{w} - w - 1 \tag{2.62}$$

$$\frac{d\theta}{d\tau} = \frac{2\theta}{w} + (n - 1) \theta \tag{2.63}$$

$$w = \theta = 0, \quad \tau = 0 \qquad (2.64)$$

The method of obtaining η for several values of ϕ and B_i is as follows:

1. Integrate equations 2.62 - 2.64 to obtain w and θ at different values of τ; for this particular case each value of w and θ can be regarded as the value at the surface.
2. From the θ value at the surface and noting the definition of θ, obtain $\theta = \phi^2 K_1$.
3. From the values of w at the surface and noting the definitions of w and K_1, obtain $w = \frac{B_i(1-K_1)}{K_1}$ for a fixed value of B_i ; this fixes the value of K_1 .
4. Using this value of K_1 in (2) to obtain ϕ.
5. Repeat the procedure to produce $\eta - \phi$ variations for different Biot numbers; for this particular case the effectiveness factor is simply obtained as $\eta = 3K_1^2 (w/\theta)$.

The results obtained using this method are presented in Figure 2.7 for 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 n^{th} order case exists. While a direct comparison of the effectiveness factors for various values of Biot number with the literature values is not possible, the values obtained are compared with those for a first order reaction (Kulkarni and Karanth, 1978) and seem to fall in the right range.

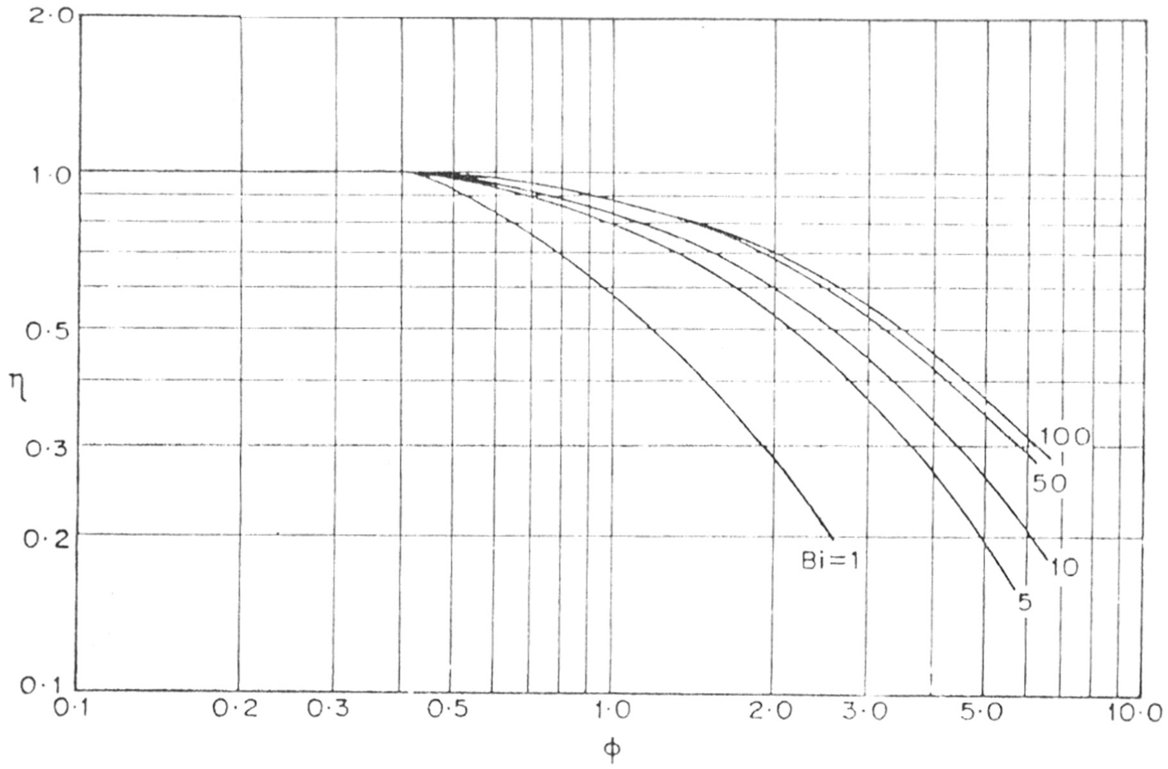


FIG. 2·7: INFLUENCE OF BIOT NUMBER ON EFFECTIVENESS FACTOR – THIELE MODULUS CURVE

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

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

$$FC_{AF}\,(a_f - 1) = V\,k_g\,a_v\,(1 - a_s) \qquad (2.65)$$

$$\nabla_x^2\,a_s = \phi^2\,f\,(a) \qquad (2.66)$$

$$\begin{aligned} \frac{da_s}{dx} &= B_i\,(1-a_s), \quad x = 1\,, \\ \frac{da_s}{dx} &= 0, \quad x = 0 \end{aligned} \qquad (2.67)$$

It is possible to write

$$k_g\,a_v\,(1 - a_s) = \eta\,r \qquad (2.68)$$

where r represents the rate corresponding to the surface conditions of the particle. The value of η for several difficult rate forms can be obtained using the method presented in earlier sections. For a typical rate form of the type $f\,(a_s) = a_s/(1 + K_A' a_s)^2$, equation 2.68 can be written as

$$\frac{\alpha_1}{\eta}\,(1-a_s) = \frac{a_s}{(1 + K_A' a_s)^2} \qquad (2.69)$$

A simple graphical procedure of plotting the lhs and rhs against concentration can then be used to locate the roots of equation 2.69. The rhs of equation 2.69 represents the rate function and shows a maximum, while the lhs is a straight line with slope of $(-\alpha_1/\eta)$. Qualitative plots of these functions are shown in Figure 2.8. It is seen that the straight line (lhs of equation 2.51) touches the rate curve at two points. Invoking the equality of the slopes for the rate function (rhs) and the straight line (lhs) 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 (α_1/η) where

$$\left(\frac{\alpha_1}{\eta}\right)^+ = \frac{a_{s1}}{(1+K_A' a_{s1})^2} \; \frac{1}{1-a_{s2}} \qquad (2.70)$$

$$\left(\frac{\alpha_1}{\eta}\right)_- = \frac{a_{s2}}{(1+K_A' a_{s2})^2} \; \frac{1}{1-a_{s2}} \qquad (2.71)$$

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 2.70 and 2.71 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 a particle problem gives rise to three different values of η. Depending on the initial conditions the particle effectiveness will approach either the higher

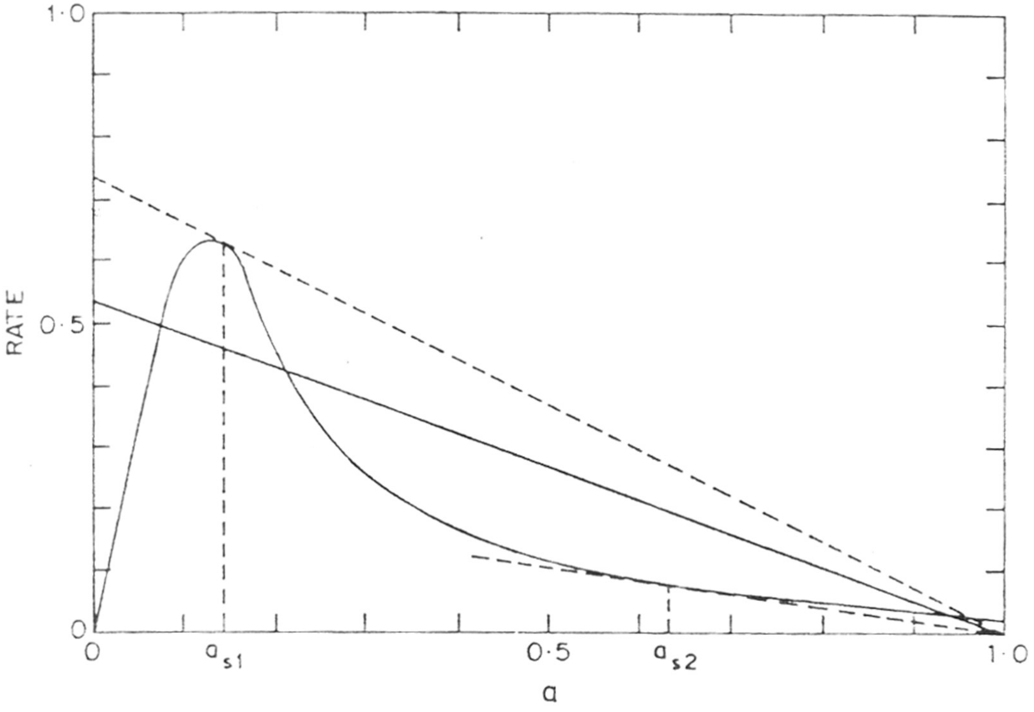


FIG. 2·8: VARIATION OF RATE WITH CONCENTRATION [EQUATION(2·69)] (say η_1) or the lower (say η_2) value. Since all particles are subjected to the same environment and initial condition, the same value of η (either η_1 or η_2) exists in all the particles. Corresponding to these two values of η two different regions of (α_1/n) can exist for the reactor problem. It is also possible for the two 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 $\eta - \phi$ for a given B_i , it is thus possible to obtain information about reactor behaviour.

2.4 Conclusions

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

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 analysed 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.

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

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CHAPTER- 3

APPLICATION TO BIDISPERSED CATALYST

CHAPTER 3

APPLICATION TO BIDISPERSED CATALYSTS

The present chapter 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 bimodal pore structure. In gas-solid noncatalytic reactions this situation arises when particle-pellet (grain) models are used to describe the behaviour. Besides, in many biochemical systems involving encapsulated enzymes, such a situation is fairly common.

3.1 The Case of Langmuir-Hinshelwood Kinetics

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 effectiveness factor 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 n^{th} order nonlinear kinetics (Jayaraman et al, 1981, 1983) in a macro-microparticle system are available, no information on L-H type of kinetics which is more rational for catalytic systems exists.

The conservation equations can be written as

Microparticle:

$$\frac{D_{eA}}{X^2}\frac{d}{dX}\left[X^2\frac{dC_A}{dX}\right] = \frac{kC_A}{(1+K_AC_A)} \qquad (3.1)$$

$$C_A = C_A' , \quad X = r_i ; \qquad \frac{dC_A}{dX} = 0, \quad X = 0 \qquad (3.2)$$

Macroparticle:

$$\frac{D_{aA}}{Y^2}\frac{d}{dY}\left[Y^2\frac{dC_A'}{dY}\right] = \frac{3(1-\epsilon)}{r_i}\left.\frac{dC_A}{dX}\right|_{X=r_i} \qquad (3.3)$$

$$C_A' = C_{AS} , \quad Y = R ; \qquad \frac{dC_A'}{dY} = 0, \quad Y = 0 \qquad (3.4)$$

Nondimensionlising C_A and C_A' with respect to the surface concentration C_{AS}, and X and Y with respect to the micro and macroparticle radii r_i and R, respectively, we get the following dimensionless equations:

Microparticle:

$$\nabla_x^2 c_i = \frac{\phi^2 c_i}{(1+K_A' c_i)} \qquad (3.5)$$

$$c_i = c_a , \quad x = 1 ; \qquad \frac{dc_i}{dx} = 0, \quad x = 0 \qquad (3.6)$$

Macroparticle:

$$\nabla_y^2 c_a = \alpha \left.\frac{dc_i}{dx}\right|_{x=1} \qquad (3.7)$$

$$C_a = 1 \;, \quad y = 1 \;; \qquad \frac{dC_a}{d\,y} = 0 \;, \quad y = 0 \qquad (3.8)$$

The set of equations 3.5-3.8 are nonlinear in the source term and involve the coupled boundary condition given by equation 3.6. The conventional method of solution requires trial and error on both equations 3.5 and 3.7 such that the boundary conditions are satisfied. Generally a large amount of computer time is required to obtain the desired solution.

In this work we avoid trial and error completely by converting the boundary value problem given by equations 3.5 and 3.6 into an equivalent initial value problem by using suitable transformations. The equivalent initial value problem is then solved to obtain $\left.\frac{dC_i}{dx}\right|_{x=1}$ required in equation 3.7 which is subsequently integrated using Weisz and 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 $\eta - \phi$ 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. Here we have avoided this by employing an alternative procedure.

Substituting

$$\frac{C_i}{C_a} = (1 + Z) \qquad (3.9)$$

equation 3.5 can be written as

$$\nabla_x^2 Z = \frac{\phi^2 (1 + Z)}{1 + K'_A C_a (1 + Z)} \qquad (3.10)$$

Using the transformations

$$w = \frac{x\,(dZ/dx)}{1 + K'_A C_a (1+Z)} , \quad \theta = \frac{\phi^2 x^2 (1+Z)}{1 + K'_A C_a (1 + Z)}$$

(3.11)

$$\tau = \ln \frac{1 + K'_A C_a (1 + Z)}{1 + K'_A C_a (1 + Z_o)}$$

equations 3.5 - 3.6 become

$$\frac{dw}{d\tau} = \frac{1}{K'_A C_a} \left[\frac{\theta}{w} - K'_A C_a w - 1 \right] \qquad (3.12)$$

$$\frac{d\theta}{d\tau} = \frac{1}{K'_A C_A} \left[\frac{2\theta}{w} + \frac{\theta e^{\tau} (1+K'_A C_a (1+Z_o))\, K'_A C_a}{[e^{\tau} (1+K'_A C_a (1+Z_o)) - 1]} - 2\theta K'_A C_a \right]$$

(3.13)

$$w = \theta = 0 \text{ at } \tau = 0 \qquad (3.14)$$

The initial value problem given by equations 3.12 - 3.14 can be solved using the following procedure:

1. Fix the value of K_A' .
2. Assume a value of Z_o; this fixes the value of τ_s .
3. Assume a value of C_a ; this fixes the value of $K_A'C_a$.
4. Integrate equations 3.12 - 3.14 from $\tau = 0$ to $\tau = \tau_s$ to obtain w and θ at the surface.
5. w at the surface gives $\left.\frac{dC_i}{dx}\right|_{x=1} = w_s(1+K_A'C_a)$.
6. θ at the surface gives ϕ^2 .

The above procedure was adopted with several values of C_a and $(1+Z_o)$ (in steps 2 and 3) to generate $\left.\frac{dC_i}{dx}\right|_{x=1}$ for different values of K_A' and ϕ. Representative calculations for $K_A' = 50$, 75 and 100 and $\phi = 5$, 10, 13, 16 are analysed further.

It is apparent from these calculations that a definite relationship exists between $\left.\frac{dC_i}{dx}\right|_{x=1}$ and C_a , and to elucidate this relationship further they are plotted on a log-log scale in Figures 3.1, 3.2 and 3.3 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' and constant values of ϕ where again a straight line as shown in Figure 3.4 results. The intercept of this figure clearly shows a dependence on

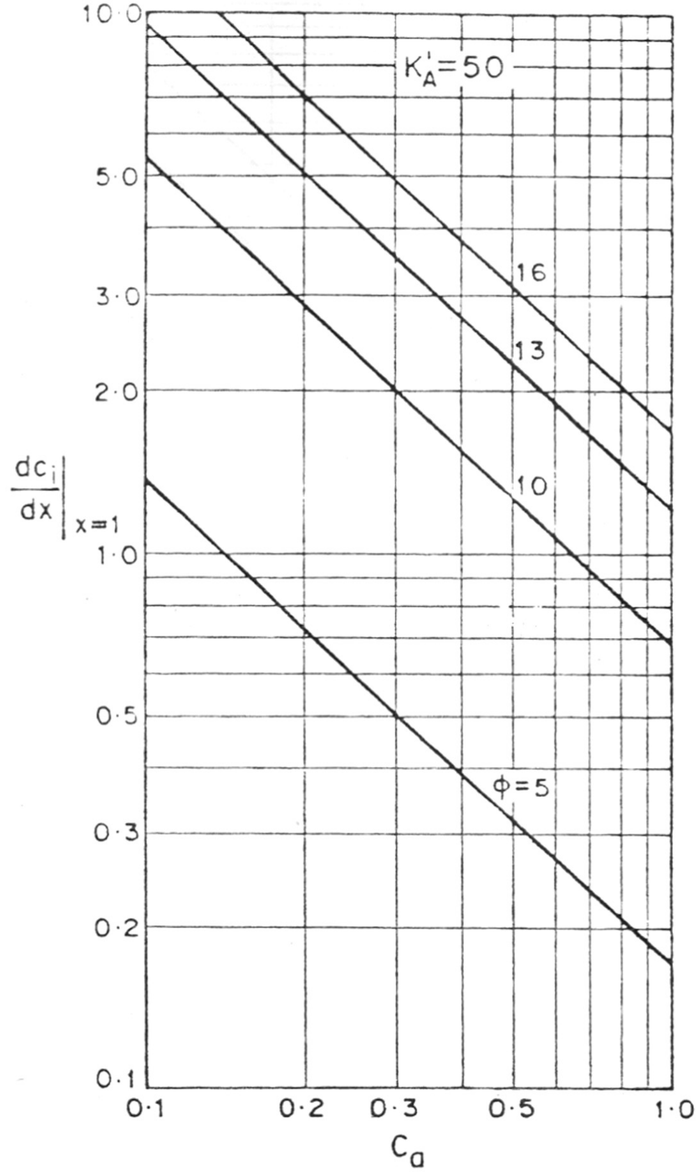

FIG. 3·1: VARIATION OF FLUX AT THE SURFACE OF MICROPORE WITH MACROPORE CONCENTRATION AT THE SURFACE OF MICROPORE AT $K'_A = 50$

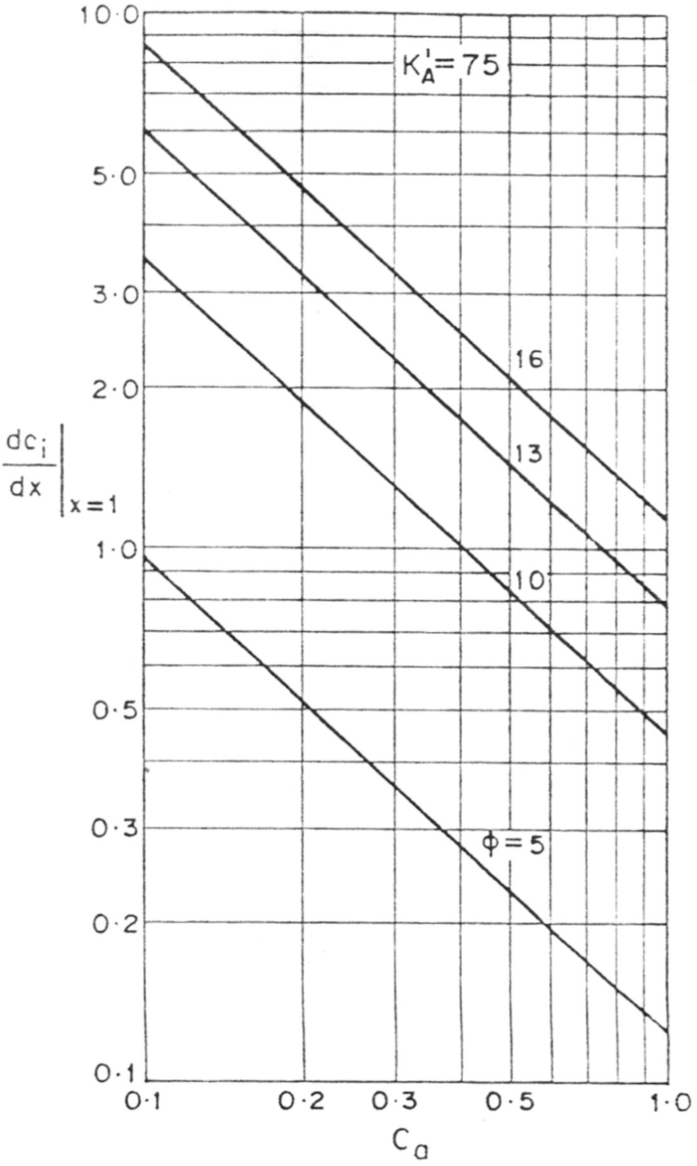

FIG. 3·2: VARIATION OF FLUX AT THE SURFACE OF MICROPORE WITH MACROPORE CONCENTRATION AT THE SURFACE OF MICROPORF AT $K_A' = 75$

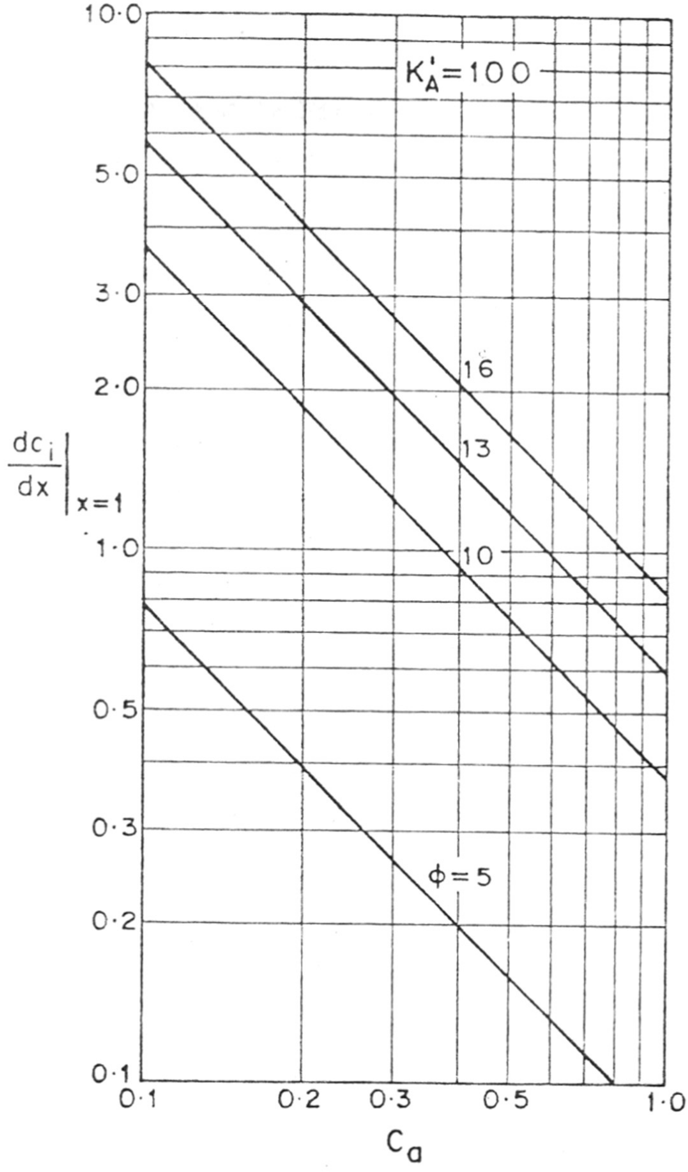

FIG. 3·3: VARIATION OF FLUX AT THE SURFACE OF MICROPORE WITH MACROPORE CONCENTRATION AT THE SURFACE OF MICROPORE AT $K_A' = 100$

ϕ which is plotted in Figure 3.5. Utilising the linear relationships shown in Figures 3.1 to 3.5, the flux at the pore mouth of a microparticle can be related (by regression analysis) to the corresponding macroparticle concentration C_a through the parameters K_A' and ϕ as follows:

$$\left.\frac{dC_1}{dx}\right|_{x=1} = K_A'^{-1}\,\phi^{1.5}\,C_a^{-1} \qquad (3.15)$$

It is interesting to note that the negative slope of the curves in Figure 3.4 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) thus occurs in the system with bimodal pore distribution. Earlier, Jayaraman <u>et al</u> (1983) had observed a similar falsification when a zero order reaction is carried out in a micro-macroparticle system. This falsification of the reaction order induced by the bipore distribution therefore gives rise to certain additional features of the system. In the present case the simple L-H kinetics tends to exhibit multiplicity behaviour corresponding to that of negative first order kinetics.

Equation 3.15 can now be substituted in 3.7 to obtain

$$\nabla_y^2\, C_a = \phi_m^2\, C_a^{-1} \qquad (3.16)$$

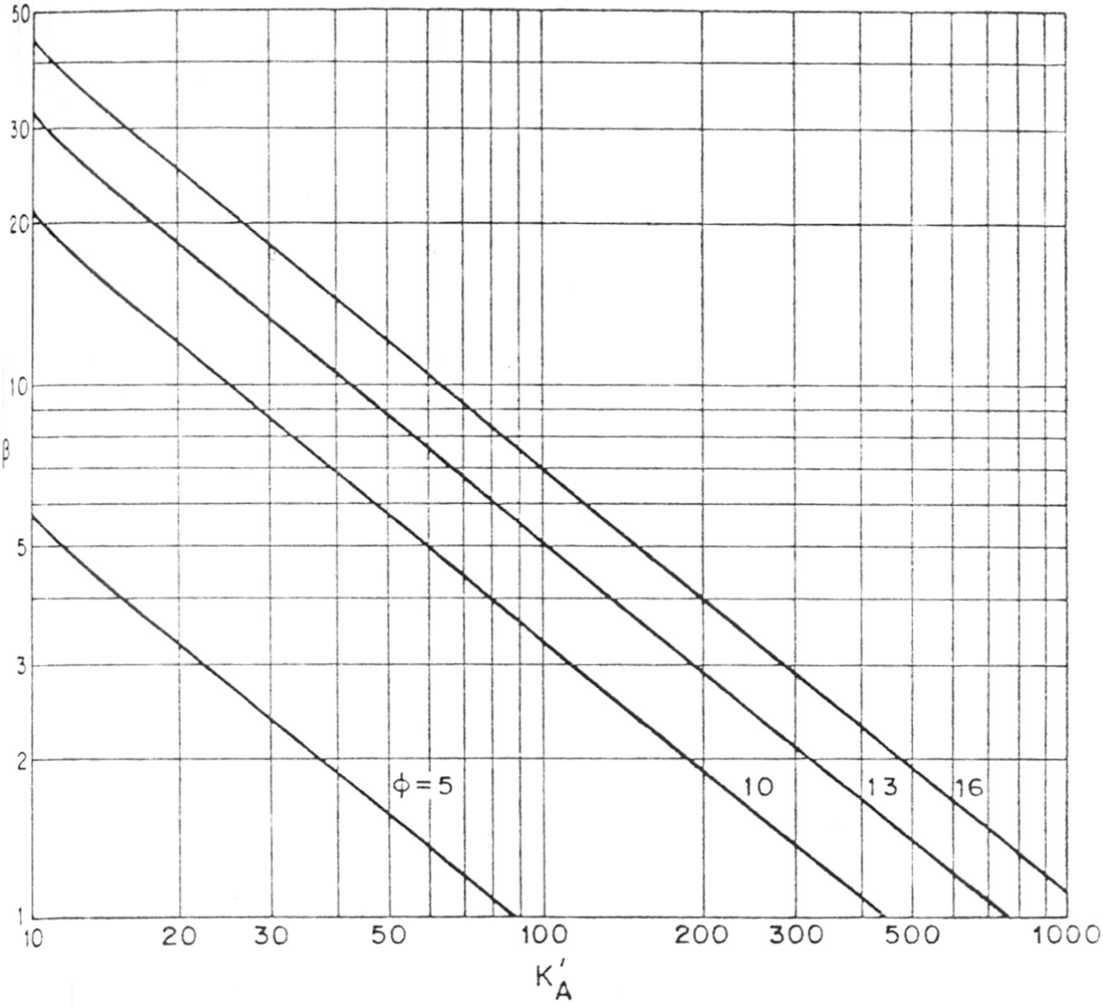

FIG. 3·4: VARIATION OF INTERCEPT IN FIGS. 3·1 – 3·3 WITH K'_A AT CONSTANT VALUES OF ϕ

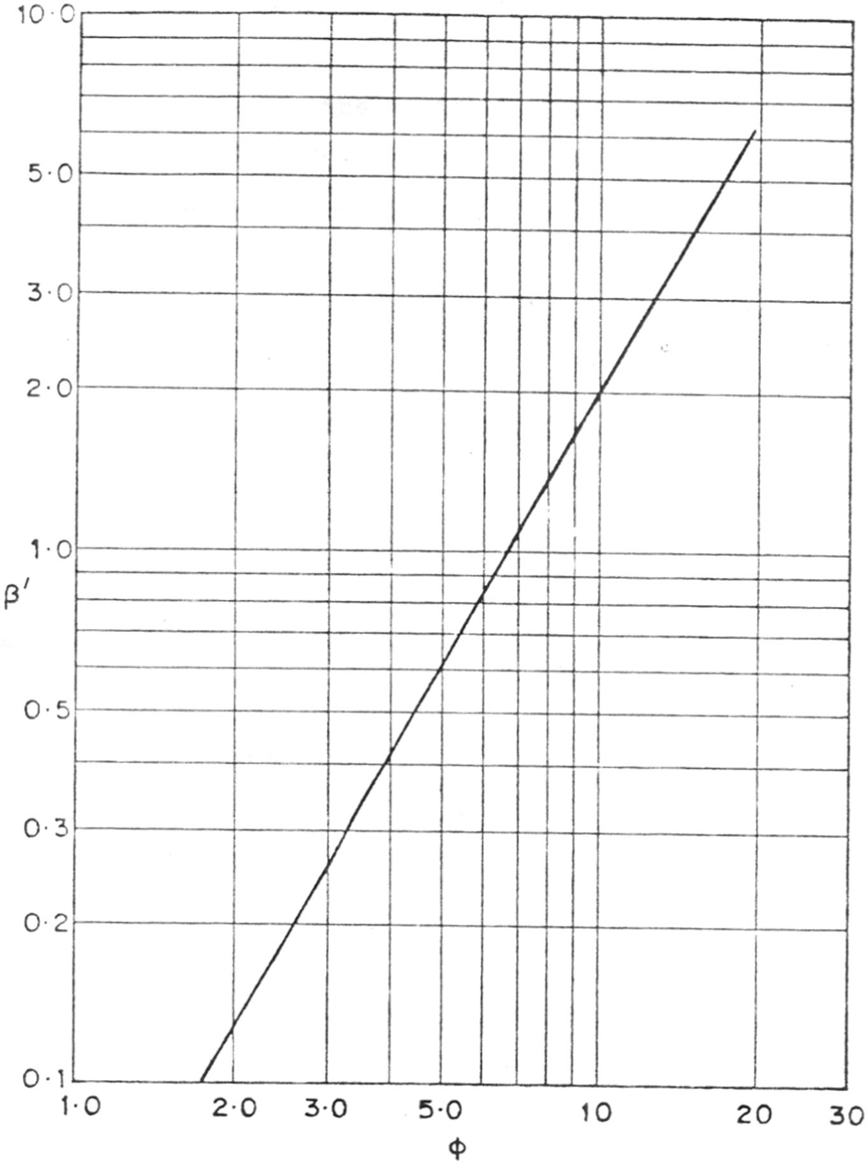

FIG. 3·5: VARIATION OF INTERCEPT IN FIG. 3·4 WITH φ where ϕ_m represents the modified Thiele modulus defined as equal to $(K_A^{-1}\,\phi^{1.5\alpha})$. Equation 3.16 can be converted into two first order equations using the transformations

$$u = \frac{y(dCa/dy)}{(1 + Z)}$$

$$v = \frac{\phi_m^2\, y^2}{(1 + Z)^2} \qquad (3.17)$$

$$\tau_1 = \ln \frac{1 + Z}{1 + Z_o}$$

as

$$\frac{du}{d\tau_1} = \frac{v}{u} - 1 - u \qquad (3.18)$$

$$\frac{dv}{d\tau_1} = \frac{2v}{u} - 2v \qquad (3.19)$$

$$u = v = 0\,, \quad \tau_1 = 0 \qquad (3.20)$$

3.2 Results and Discussion

Variations of u and v with τ_1 are obtained and are presented as a phase plane plot in Figure 3.6. This figure clearly shows the critical point to be a stable focus with a range of v and hence ϕ_m values for which multiplicity is possible. The corresponding $\eta - \phi_m$ curves can also be obtained from this figure using the relation $\eta = 3u/v$ and are shown in Figure 3.7. The striking advantage of Figure 3.7 is that the whole parameter

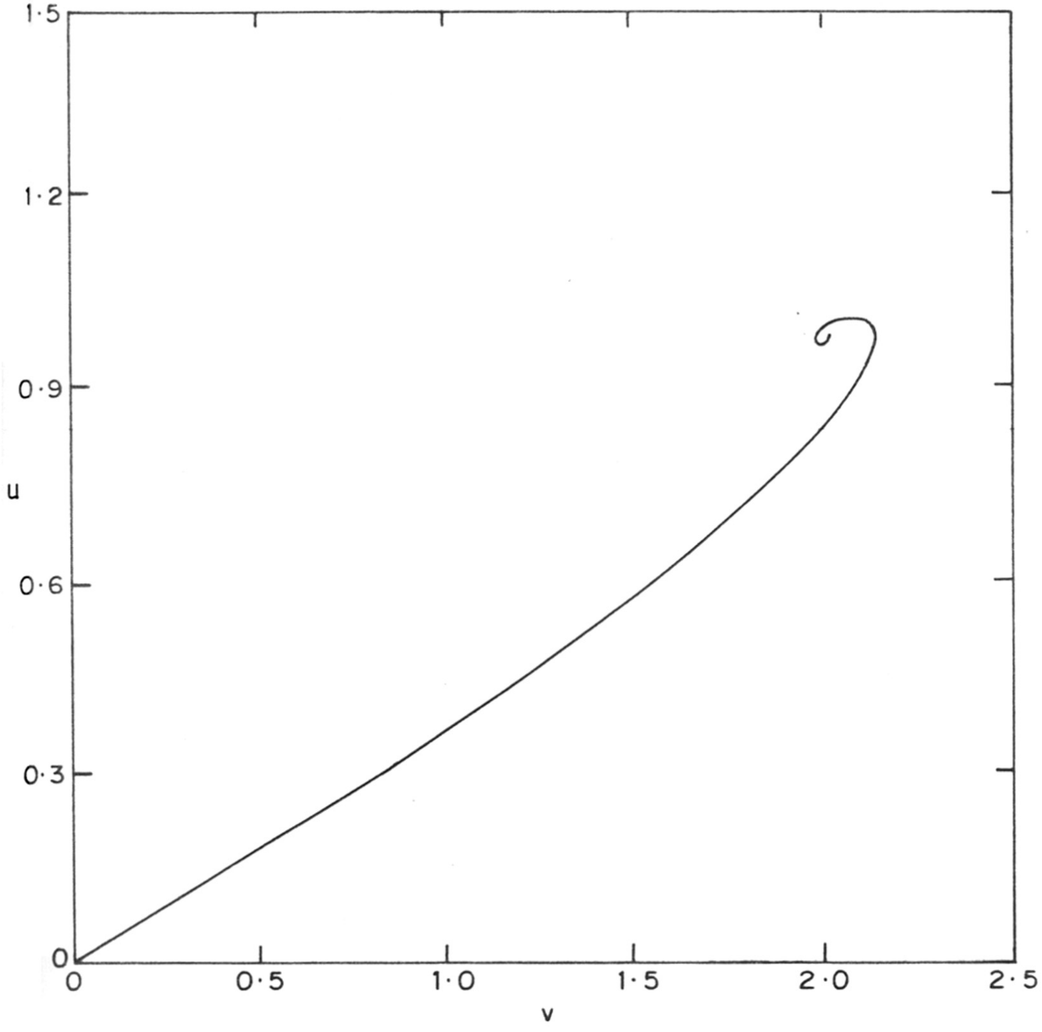

FIG. 3·6: PHASE PLANE PLOT OF u Vs. v

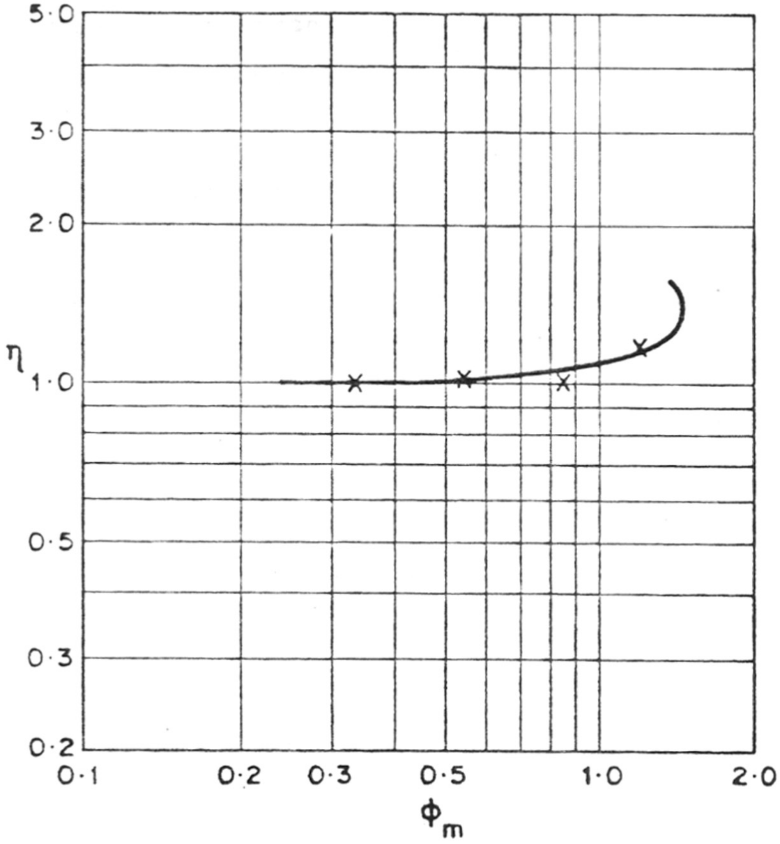

FIG. 3·7: EFFECTIVENESS FACTOR vs. MODIFIED THIELE MODULUS space for K_A', ϕ and α is condensed into a single curve leading to a very compact representation of the variation of effectiveness factor with the parameters of the system.

The results in Figure 3.7 have been obtained by making use of the relationship for $\left.\frac{dC_i}{dx}\right|_{x=1}$ given by equation 3.16. 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 macroparticle equation for subsequent integration. In order to show its validity the macroparticle equation 3.7 has been integrated using the Weisz-Hicks (1962) method.

The procedure is briefly as follows:

1. Obtain $\left.\frac{dC_i}{dx}\right|_{x=1}$ for an assumed value of C_a (at $x = 1$, $y = 0$) for fixed values of K_A' and ϕ.
2. Use this point value of $\left.\frac{dC_i}{dx}\right|_{x=1}$ in equation 3.7 and integrate using Weisz and Hicks' method to obtain α and $(dC_a/dy)_{y=1}$. The value of η for known α, ϕ and K_A' is then obtained using the relation

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

The values of η thus obtained are also marked in Figure 3.7 as crosses. In view of the close agreement between the η values obtained using the rigorous numerical method and equation 3.15 it is apparent that the simple method suggested can be conveniently used.

3.3 Conclusions

The transformation used for L-H kinetics in a bidispersed catalyst 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 n 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 monoporous 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.

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NOTATION

a	dimensionless concentration of species A
a_1	transformed concentration variable defined by equation 2.56
a_s	dimensionless concentration of species A at the catalyst surface
a_f	dimensionless inlet concentration
a_v	gas-solid interfacial area
b	dimensionless concentration of species B
B_i	Biot number defined as $k_g R/D_{eA}$
C_a	dimensionless concentration in the macroparticle
C_i	dimensionless concentration in the microparticle
C_A	concentration of species A
C_B	concentration of species B
C_A'	concentration of species A in the macroparticle
C_{AS}	concentration of species A at the surface of catalyst
C_{BS}	concentration of species B at the surface of catalyst
C_T	total concentration in the gas phase
C_{AF}	concentration of species A in the inlet stream
D_{aA}	effective diffusivity of A in the macroparticle
D_{eA}	effective diffusivity of A
D_{eB}	effective diffusivity of B
F	flow rate
$f(a_s)$	rate function defined by equation 2.66
k	rate constant

K_1	parameter defined in equation 2.56
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
K_B'	dimensionless adsorption equilibrium constant for species B
k_g	mass-transfer coefficient
n	order of reaction
p	parameter defined by equation 2.34
q	parameter defined by equation 2.31
q_1	parameter defined by equation 2.31
r	general term for rate
R	radius of the pellet
$\bar{r}$	dimensionless rate
r_i	general notation for the radius
u	transformation defined by equation 2.61
v	transformation defined by equation 2.61
V	volume of the reactor
w	transformation
x	general notation used to define dimensionless distance parameter
y	dimensionless distance specifically used in the macropore
X	general notation used to define distance parameter
Y	distance parameter specifically used in the macropore
Z	transformed concentration as defined in the text and table
Z_o	value of Z at the center of the pellet

Greek symbols

α	parameter defined as $3(1-\epsilon)\frac{D_{eA}}{D_{aA}}\frac{R^2}{r_i^2}$
α_1	parameter defined as $k_g a_v a_s$
β	intercept in Figures (3.1 - 3.3)
β'	intercept in Figure 3.4
η	effectiveness factor
ϵ	porosity of the pellet
τ	transformation
τ_1	transformation
ν	stoichiometric coefficient
ν_1	parameter defined as $\frac{D_{eA}}{D_{eB}}\nu$
ϕ	general parameter used to define Thiele modulus
ϕ_m	modified Thiele modulus defined as $K_A'\phi^{1.5}$
∇^2	Laplacian operator
θ	transformation

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SECTION II

EFFECTIVENESS FACTORS IN BIDISPERSED CATALYSIS BY THE METHOD OF WEIGHTED RESIDUALS

CHAPTER-4

INTRODUCTION

CHAPTER 4

INTRODUCTION

Many supported catalysts, due to their method of preparation viz. compaction of porous particles into pellets, are characterised by bidispersed size distribution, with microparticles lying inside the porous particles and macroparticles between single or agglomerated particles. Considerable work on diffusion and adsorption in bidispersed catalysts has been reported in the literature (Hashimoto et al, 1976; Uyanik, 1977; Dogu and Smith, 1975; Hashimoto and Smith, 1974), and both the micro- and macroparticle diffusivities can be determined experimentally (see, for example, MacDonald and Habgood, 1972; Dogu and Smith, 1975; Ma and Lee, 1976; Ravi Kumar et al,1982). Studies on the effectiveness of these catalysts have also been numerous. Carberry (1962) evaluated the effectiveness factor for reversible first order reaction in a biporous catalyst. Mingle and Smith (1961) employed several pore distribution functions and obtained a nonisothermal effectiveness factor. Wakao and Smith (1964) studied the effective diffusivity for diffusion in bidispersed porous pellets under reaction conditions and showed the need for information of particle size distribution to predict the effectiveness factor. Thus Silveston & Hashimoto (1975) have incorporated particle size distribution and evaluated the micro- macro particle effectiveness factor.

In a departure from these conventional studies, Ors and Dogu (1979) defined an additional parameter α, the ratio of diffusion times in the micro- and macroparticle regions, and presented an analytical equation for effectiveness factor for a simple first order reaction. The analysis has been subsequently extended to include nonlinear rate forms involving power law kinetics (Jayaraman et al, 1981, 1983).

In this section the effectiveness factors for these types of catalysts with added complexities such as diffusion coefficient variation with concentration (or distance) has been studied (Chapter 5). The subsequent two chapters analyse the role of nonisothermal effects and catalyst fouling. All these complications seem to be pertinent to practical situations and no information regarding the behaviour of biporous pellets under these conditions exists. A general sketch of the micro-macro particle system is shown in Figure 4.1.

Inclusion of these effects in the analysis of the micro-macro effectiveness factor leads to a coupled two point boundary value problem that requires trial and error on the microparticle equations for each integration step of the macroparticle equation, which itself needs trial and error solution. This point has been elucidated in Chapter 5 of this section and it suffices to state here that the conventional finite difference methods become too cumbersome and

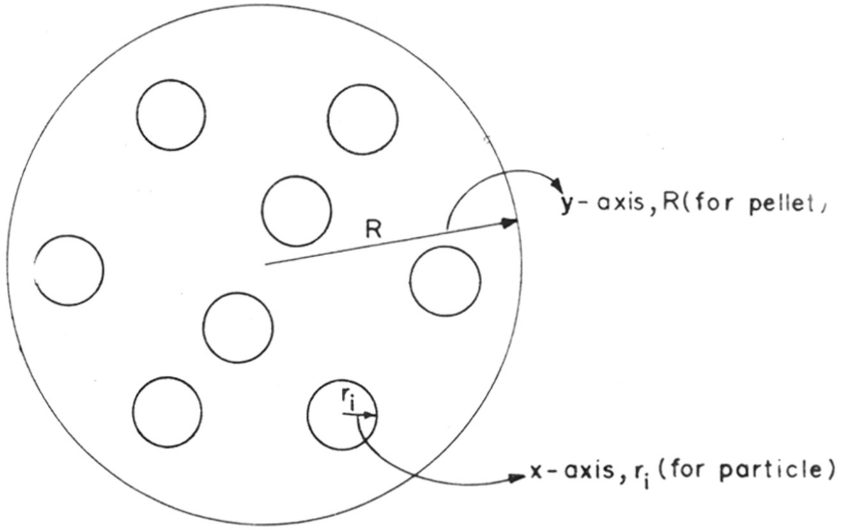

FIG. 4·1: SCHEMATIC DIAGRAM SHOWING MICRO-MACRO PARTICLES IN A PELLET almost impossible to use for obtaining solutions to these problems. In the present work, we employ the methods of weighted residuals (Villadsen and Stewart, 1967; Villadsen and Michelsen, 1978)- more specifically, the Galerkin method- and present comprehensive solutions to these problems with first order main reaction. The order of the method employed is restricted to <u>two</u> to avoid excessive computation. This, of course, restricts the applicability of the results to non-too-large variations in the parameter values. For ranges of parameter values lying beyond those investigated in this work, it would be necessary to employ higher order approximation; however, the results obtained for the parameter ranges are essentially accurate.

The details of the Galerkin method used in this section are given below.

4.1 The Galerkin Method

The method is illustrated for a first order reaction occurring in a spherical catalyst pellet. The dimensionless conservation equations for the above case will be

$$\frac{d^2C}{dx^2} + \frac{2}{x}\frac{dC}{dx} = \phi^2 C \qquad (4.1)$$

with the boundary conditions

$$x = 0, \ \frac{dC}{dx} = 0 \ , \ x = 1 \ , \ C = 1 \qquad (4.2)$$

By using the transformation $u = x^2$ equation 4.1 is converted to

$$4u \frac{d^2C}{du^2} + 6 \frac{dC}{du} = \phi^2 C \tag{4.3}$$

Now the concentration C is defined by the polynomial

$$C = 1 + (1-u) \sum_{i=1}^{N} a_i u^{i-1} , \quad i = 1,2 \ldots N \tag{4.4}$$

such that the boundary conditions given by equation 4.2 are satisfied. The residual R_N is obtained as

$$R_N(a, u) = \sum_{i=1}^{N} a_i \left[(i-1)^2 u^{i-2} - i^2 u^{i-1} \right] - \phi^2 \left[1 + (1-u) \sum_{i=1}^{N} a_i u^{i-1} \right] \tag{4.5}$$

Now R_N is made orthogonal on $\frac{\partial C}{\partial a_i}$ $i = 1,2 \ldots N$ over the volume of the spherical particle. Thus, we get

$$\int_0^1 R_N (a,u) (1-u) u^{i-1} u^{1/2} du = 0, \quad i = 1,2 \ldots N \tag{4.6}$$

These N equations containing N coefficients are then solved to obtain N coefficients.

Sometimes it is difficult to integrate these equations; in such cases these are to be solved by quadrature methods.

Equation 4.6 can be equivalently written as

$$\int_0^1 F_j(u)\,(1-u)\,u^{1/2}\,du = \sum_{k=1}^{M} w_k F_j(u_k) = 0 \qquad (4.7)$$

where $F_j(u) = R_N\,(a,u)\,u^{j-1}$, $j = 1,2 \ldots N$, and M has any value $\geqslant N$. The u_k's are chosen to be zeros of the Jacobi polynomial $P_N^{(1,1/2)}$. Equation 4.7 is solved to obtain the coefficients $a_1, a_2, \ldots . a_N$.

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CHAPTER – 5

STUDY OF DIFFUSIVITY VARIATIONS

CHAPTER 5

STUDY OF DIFFUSIVITY VARIATIONS

In many systems of practical importance such as the ones using synthetic zeolites, it is known that sharp diffusivity variations occur within the pellet. The effective diffusivity within the pellet cannot therefore be treated as constant and some modification to account for this variation should be included in the analysis. In general, the diffusivity variation with concentration is fairly complex (Gelbin and Fiedler, 1980). However, to get a measure of the qualitative influence, it is customary to assume linear or simple exponential dependence (Lin, 1979). Inverse dependence on concentration has been reported by Ruthven and Derrah (1975), while diffusivity going through a minimum with sorbate concentration has been observed by Ruthven and Doetsch (1976). It appears therefore that no general equation that can describe the diffusivity variations can be obtained and recourse to empirical formulation of diffusivity variations with concentration is necessary. An alternative method of accounting for diffusivity variation with concentration is to empirically relate the diffusivity to the distance variable in the pellet. Such a formulation has the advantage that diffusivity variations due to porosity variations can also be included.

In the present study, we consider the inverse dependence of diffusivity on concentration, as well as the following empirical variations of diffusivity with the distance:

$$\begin{aligned} D_i &= D_{io}\,(p - qxy) \\ D_i &= D_{io}\,(p - qy)^n \qquad\qquad (5.1) \\ D_i &= D_{io}\,(\exp(qy)) \end{aligned}$$

where x and y refer to the distance coordinates in the micro- and macroparticles, respectively, and p, q and n are arbitrary constants. It is obvious from these relationships that the first case assumes that the microparticle diffusivity not only varies within the microparticle but also depends on the location of the microparticle in the overall pellet. Cases 2 and 3, on the other hand, assume that the diffusivity varies in relation to the distance in the macroparticle.

5.1 Diffusivity Variations with Distance

5.1.1 Case 1 : Diffusivity variation with respect to both micro- and macroparticle distances

The conservation equations for the reactant species A in the micro-macroparticle system (sphere) subject to the diffusivity variations given by the rate law

$$D_i = D_{io}\,(p - qxy) \qquad (5.2)$$

can be written as

Microparticle:

$$\frac{D_{io}}{X^2}\,\frac{d}{dX}\left[X^2\,(p - qxy)\right]\frac{dC}{dX} = kC \qquad (5.3)$$

$$C = C_A\,,\quad X = r_i\;;\quad \frac{dC}{dX} = 0,\quad X = 0 \qquad (5.4)$$

Nondimensionalising X with respect to r_i and C with respect to C_{AS} and solving, equations 5.3 - 5.4 become

$$\frac{d^2C_i}{dx^2} + \left[\frac{2(p - qxy) - qxy}{x\,(p - qxy)}\right]\frac{dC_i}{dx} = \frac{\phi^2 C_i}{(p-qxy)} \qquad (5.5)$$

$$C_i = C_a,\; x = 1;\quad \frac{dC_i}{dx} = 0,\; x = 0 \qquad (5.6)$$

Macroparticle:

$$\frac{D_a}{Y^2}\,\frac{d}{dY}\left[Y^2\,\frac{dC_A}{dY}\right] = \frac{3(1-\epsilon)}{r_i}\,D_i\left.\frac{dC}{dX}\right|_{X = r_i} \qquad (5.7)$$

$$C_A = C_{AS}\,,\quad Y = R\;;\quad dC_A/dY = 0,\quad Y = 0 \qquad (5.8)$$

The dimensionless form of these equations can be written as

$$\frac{d^2C_a}{dy^2} + \frac{2}{y}\frac{dC_a}{dy} = \alpha(p-qxy)\left.\frac{dC_i}{dx}\right|_{x=1} \qquad (5.9)$$

$$C_a = 1, \quad y = 1; \quad \frac{dC_a}{dy} = 0, \quad y = 0 \qquad (5.10)$$

where C_i and C_a refer to the dimensionless concentrations in the micro- and macroparticles defined with respect to the concentration at the surface of the pellet. It is important to note that the macroparticle distance variable y appears in the microparticle equation. A rigorous solution of these equations would require the following procedure.

For fixed values of the other parameters, p,q and ϕ : (i) Assume a value of C_i at the center of the microparticle and pellet as $C_i = C_{io}$ $(x=0, y=0)$. (ii) Integrate the microparticle equation to reach the surface of the microparticle (x=1) and obtain $C_i = C_{a_1}$ $(x=1, y=0)$. (iii) Use this value of C_{a_1} in the macroparticle equation to obtain the next increment in y $(y=y_1)$ and $C_a = C_{a_2}$. (iv) Revert to the microparticle equation, and for $y=y_1$ and assuming a value of C_i at $x = 0$ integrate till $x=1$ so as to obtain C_i $(x=1, y=y_1) = C_{a_2}$. This requires trial and error solution of the microparticle equation. (v) Repeat the integration procedure for the macroparticle to get the next increment in y and the corresponding C_a, which is then used in the microparticle equation. Continue this procedure till $y=1$ is reached. The specified boundary condition at the surface of the pellet requires that at y=1, C_a should be equal to one. At the end of the integration procedure, if this condition is not satisfied, the whole set of operations should be repeated so as to satisfy this condition. It is obvious that considerable trial and error would be involved with no certainty of obtaining a solution. It is desirable therefore to devise a simpler method that would yield a solution to this problem.

In order to avoid the cumbersome trial and error, the present work employs one of the methods of weighted residuals, viz. the Galerkin method. It is assumed that the concentration in the microparticle is described by the polynomial

$$C_i = C_a + a_1\ (1-u) + a_2 u\ (1-u) \qquad (5.11)$$

where $u=x^2$ and a_1 and a_2 refer to the polynomial coefficients to be determined. Using equation 5.11 in 5.5,

$$u\frac{d^2C_i}{du^2} + \frac{1}{2}\left[1 + \frac{2(p-qy\sqrt{u}) - qy\sqrt{u}}{(p-qy\sqrt{u})}\right]\frac{dC_i}{du} = \frac{0.25\ \phi^2}{(p-qy\sqrt{u})}\left[C_a + a_1\ (1-u) + a_2\ u(1-u)\right] \qquad (5.12)$$

Substituting the values of dC_i/du and $\frac{d^2C_i}{du^2}$ given by

$$\frac{dC_1}{du} = - a_1 + a_2 - 2a_2 u \ , \quad \frac{d^2C_1}{du^2} = - 2a_2$$

the residual is obtained as

$$R_2 = a_2 \left[-2u + 0.5 \left\{ 1 + \frac{2(p-qy\sqrt{u})-qy\sqrt{u}}{(p-qy\sqrt{u})} \right\} (1-2u) - \frac{u(1-u)\phi^2 0.25}{(p-qy\sqrt{u})} \right]$$

$$- a_1 \left[0.5 \left\{ 1 + \frac{2(p-qy\sqrt{u})-qy\sqrt{u}}{(p-qy\sqrt{u})} \right\} + \frac{(1-u)\phi^2 0.25}{(p-qy\sqrt{u})} \right] - \frac{0.25\phi^2 C_a}{p-qy\sqrt{u}}$$

(5.13)

To get the best approximation profile the residual is minimised over the entire volume of the pellet:

$$\int_0^1 R_2 (a,u) (1-u) u^{1/2} du = 0 \qquad (5.14)$$

$$\int_0^1 R_2 (a,u) (1-u)u\, u^{1/2} du = 0 \qquad (5.15)$$

As described in Chapter 4, equations 5.13 and 5.14 can be equivalently written as

$$\int_0^1 F_1 (u) (1-u) u^{1/2} du = 0 \qquad (5.16)$$

$$\int_0^1 F_2 (u) (1-u) u^{1/2} du = 0 \qquad (5.17)$$

where $F_1(u) = R_2(a,u)$ and $F_2(u) = uR_2(a,u)$ which are then solved by quadrature

$$\sum_{k=1}^{M} F_1(u_k)wk = 0 \tag{5.18}$$

$$\sum_{k=1}^{M} F_2\ (u_k)w_k = 0 \tag{5.19}$$

Here $M = 2$, u_k's are chosen to be the roots of the Jacobi polynomial $p_2^{(1,1/2)}$. The resulting algebraic equations are then solved to get the polynomial coefficients a_1 and a_2 as

$$a_1 = f_1\ (u)\ C_a\ ,\ \ a_2 = f_2\ (u)\ C_a \tag{5.20}$$

where the functions f_1 and f_2 are defined as

$$f_1 = -\frac{C_1+f_2A_1}{B_1}\ ,\quad f_2 = \frac{(B_2C_1-B_1C_2)}{(A_2B_1-A_1B_2)}$$

and

$$A_1 = \sum_{k=1}^{M+2} 2u_k-0.5\left\{1+\frac{2(p-qy\sqrt{u_k})-qy\sqrt{u_k}}{(p-qy\sqrt{u_k})}\right\}+\frac{u_k(1-u_k)0.25\phi^2}{(p-qy\sqrt{u_k})}$$

$$A_2 = \sum_{k=1}^{M+2} u_k\left[2u_k-0.5\left\{1+\frac{2(p-qy\sqrt{u_k})-qy\sqrt{u_k}}{(p-qy\sqrt{u_k})}\right\}+\frac{u_k(1-u_k)0.25\phi^2}{(p-qy\sqrt{u_k})}\right]$$

$$B_1 = \sum_{k=1}^{M+2} 0.5 \left\{ 1 + \frac{2(p-qy\sqrt{\bar{u}_k})-qy\sqrt{\bar{u}_k}}{(p-qy\sqrt{\bar{u}_k})} \right\} - \frac{(1-u_k)\phi^2 0.25}{(p-qy\sqrt{\bar{u}_k})}$$

$$B_2 = \sum_{k=1}^{M+2} u_k \left[0.5 \left\{ 1 + \frac{2(p-qy\sqrt{\bar{u}_k})-qy\sqrt{\bar{u}_k}}{(p-qy\sqrt{\bar{u}_k})} \right\} - \frac{(1-u_k)\phi^2 0.25}{(p-qy\sqrt{\bar{u}_k})} \right]$$

$$C_1 = \sum_{k=1}^{M+2} \frac{0.25\,\phi^2}{(p-qy\sqrt{\bar{u}_k})} , \quad C_2 = \sum_{k=1}^{M+2} u_k \frac{0.25\,\phi^2}{(p-qy\sqrt{\bar{u}_k})} \tag{5.21}$$

It is seen from the definitions of parameters that the parameters a_1 and a_2 are functions of position in the macroparticles. The concentration profile (equation 5.11) can then be written as

$$\frac{C_i}{C_a} = 1 + f_1\,(1-u) + f_2 u(1-u) \tag{5.22}$$

It is possible in this particular case to separate the macroparticle concentration and explicitly express C_i in a form such as given by equation 5.22 . In most other cases that follow, it may not be possible to analytically obtain a form similar to equation 5.22. It is necessary in these cases to employ Newton-Raphson or other suitable techniques to obtain the polynomial coefficients.

Once the coefficients a_1 and a_2, and hence the concentration profile for C_i, are known, we can proceed to calculate $(dC_i/dx)_{x=1}$ required in the macroparticle equation (equation 5.9). The MWR methods are, however, known to give better estimates of the effectiveness factor using the integral representations than from the calculations of the flux (Villadsen and Michelsen, 1978). To avoid any error the rhs of equation 5.9 is written in terms of the microparticle effectiveness factor $(\alpha/3\ (\phi^2 \eta_i C_a))$. The microparticle effectiveness factor required is then simply obtained as

$$\eta_i = \frac{1}{C_a} \int_0^1 C_i \, dx^3 \qquad (5.23)$$

which can be analytically evaluated for the present case as

$$\eta_i = 1 + \frac{2}{5} f_1(y) + \frac{6}{35} f_2(y) \qquad (5.24)$$

Again, in most cases, equation 5.23 cannot be evaluated analytically and may have to be solved using quadratures.

The analytical nature of equation 5.24 facilitates the further solution of equation 5.9 which for an assumed polynomial

$$C_a = 1 + b_1 (1-t) + b_2 (1-t) t, \quad t = y^2 \qquad (5.25)$$

becomes

$$u\frac{d^2C_a}{dt^2} + \frac{3}{2}\frac{dC_a}{dt} = \frac{0.25\alpha\phi^2}{3}\eta_1\,(1+b_1(1-t)+b_2t(1-t)) \tag{5.26}$$

The corresponding residual R_2 calculated is

$$R_2 = b_2\left[2t-(1-2t)\frac{3}{2} + t(1-t)p_1\right] + b_1\left[\frac{3}{2}+(1-t)p_1\right] - p_1 \tag{5.27}$$

where $$p_1 = \frac{0.25\,\phi^2\alpha\eta_1}{3}$$

It is seen from equation 5.27 that the residual R_2 involves the microparticle effectiveness factor and depends on the value of t (or y). η_1 therefore needs to be evaluated for each collocation point t_k in the macroparticle equation. Once the function R_2 is identified, we can calculate the functions F_j and evaluate the integral equations 5.16 - 5.17 using Gaussian quadrature. The points t_k are again chosen to be the roots of the polynomial $p_2^{(1,1/2)}$. The solution to equations 5.16 - 5.17 for these functions gives a set of algebraic equations which have been solved to obtain the roots b_1 and b_2.

Once the coefficients b_1 and b_2 are estimated, the overall effectiveness can be obtained as

$$\eta = \frac{\int_0^1 \eta_1 C_a \, dy^3}{\int_0^1 \eta_1 (C_a) C_{a=1} \, dy^3} \qquad (5.28)$$

The effectiveness factor can be obtained using the method of quadratures.

The effectiveness factor η is obtained as a function of ϕ for several values of α. To account for different variations of diffusivities, the parameter q has also been varied. Both positive and negative values of q are analysed. The positive values of q correspond to the case where the microparticle diffusivity increases towards the center of the pellet, while negative values of q connote the reverse. The results obtained are presented in Figure 5.1 and discussed below.

Results and discussion

For the value of $q = 0$, the particular form of diffusivity variations reduces to the case of constant diffusivity, which has been analysed earlier by Ors and Dogu (1979). The results obtained using the present method match with those of Ors and Dogu (1979) for values of α and ϕ equal to or less than 10. At higher values of α or ϕ, more terms would have to be included in the profiles for C_1 and C_a.

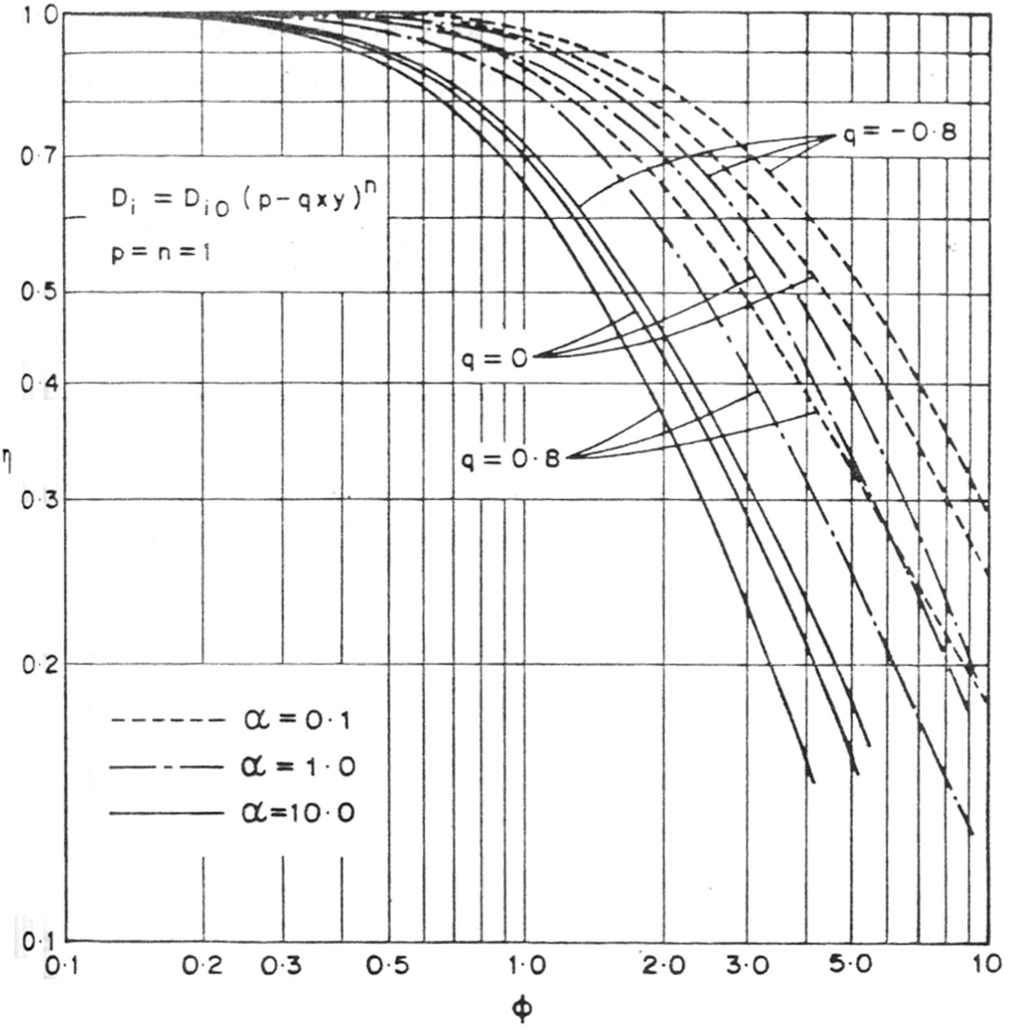

FIG. 5·1: EFFECT OF DIFFUSIVITY VARIATION OF THE FORM $D_i = D_{io}(p-xy)$ ON THE EFFECTIVENESS FACTOR – THIELE MODULUS CURVE FOR VARIOUS VALUES OF α

It is also seen from this figure that for a given value of α the curves with positive values of q lie inside the curve q = 0. Likewise the curves with negative values of q lie outside the curve q = 0. Also, for a given value of q, the deviation from the q = 0 curve is greater for positive values than for negative values of q. This deviation is smaller at lower values of ϕ and increases with increase in ϕ. On increasing the value of α, for given values of q (both +ve or -ve) and ϕ these curves move closer to the curve q = 0. This result in general implies that increase in the parameter α nullifies any effect of diffusivity variation. At lower values of α, and especially for higher values of ϕ, however, the diffusivity variations cannot in general be ignored.

5.1.2 Case 2: Diffusivity variation with respect to macroparticle distance only

We shall now consider diffusivity variation of the form $D_i = D_{io} f(y)$, where the function f(y) depicts linear or exponential variation with regard to the macroparticle distance variable. The conservation equations for this case can be written as

Microparticle:

$$\frac{D_{io}}{X^2} \frac{d}{dX} \left[X^2 \quad \frac{dC}{dX} \right] = \frac{kC}{f(y)} \qquad (5.29)$$

$$C = C_A, \quad X = r_i \; ; \quad \frac{dC}{dX} = 0, \quad X = 0 \qquad (5.30)$$

Macroparticle:

$$\frac{D_a}{Y^2}\frac{d}{dY}\left[Y^2\frac{dC_A}{dY}\right] = \frac{3(1-\epsilon)}{r_i} D_i \left.\frac{dC}{dX}\right|_{X=r_i} \qquad (5.31)$$

$$C_A = C_{AS}\ ,\ Y = R\ ;\quad \frac{dC_A}{dY} = 0\ ,\ Y = 0 \qquad (5.32)$$

The corresponding nondimensional equations are

$$\nabla_x^2 C_i = \frac{\phi^2}{f(y)} C_i \qquad (5.33)$$

$$C_i = C_a,\ x = 1\ ;\quad \frac{dC_i}{dx} = 0\ ,\ x = 0 \qquad (5.34)$$

$$\nabla_y^2 C_a = \alpha f(y) \left.\frac{dC_i}{dx}\right|_{x=1} \qquad (5.35)$$

$$C_a = 1\ ,\ y = 1;\quad \frac{dC_a}{dy} = 0\ ,\ y = 0 \qquad (5.36)$$

Equations 5.32 - 5.34 can be analytically solved to obtain

$$C_i = \frac{C_a}{x}\,\frac{\sinh\left(\frac{\phi}{\sqrt{f(y)}}\,x\right)}{\sinh\left(\frac{\phi}{\sqrt{f(y)}}\right)} \qquad (5.37)$$

Substituting for C_i from equation 5.37 in 5.35 and again employing a two-parameter polynomial similar to equation 5.25, we get

$$u \frac{d^2C_a}{du^2} + \frac{3}{2} \frac{dC_a}{du} - Q\,C_a = 0 \qquad (5.38)$$

$$R_2 = a_2\,(2u - 1.5 + 3u + u(1-u)\,Q\,) + a_1(1.5+(1-u)Q)+Q \qquad (5.39)$$

where $$Q = 0.25\,\alpha\,f(y)\left[\frac{\phi}{\sqrt{f(y)}} \coth \frac{\phi}{\sqrt{f(y)}} - 1\right]$$

Once R_2 is known, following a procedure similar to that for case 1, the overall η is estimated as

$$\eta = -\frac{18\,(b_1 + b_2)}{\alpha\,\phi^2} \qquad (5.40)$$

The effectiveness factor calculated using equation (5.40) is somewhat inaccurate due to the approximate nature of the equation. However, for ranges of parameter values studied here, both the integral form and equation (5.40) yield almost identical result.

Several cases depicting the variations in the $\eta - \phi$ curves for different values of α have been generated for the functions $f(y) = (p-qy)^n$ and $f(y) = \exp(qy)$, with both positive and negative values of q and n. These are shown in Figures 5.2 - 5.5 and the results are summarised below.

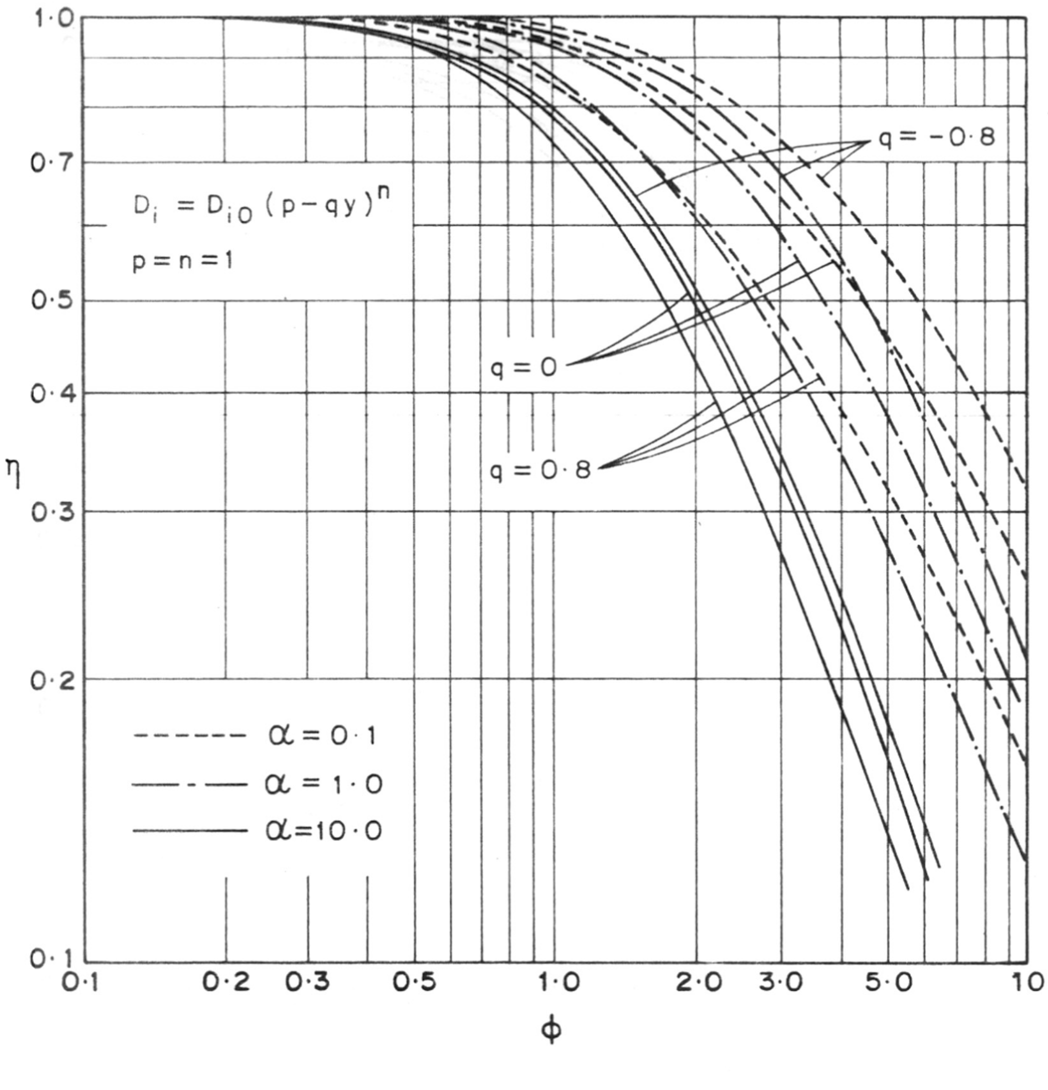

FIG. 5·2: EFFECT OF DIFFUSIVITY VARIATION OF THE FORM $D_i = D_{i0}(p-y)$ ON THE EFFECTIVENESS FACTOR – THIELE MODULUS CURVE FOR VARIOUS VALUES OF α

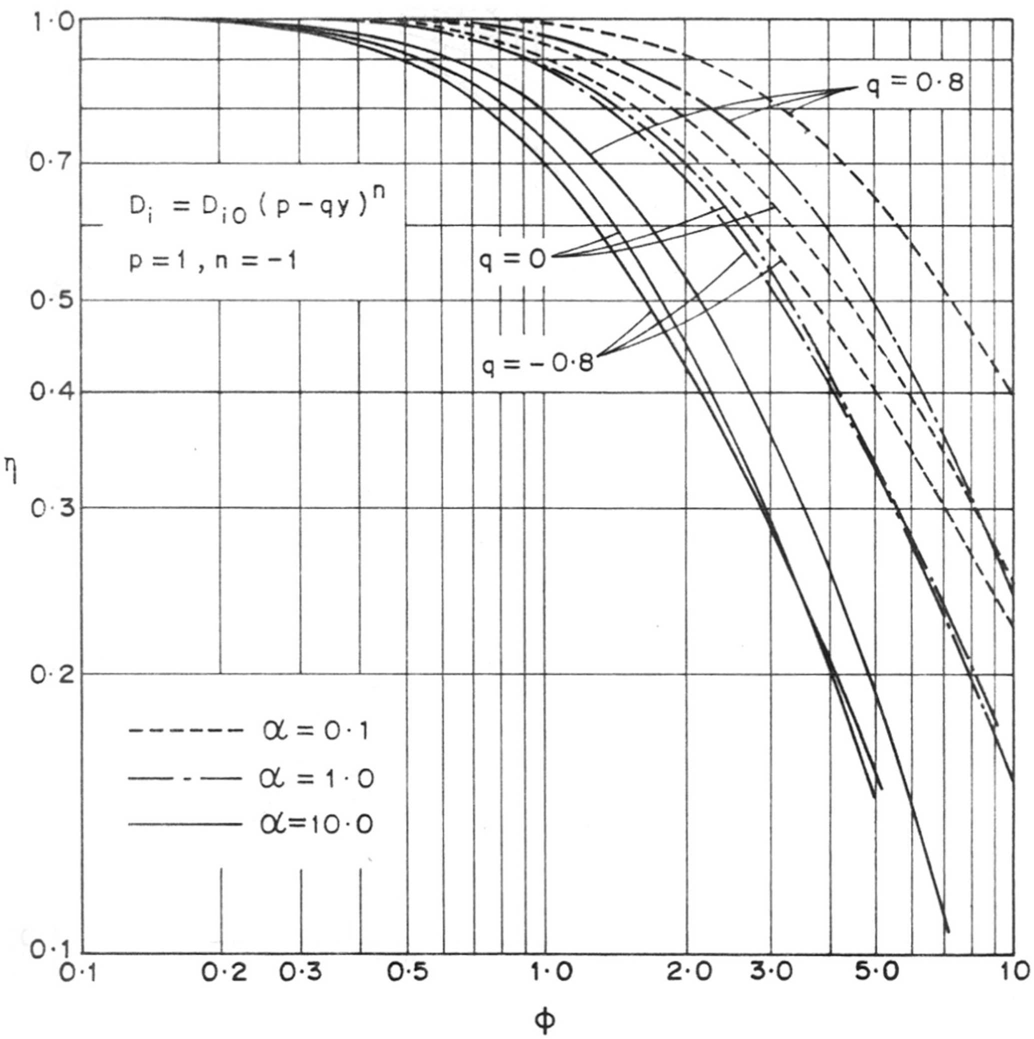

FIG. 5·3: EFFECT OF DIFFUSIVITY VARIATION OF THE FORM $D_i = D_{io}(p-y)^{-1}$ ON THE EFFECTIVENESS FACTOR – THIELE MODULUS CURVE FOR VARIOUS VALUES OF α

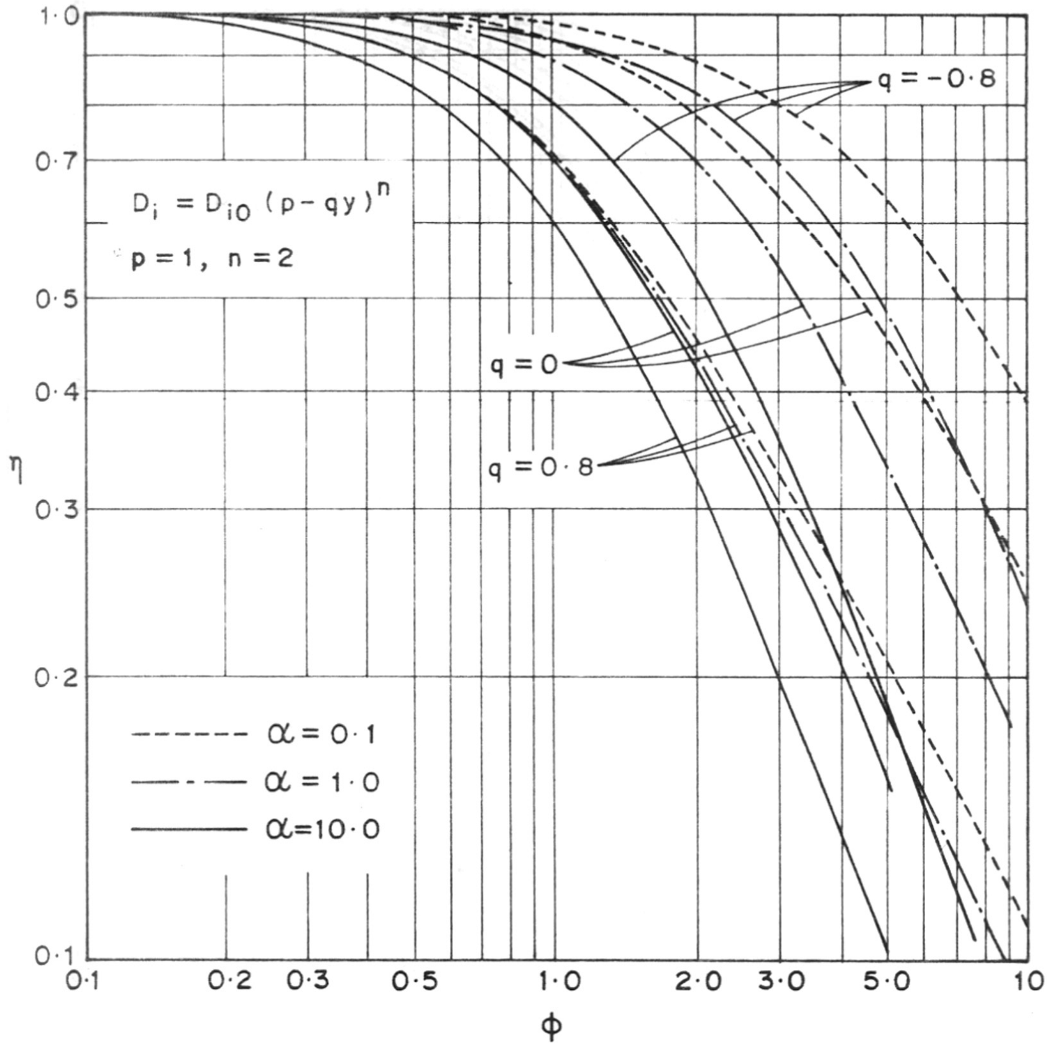

FIG. 5·4: EFFECT OF DIFFUSIVITY VARIATION OF THE FORM $D_i = D_{i0}(p-y)^2$ ON THE EFFECTIVENESS FACTOR – THIELE MODULUS CURVE FOR VARIOUS VALUES OF α

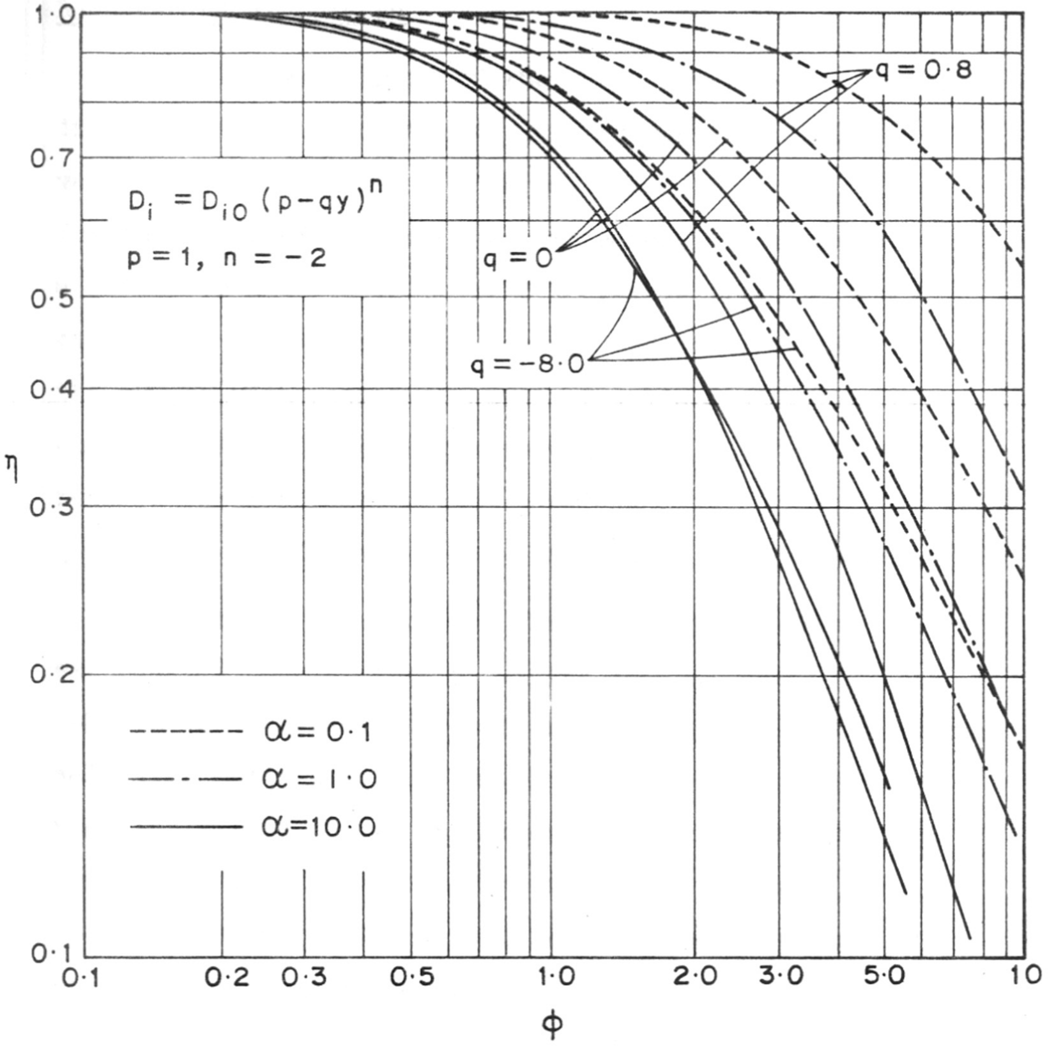

FIG. 5·5: EFFECT OF DIFFUSIVITY VARIATION OF THE FORM $D_i = D_{i0}\,(p-y)^{-2}$ ON THE EFFECTIVENESS FACTOR – THIELE MODULUS CURVE FOR VARIOUS VALUES OF α

Results and discussion

The general trend of the η-ϕ curves is that with increase in the parameter α, the curves for different values of q (and fixed n) moved closer together. Also, for any value of α, as $|n|$ increases, the deviation for a given +ve and -ve value of q increases from the q = 0 curve. As in the previous case for positive values of n, the curves with positive values of q lie inside the q=0 curve and outside for negative values of q. This trend is reversed when n takes negative values (i.e. curves for q(+ve) lie outside and q(-ve) lie inside the q = 0 curve).

In the case where the function f(y) takes an exponential form (Figure 5.6), the general trend of the η-ϕ curves observed suggests that the curves with positive values of q lie outside the q = 0 curve and inside for negative values of q. The observed trend is opposite to that for the linear case. The result is, however, in conformity with the fact that for cases where values of diffusivity increase towards the center the curves lie inside the q = 0 curve and outside for the reverse case. In other words, the effectiveness factor for the same values of other parameters (such as α, ϕ, etc.) decreases when the diffusivity variations are such that a minimum value exists at the surface with progressive increase towards the center.

It is seen from Figure 5.6 for this case that considerable deviations in the effectiveness factor can exist

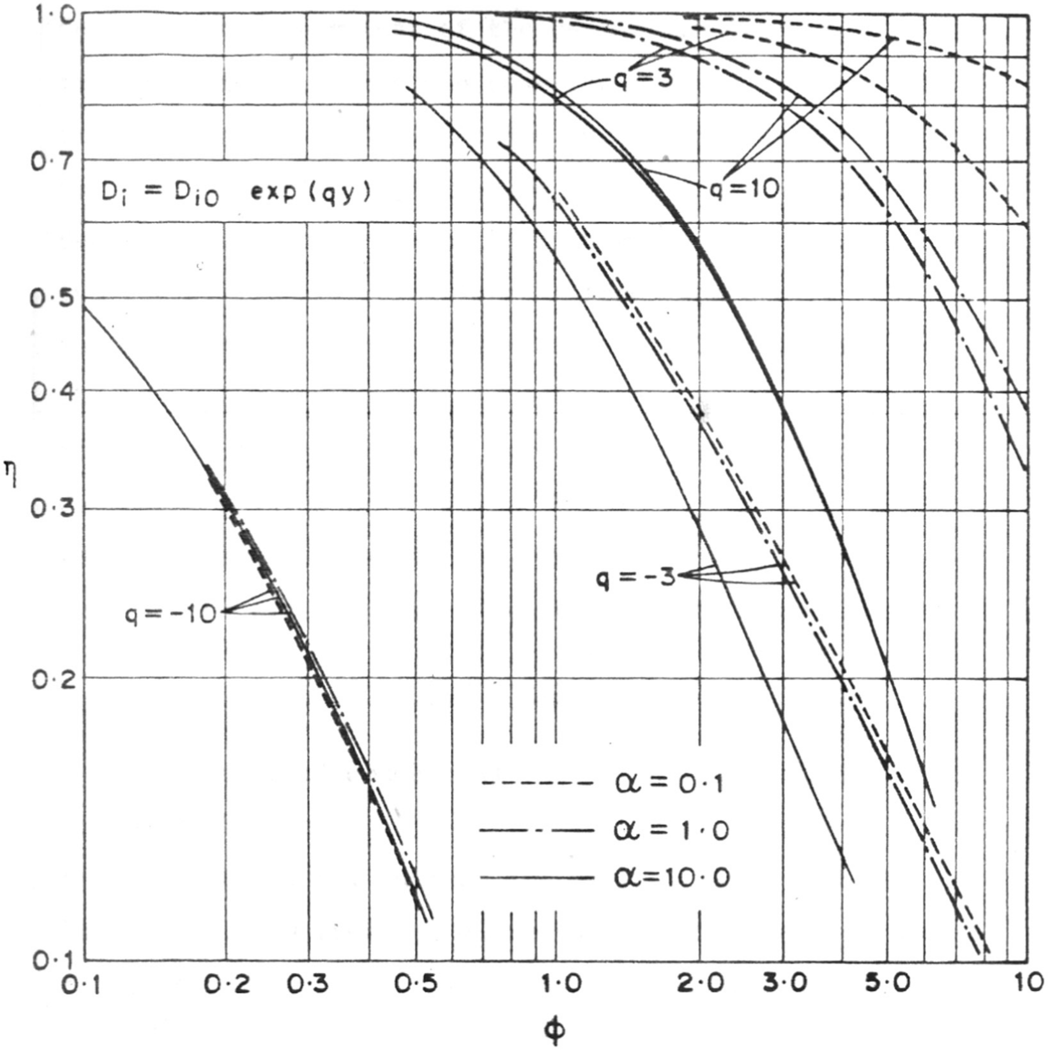

FIG. 5·6: EFFECT OF DIFFUSIVITY VARIATION OF THE FORM $D_i = D_{i0} \exp(qy)$ ON THE EFFECTIVENESS FACTOR–THIELE MODULUS CURVE FOR VARIOUS VALUES OF α

depending on the values of the parameters α and ϕ. The figure typically shows the case for $q = \pm 3$ and $q = \pm 10$ for different α values. As the parameter α increases the relative deviations between the curves for $q = 3$ and 10 decrease, and at sufficiently high value of α ($\alpha > 10$) the two curves are indistinguishable from each other. This result suggests that a severe diffusional limitation in the micropore annhilates any effect due to diffusivity variations for a catalytic system where the diffusivity decreases towards the center. The same, however, cannot be said for the reverse case, where substantial differences in the effectiveness factor exist at high values of .

5.2 Diffusivity Variation with Concentration

In several commercial catalysts, particularly those involving the use of synthetic zeolites, it has been experimentally observed (Ruthven and Derrah, 1975; Ruthven and Doetsch, 1976) that the diffusivity varies inversely with the concentration of the sorbate and can be adequately described by the relation $D_i = D_{io}/C$ where D_{io} represents the concentration independent diffusivity. Incorporating this variation of microparticle diffusivity in the conservation equations for the micro-macroparticles, the equations for a simple first order reaction can be written as

Microparticle:

$$\frac{D_{io}}{X^2}\,\frac{d}{dX}\left[X^2\frac{1}{C}\frac{dC}{dX}\right] = kC \qquad (5.41)$$

$$C = C_A \;, \quad X = r_i \;; \quad \frac{dC}{dX} = 0 \;, \quad X = 0 \qquad (5.42)$$

the corresponding dimensionless form is

$$\frac{d^2C_i}{dx^2} + \frac{2}{x}\,\frac{dC_i}{dx} - \frac{1}{C_i}\left(\frac{dC_i}{dx}\right)^2 = \phi_1^2\, C_i^2 \qquad (5.43)$$

$$C_i = C_a \;, \quad x = 1 \;; \quad \frac{dC_i}{dx} = 0 \;, \quad x = 0 \qquad (5.44)$$

Here the definition of ϕ_1 is modified suitably and is given as

$$\phi_1 = r_i \sqrt{\frac{kC_{AS}}{D_{io}}}$$

Macroparticle:

$$\frac{D_a}{Y^2}\,\frac{d}{dY}\left[Y^2\,\frac{dC_A}{dY}\right] = \frac{3(1-\epsilon)}{r_i}\,\left.\frac{dC}{dX}\right|_{X=r_i} \qquad (5.45)$$

$$C_A = C_{AS} \;, \quad Y = R \;; \quad \frac{dC_A}{dY} = 0 \;, \quad Y = 0 \qquad (5.46)$$

The dimensionless form is

$$\frac{d^2C_a}{dy^2} + \frac{2}{y}\,\frac{dC_a}{dy} = \left.\frac{dC_i}{dx}\right|_{x=1} \qquad (5.47)$$

$$C_a = 1,\; y = 1 \;; \quad \frac{dC_a}{dy} = 0,\quad y = 0 \qquad (5.48)$$

where C_i and C_a represent the dimensionless concentrations with respect to the pellet surface.

Following the method suggested in the earlier cases the microparticle equation has been solved using the Galerkin method to obtain the flux $(dC_i/dx)_{x=1}$ for different values of C_a and ϕ. This information is then used in the macroparticle equation(equation 5.47) which is solved using the Weisz-Hicks (1962) method to obtain the overall effectiveness factor.

Results and discussion

The results are presented in Figure 5.7 as $\eta - \alpha$ curves for several values of ϕ.

An interesting observation from this figure is that at low values of ϕ ($\phi < 1$), the effectiveness factor exceeds unity for $\alpha < 10$. The curves then show a monotonic decrease on further increase of α. In view of the inverse concentration dependence of diffusivity, such a case, viz. $\eta > 1$, is expected, but no evidence of multiple solutions could be generated in the present work.

5.3 Conclusions

To summarise, in the present chapter four different forms of diffusivity variations within the pellet have been considered and analysed using the Galerkin method to obtain

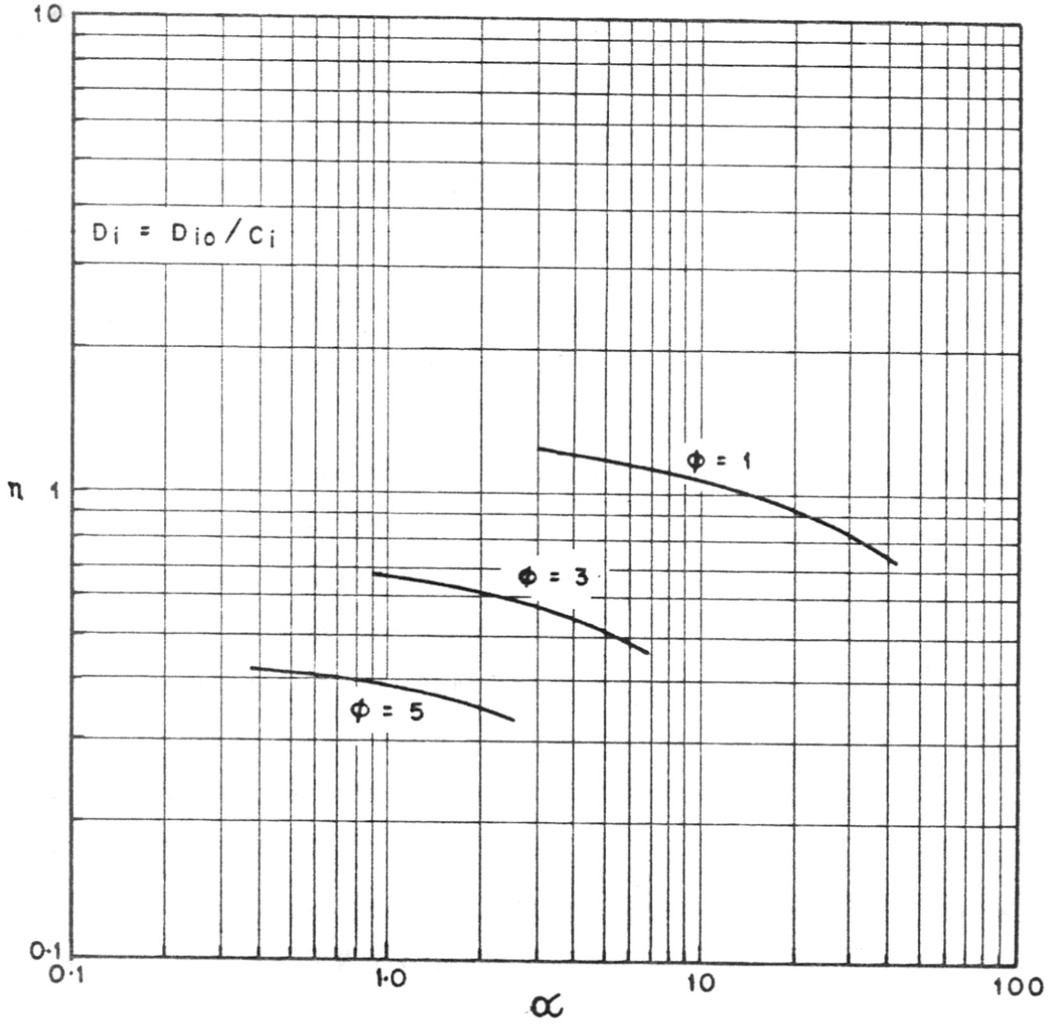

FIG. 5·7 EFFECTIVENESS FACTOR AS A FUNCTION OF α FOR DIFFERENT VALUES OF THIELE MODULUS the variation of the effectiveness factor with system parameters such as α and ϕ. While the individual cases are discussed appropriately, the important general conclusions are:

(1) Diffusivity variations can lead to significant variations in the effectiveness factor values in relation to those obtained with constant diffusivity.

(2) In general, at any value of the Thiele modulus, increasing the diffusive resistance in the microparticle (increasing α) leads to a lowering of the effectiveness factor.

(3) Higher values of the effectiveness factor than those at constant diffusivity (for given values of α and ϕ) can be obtained for a catalyst where the diffusivity decreases towards the center from the surface. This statement is valid for all the variation forms studied here and suggests an important finding, since the catalyst can be tailor-made to meet this requirement.

(4) Higher values of η are realised for cases where both α and ϕ are small.

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CHAPTER – 6

ROLE OF NONISOTHERMICITY

CHAPTER 6

ROLE OF NONISOTHERMICITY

The problem of estimation of effectiveness factors under nonisothermal conditions has been studied over the past few years. Texts like those of Aris (1975), Froment and Bischoff (1979) and Doraiswamy and Sharma (1983) have discussed first order reaction taking into account different geometries in a catalyst particle under these conditions.

Weisz and Hicks (1962) used a simple method to obtain effectiveness factors for a first order reaction in a nonisothermal catalyst pellet and plotted the results in terms of effectiveness factor vs. Thiele modulus for various values of other parameters. Subsequently, orthogonal collocation was used (Pattersen and Creswell, 1971) for a nonisothermal reaction of arbitrary kinetics in a catalyst pellet.

The phenomenon of multiplicity of steady states is observed under nonisothermal conditions for some ranges of the parameters of the system. The existence of five steady states has been noticed for bimolecular Langmuir-Hinshelwood kinetics in the simultaneous but independent works of Elnashaie and Mahfouz (1978) and Pereira and Varma (1978). Pereira and Varma (1978) have shown that even for isothermal and modestly nonisothermal bimolecular Langmuir-Hinshelwood kinetics existence of five steady states is possible. The multiplicity pattern is found to be 1-3-5-3-1.

Wong and Szepe (1982) studied the general nonisothermal case of bimolecular Langmuir-Hinshelwood kinetics for exothermic as well as endothermic reactions and observed that even for endothermic reactions multiplicity exists in a region where $\eta < 1$.

More complex cases of isothermal and nonisothermal effectiveness factor such as for redox kinetics have been studied by Lakshman and Chanda (1984).

So far the study of effectiveness factors under nonisothermal conditions has been restricted to monoporous catalyst pellets (except that of Mingle and Smith, 1961). Since the catalysts used in industry are mostly bidispersed there is need to study nonisothermal effects in this type of catalysts.

In the present work we have studied a simple first order irreversible, exothermic reaction in a bidispersed catalyst. Due to the bidispersed nature of the catalyst, in addition to the usual parameters such as γ, α , β , a new parameter α_T has been introduced which defines the ratio of thermal conductivity time for heat in the microparticle to that in the macroparticle. The inclusion of an additional parameter is expected to enhance the complexities such as multiplicity patterns further. Here even for a first order reaction five steady states can occur under conditions of no external transport limitations, which is otherwise absent in the monopore case. α_T has an interesting influence on the $\eta - \alpha$ curve and an unusual multiplicity pattern 1-3-5-3-5-3-1 is obtained with two regions of five steady states.

6.1 Analysis of the Problem

The mass and heat balance equations for the micro-macroparticle system can be written as

Microparticle:

Mass balance

$$\frac{D_{io}}{X^2} \frac{d}{dX} \left[X^2 \frac{dC}{dX} \right] = kC \qquad (6.1)$$

$$C = C_A \ , \quad X = r_i \ ; \quad \frac{dC}{dX} = 0 \ , \quad X = 0 \qquad (6.2)$$

Heat balance

$$\frac{k_e}{X^2} \frac{d}{dX} \left[X^2 \frac{dT}{dX} \right] = (-\Delta H) \, kC \qquad (6.3)$$

$$T = T_s \ , \ X = r_i \ ; \quad \frac{dT}{dX} = 0, \quad X = 0 \qquad (6.4)$$

where $k = k_o \exp(-E/R_g T) \ , \quad \frac{k(T_s^s)}{k(T)} = \exp(-\gamma(1 - \frac{1}{T_i}))$

(6.5)

After proper nondimensionlisation, the equations take the form

$$\nabla_x^2 C_i = \phi^2 \exp \left(\gamma (1 - \frac{1}{T_i} \right) C_i \qquad (6.6)$$

$$C_i = C_a \ , \ x = 1 \ ; \ \frac{dC_i}{dx} = 0 \ , \ x = 0 \qquad (6.7)$$

$$\nabla_x^2 T_i = - \phi^2 \left[\exp \left(\gamma (1 - \frac{1}{T_i}) \right) \right] C_i \qquad (6.8)$$

$$T_i = T_a \ , \ x = 1 \ ; \ \frac{dT_i}{dx} = 0, \ x = 0 \qquad (6.9)$$

where $$\beta = \frac{D_{io} (-\triangle H) C_{AS}}{k_e T_s^s} \quad \text{and} \quad \gamma = \frac{E}{R_g T_s^s} \qquad (6.10)$$

Macroparticle:

Mass balance

$$\frac{D_a}{Y^2} \frac{d}{dY} \left[Y^2 \frac{dC_A}{dY} \right] = \frac{3^{(1-\epsilon)}}{r_i} \left. \frac{dC}{dX} \right|_{X=r_i}$$

$$(6.11)$$

$$C_A = C_{AS} \ , \ Y = R \ ; \ dC_A/dY = 0 \ , \ Y = 0 \qquad (6.12)$$

Heat balance

$$\frac{k_a}{Y^2} \frac{d}{dY} \left[Y^2 \frac{dT_s}{dY} \right] = \frac{3^{(1-\epsilon)} k_e}{r_i} \left. \frac{dT}{dX} \right|_{X=r_i} \qquad (6.13)$$

$$T_s = T_s^s \, , \quad Y = R \; ; \quad \frac{dT_s}{dX} = 0 \, , \quad Y = 0 \qquad (6.14)$$

The corresponding dimensionless equations are

$$\nabla_y^2 C_a = \alpha \left. \frac{dC_i}{dx} \right|_{x=1} \qquad (6.15)$$

$$C_a = 1, \quad y = 1; \quad dC_a/dy = 0 \, , \quad y = 0 \qquad (6.16)$$

$$\nabla_y^2 T_a = \alpha_T \left. \frac{dT_i}{dx} \right|_{x=1} \qquad (6.17)$$

$$T_a = 1 \, , \quad y = 1 \; ; \quad \frac{dT_a}{dy} = 0 \, , \; y = 0 \qquad (6.18)$$

where

$$\alpha_T = 3 \, (1 - \epsilon) \, \frac{k_e}{k_a} \, \frac{R^2}{r_i^2} \qquad (6.19)$$

Equations 6.6 and 6.8 can be combined by using the boundary conditions, (equations 6.7 and 6.9), to eliminate T_i in terms of C_i and the following relation is obtained :

$$T_i = T_a + \beta (C_a - C_i) \qquad (6.20)$$

Similarly, T_a is eliminated in terms of C_a by using equations 6.15 - 6.18 :

$$T_a = 1 + \frac{\alpha_T}{\alpha} \, \beta \, (1 - C_a) \qquad (6.21)$$

By using equations 6.20 and 6.21 in 6.6 the final set of equations will be

$$\nabla_x^2 C_i = \phi^2 \left[\exp \left\{ \gamma \left(1 - \frac{1}{1 + \frac{\alpha_T}{\alpha} \beta (1 - C_a) + \beta (C_a - C_i)} \right) \right\} \right. \tag{6.22}$$

$$C_i = C_a \ , \quad x = 1 \ ; \quad \frac{dC_i}{dx} = 0 \ , \quad x = 0 \tag{6.23}$$

which has to be solved along with equations 6.15 - 6.16 .

Here the concentration and temperature in the micro- and macroparticle system are nondimensionalised with respect to concentration and temperature at the surface of the pellet. α denotes the ratio of the diffusion times for mass in the microparticle to that in the macroparticle region, while α_T refers to the ratio of the thermal conductivity times for heat. The ratio D_i/D_a appearing in α is usually less than unity, while the ratio k_e/k_a appearing in α_T is usually far greater than unity. The ratio α_T/α is therefore always greater than unity in practical systems.

By applying polynomial approximation, C_i is given by

$$C_i = C_a + a_1 (1-u) + a_2 u(1-u), \ u = x^2 \tag{6.24}$$

The microparticle equation can then be written as

$$u \frac{d^2C_i}{du^2} + 1.5 \frac{dC_i}{du} = 0.25\phi^2 C_i \exp\left\{\gamma\left(1 - \frac{1}{1 + \frac{\alpha_T}{\alpha}\beta(1-C_a) + \beta(C_a - C_i)}\right)\right\} \tag{6.25}$$

The corresponding residual is obtained as

$$R_2 = 6(a_2 - a_1) - 20a_2u - \phi^2 C_i \exp\left\{\gamma\left(1 - \frac{1}{1 + \frac{\alpha_T}{\alpha}\beta(1-C_a) + \beta(C_a - C_i)}\right)\right\} \tag{6.26}$$

Applying the Galerkin method we get the following two equations:

$$\int_0^1 R_2\ (a,u)\ u^{1/2}\ du \tag{6.27}$$

$$\int_0^1 R_2\ (a,u)u\ u^{1/2}\ du \tag{6.28}$$

which are solved to get the values of a_1 and a_2. Once the C_i profile is known $\left.\frac{dC_i}{dx}\right|_{x=1}$ is calculated for several values of C_a for a particular set of other parameter values (γ, β, α_T/α, ϕ). The tables of $\left.\frac{dC_i}{dx}\right|_{x=1}$ vs. C_a for different sets of parameters are given in Tables 6.1 - 6.7. It is seen that for lower values of ϕ for other parameter ranges (studied here), $\left.\frac{dC_i}{dx}\right|_{x=1}$ vs. C_a curves pass through maxima.

To solve the macroparticle equation it is seen that $\left.\frac{dC_i}{dx}\right|_{x=1}$ depends on C_a . For that, a large volume of data is collected and the results are interpolated to obtain $\left.\frac{dC_i}{dx}\right|_{x=1}$ for any value of C_a . For this purpose spline interpolation scheme has been used. The equation is integrated using Weisz and Hicks' (1962) method.

The effectiveness factor is finally obtained as

$$\eta = \frac{9 \left.\frac{dC_a}{dy}\right|_{y=1}}{\alpha \phi^2}$$

The results are plotted in terms of effectiveness factors vs. α for constant values of other parameters. It is seen that the final results are very sensitive to the number of interpolation points. Here caution should be exercised in obtaining sufficient number of interpolation points so that the final results are qualitatively correct.

6.2 Results and Discussion

The effectiveness factors thus calculated are presented as $\eta - \alpha$ plots showing the influence of variations in ϕ, γ, β, and α_T/α . Thus Figure 6.1 indicates the influence of ϕ on the $\eta - \alpha$ plot. The figure indicates the existence of a region of five steady states which extends

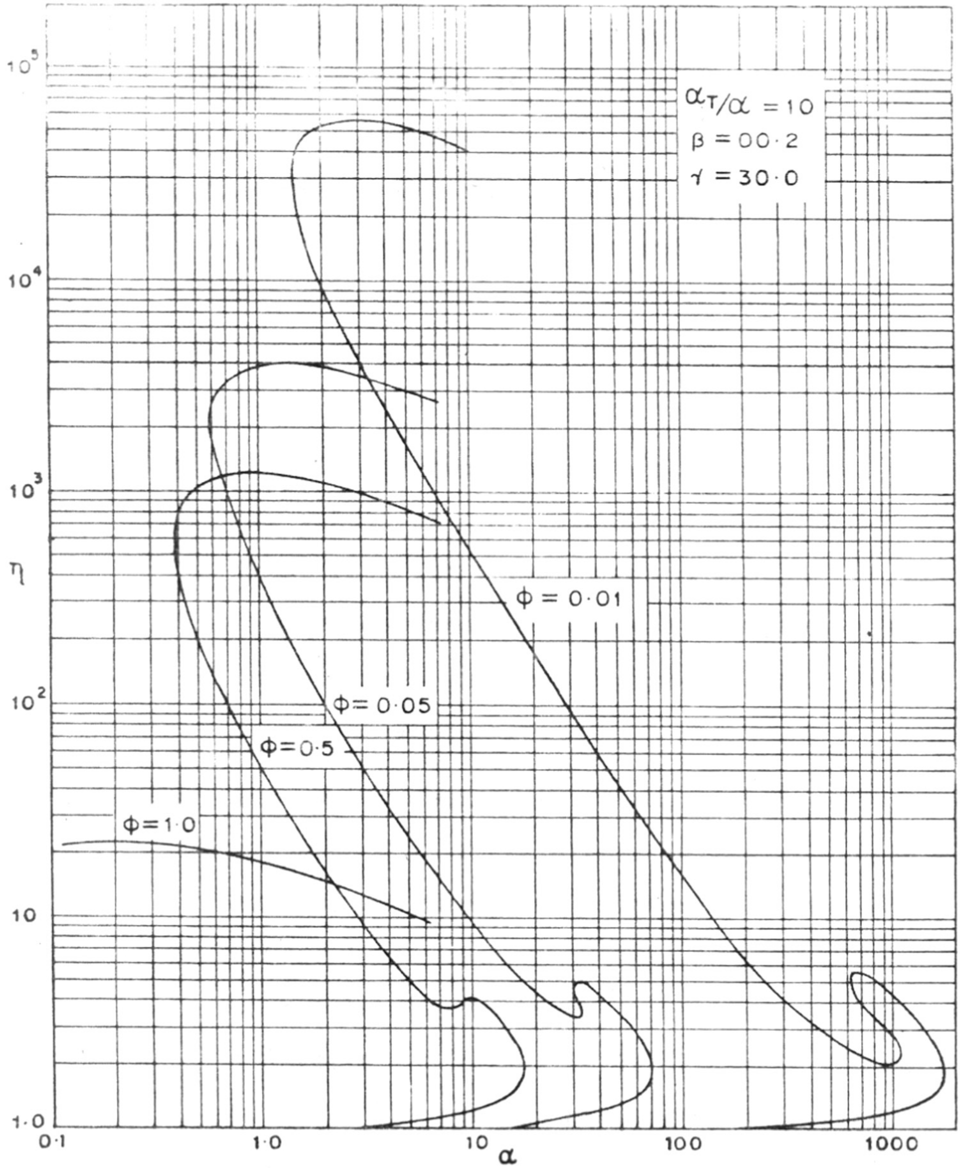

FIG. 6·1 : EFFECTIVENESS FACTORS FOR NONISOTHERMAL MICRO-MACRO PARTICLE SYSTEMS: η-α VARIATIONS WITH RESPECT TO ϕ

with decrease in ϕ. Thus for $\phi = 0.01$ the five steady state region covers the α-parameter space from $\alpha = 600$ to 1100, while for $\phi = 0.05$, it covers a narrower α - range, 30-34. For $\phi = 0.1$ the five steady state region has completely disappeared but multiplicity (3 states) still persists. For $\phi = 1$ multiplicity disappears altogether. Also, as evident from the figure, higher values of η are realised for lower values of α, especially when ϕ is also smaller.

Two points may be noted at this stage :

(1) The values of η as calculated are higher than those reported for monoporous systems. Direct comparison with the monopore case, however, is not possible due to the presence of α and α_T in the present case.

(2) The region where five steady states exist appears to shift to higher values of α when ϕ becomes smaller. The existence of five steady states in monoporous systems is known, especially when external transport limitations are present (Pereira and Varma, 1978; Elnashaie and Mahfouz, 1978). The present case reveals that the biporous nature of the catalyst can also induce five steady states in certain regions of the parameter space.

Figure 6.2 shows the influence of the ratio α_T/α on the $\eta - \alpha$ curve. The figure again reveals the existence of five

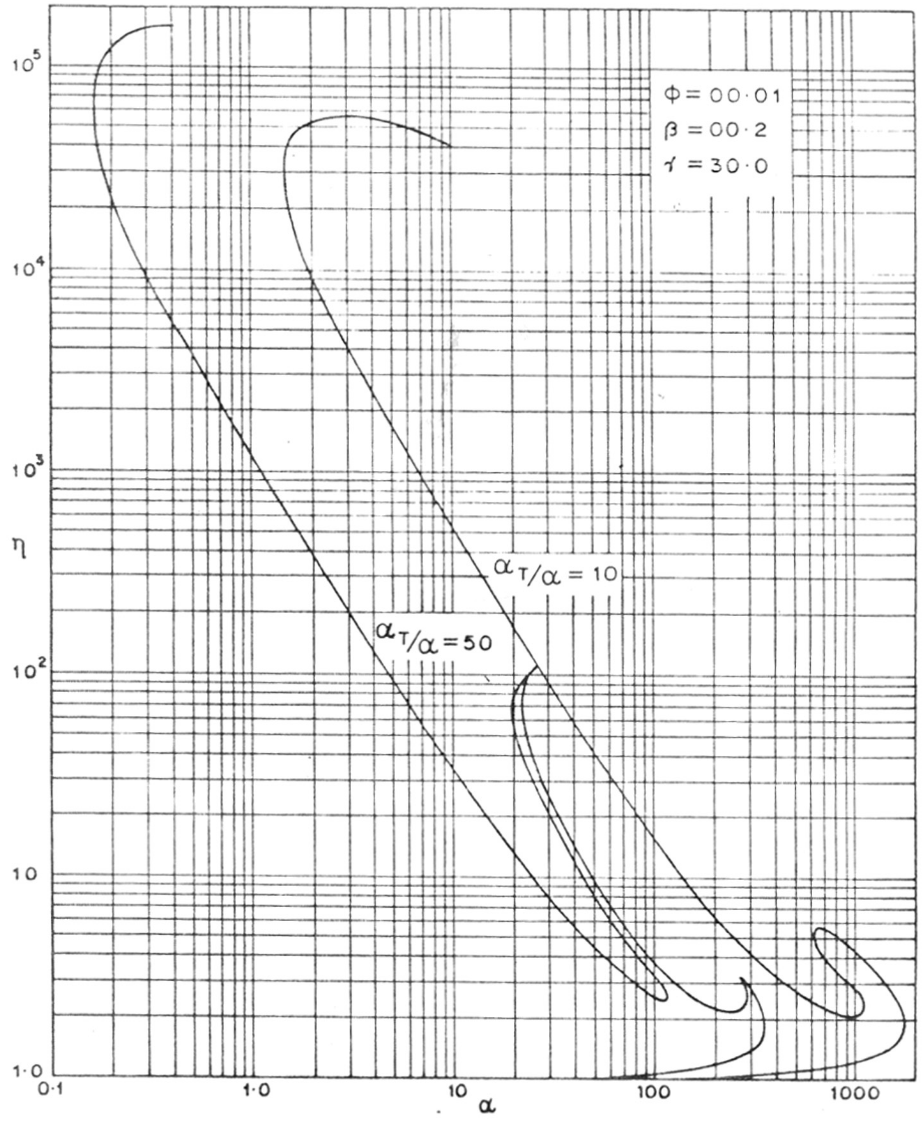

FIG. 6·2: EFFECTIVENESS FACTORS FOR NONISOTHERMAL MICRO-MACRO PARTICLE SYSTEMS: η-α VARIATIONS WITH RESPECT TO α_T/α

steady states. The curve for $\alpha_T/\alpha = 50$ is especially interesting in that it reveals two different regions in the parameter space where five steady states can prevail. On increasing α, the figure reveals the multiplicity pattern 1-3-5-3-5-3-1. Such a pattern is rather unusual and provides perhaps the first instance of its occurrence. The figure also shows that higher values of   are realised when α_T/α is larger. The five steady state region occurs at lower values of   for higher values of α_T/α, and the region in general is narrower than at lower values of the α_T/α. The intermediate states also lie closer to each other for higher values of (α_T/α).

Figure 6.3 shows the influence of β on the η-α plot. As expected, for a reaction of higher nonisothermicity, the η - α plot shifts to the left. The five steady state region occurs at lower values of α, the intermediate states move closer to each other, and higher values of η can be realised at lower values of α. Figure 6.4 shows the influence of γ. Increasing γ has the same effect as increasing β and the results indicated in Figures 6.3 and 6.4 are qualitatively in accord with those known for a monoporous system.

6.3 Conclusions

The present work reports effectiveness factors for a micro-macroparticle system in the presence of an exothermic first order reaction. The results indicate that in general

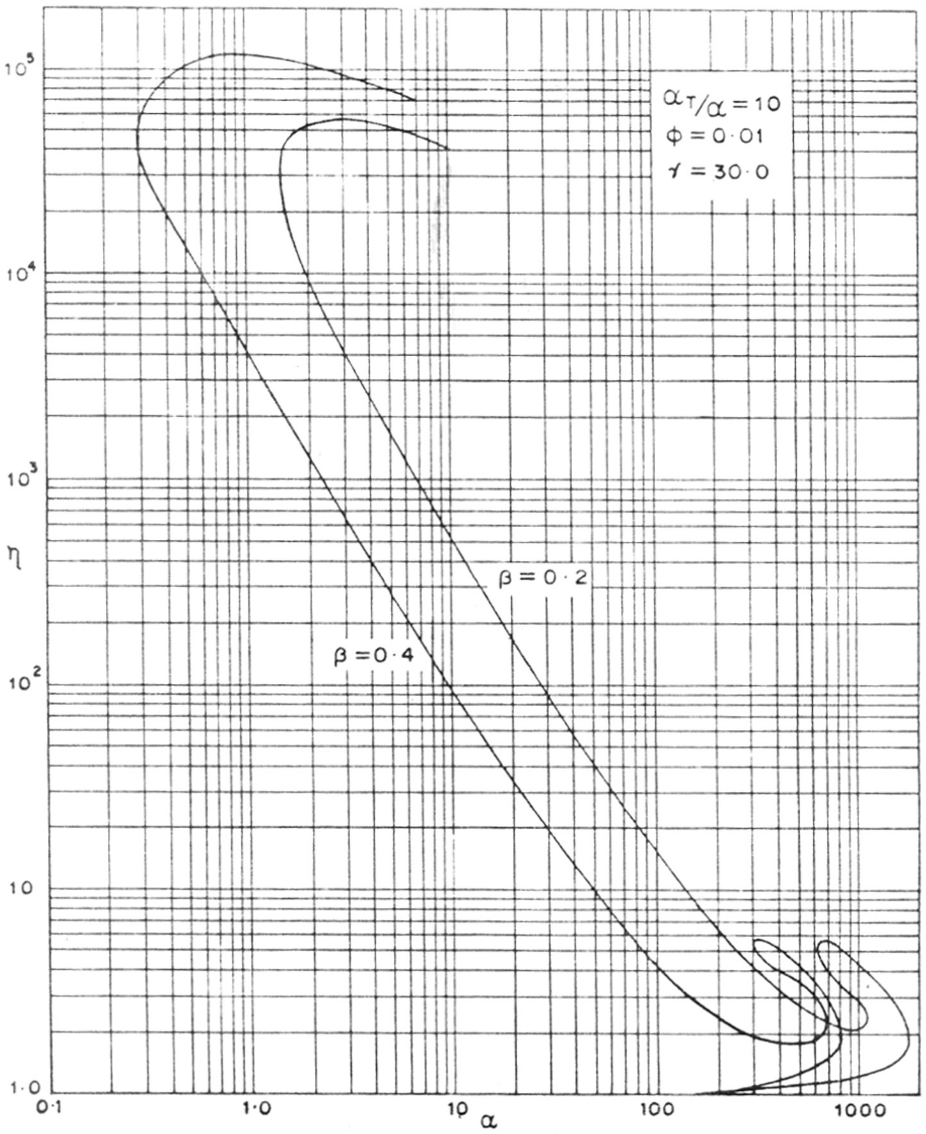

FIG. 6.3 : EFFECTIVENESS FACTORS FOR NONISOTHERMAL MICRO–MACRO PARTICLE SYSTEMS: η–α VARIATIONS WITH RESPECT TO β

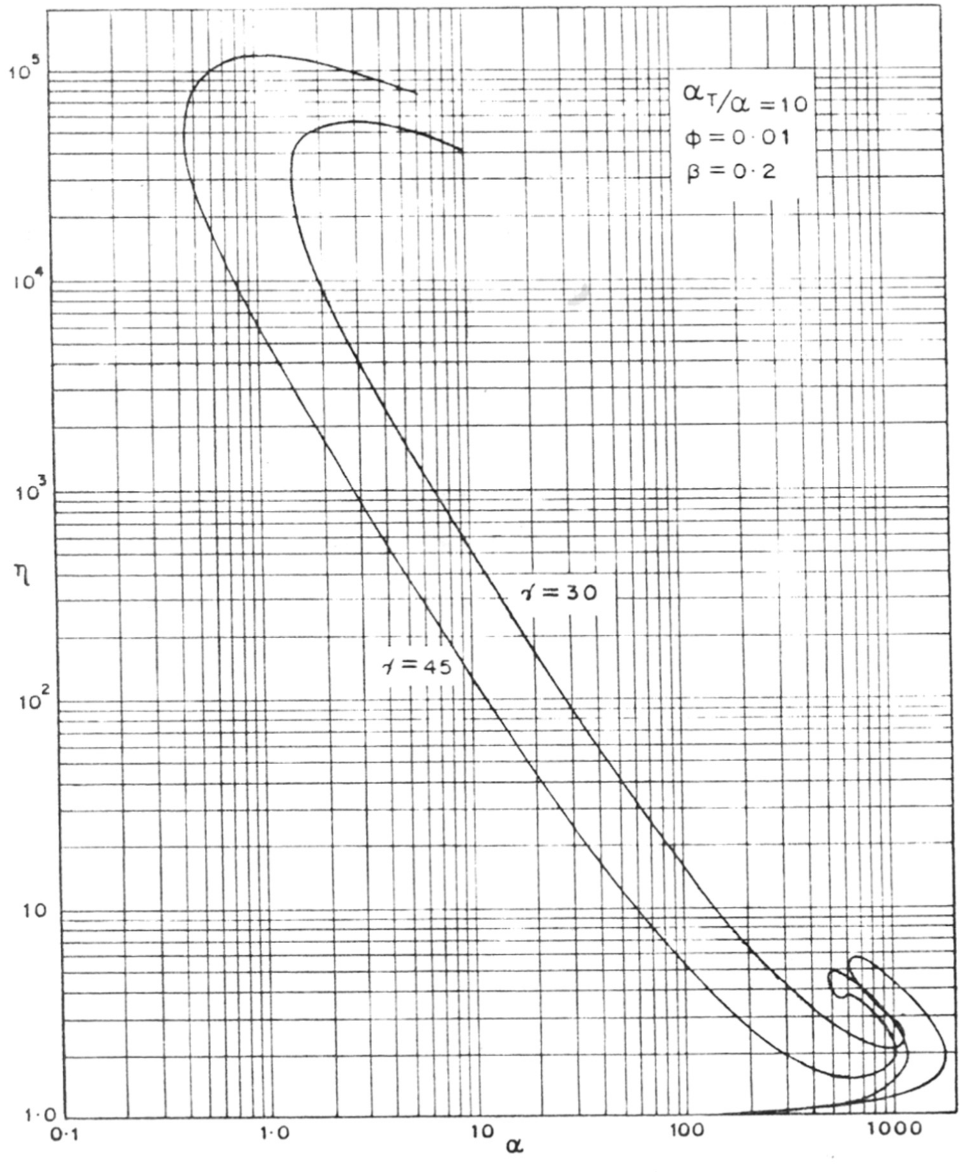

FIG. 6.4: EFFECTIVENESS FACTORS FOR NONISOTHERMAL MICRO-MACRO PARTICLE SYSTEMS: η-α VARIATIONS WITH RESPECT TO γ

higher values of η can be realised for such systems in comparison with those for monoporous systems, especially at lower values of α. The system can possess five stationary states in a certain parameter region even in the absence of external transport limitations. The influence of parameters such as ϕ, β, γ and α_T/α has been investigated and the results suggest that increase in the value of any of these parameters would shift the $\eta - \alpha$ plot to the left. The ratio α_T/α has an especially important influence in that two separate regions of five steady states can be identified. The influence of β and γ is similar to that for the monoporous system and has been quantified.

...

TABLE 6.1

$\phi=0.01$, $\beta=0.2$, $\gamma=30$, $\alpha_T/\alpha=10$

Ca	Flux
0.001	8.99 E-03
0.005	0.04498
0.01	0.0899
0.02	0.17978
0.03	0.2696
0.05	0.4498
0.07	0.629
0.1	0.8982
0.15	1.3466
0.2	1.7936
0.25	2.2382
0.3	2.6788
0.35	3.1112
0.4	3.5278
0.45	3.9192
0.5	4.229
0.55	4.3988
0.6	4.241
0.62	4.0116
0.63	3.8546
0.64	3.646
0.65	3.4070
0.66	3.1334
0.67	2.8312
0.68	2.5116
0.69	2.189
0.7	1.8712
0.72	1.30016

...

Table 6.1 contd

Ca	Flux
0.75	0.6376
0.78	0.2712
0.79	0.2008
0.8	0.14852
0.82	0.07934
0.85	0.02916
0.87	0.01461
0.875	0.011842
0.9	4.66 E-03
0.92	1.9244 E-03
0.94	7.8 E-04
0.96	2.9536 E-04
0.98	1.03574 E-04
0.99	5.943 E-05
1.00	3.32 E-05

TABLE 6.2

$\phi=0.01$, $\beta=0.2$, $\gamma=30$, $\alpha_T/\alpha=10$

Ca	Flux
0.001	8.99 E-03
0.005	0.04498
0.01	0.0899
0.03	0.2696
0.07	0.629
0.09	0.818
0.1	0.8984
0.15	1.3496
0.2	1.7936
0.25	2.249
0.3	2.6986
0.35	3.1478
0.4	3.5964
0.45	4.0492
0.55	4.9364
0.6	5.3478
0.65	5.7294
0.7	5.9976
0.75	5.9058
0.78	5.3302
0.79	4.944
0.8	4.4112
0.81	3.7725
0.83	2.2458
0.84	1.6478
0.85	1.1734
0.86	0.7472

....

Table 6.2 contd.

Ca	Flux
0.87	0.456
0.88	0.28794
0.89	0.18536
0.9	0.1198
0.92	0.04916
0.93	0.03154
0.94	0.01978
0.97	4.42 E-03
0.98	2.5952 E-03
0.99	1.48776 E-03
1.00	8.34 E-04

TABLE 6.3

$\phi = 0.1$, $\beta = 0.2$, $\gamma = 30$, $\alpha_T/\alpha = 10$

Ca	Flux
0.001	8.982 E-03
0.005	0.04498
0.01	0.0899
0.02	0.17978
0.05	0.4498
0.07	0.629
0.1	0.8984
0.15	1.3496
0.2	1.7936
0.25	2.249
0.3	2.6986
0.35	3.1478
0.4	3.5992
0.45	4.048
0.5	4.4964
0.55	4.9432
0.6	5.3862
0.65	5.819
0.7	6.2234
0.75	6.5404
0.8	6.5436
0.82	6.278
0.83	6.0108
0.84	5.589
0.85	4.9268
0.86	3.952

...

Table 6.3 contd.

Ca	Flux
0.87	2.8456
0.88	1.9642
0.89	1.3316
0.9	0.7484
0.92	0.22574
0.94	0.08306
0.95	0.05038
0.98	0.0104552
0.99	5.9766 E-03
1.00	3.3444 E-03

TABLE 6.4

$\phi = 1$, $\gamma = 30$, $\beta = 0.2$, $\alpha_T/\alpha = 10$

Ca	Flux
0.001	8.99 E-03
0.005	0.04498
0.01	0.0899
0.03	0.2696
0.05	0.4498
0.07	0.629
0.1	0.8982
0.15	1.3466
0.2	1.7936
0.25	2.248
0.3	2.6994
0.35	3.1494
0.4	3.5952
0.45	4.04928
0.5	4.499
0.55	4.949
0.6	5.3988
0.65	5.8486
0.7	6.298
0.75	6.7466
0.8	7.1924
0.85	7.6268
0.9	8.0102
0.95	8.091
0.96	7.9636
0.97	7.68417

...

Table 6.4 contd.

Ca	Flux
0.975	7.4316
0.98	7.0186
0.985	6.1874
0.986	5.8842
0.987	5.46
0.988	4.8128
0.989	3.9726
0.9892	4.38228
0.9895	3.621
0.99	3.3402
0.995	2.0572
0.997	1.8088
0.999	1.6158
0.9995	1.5738
1.00	1.5338

TABLE 6.5

$\alpha_T/\alpha = 50$, $\beta = 0.2$, $\gamma = 30$, $\phi = 0.01$

Ca	Flux
0.001	9.984 E-03
0.005	0.04498
0.007	0.06298
0.01	0.0884
0.03	0.2699
0.05	0.4498
0.07	0.62988
0.1	0.89984
0.15	1.34976
0.2	1.79964
0.25	2.24961
0.3	2.6994
0.35	3.1494
0.4	3.5992
0.45	4.0492
0.5	4.4992
0.55	4.949
0.6	5.3988
0.65	5.8488
0.7	6.2984
0.75	6.7558
0.8	7.195
0.85	7.626
0.9	7.8022
0.91	7.6172
0.92	7.1014
0.93	5.7594

....

Table 6.5 contd.

Ca	Flux
0.935	4.5214
0.94	3.0482
0.942	2.5072
0.944	2.0268
0.946	1.6052
0.95	0.916
0.951	0.7812
0.952	0.6644
0.953	0.56476
0.954	0.4812
0.955	0.4082
0. 956	0.3472
0.957	0.2954
0.958	0.2514
0.959	0.2138
0.96	0.1816
0.97	0.0338
0.975	0.013208
0.98	4.863 E-03
0.985	1.645 E-03
0.99	5.04808 E-04
0.994	1.81056 E-04
0.995	1.3853 E-04
0.996	1.05266 E-04
0.998	5.99302 E-05
0.999	4.4819 E-05
0.9992	4.226 E-05
0.9994	3.98402 E-05
0.9996	3.75516 E-05
0.9998	3.53844 E-05
0.9999	3.4344 E-05
1.0	3.3334 E-05

TABLE 6.6

$\beta = 0.4$, $\alpha_T/\alpha = 10$, $\phi = 0.01$, $\gamma = 30$

Ca	Flux
0.001	8.998 E-03
0.005	0.04498
0.007	0.062988
0.01	0.08998
0.05	0.44988
0.07	0.62988
0.1	0.8998
0.15	1.3496
0.2	1.7996
0.25	2.2496
0.3	2.6992
0.35	3.1494
0.4	3.5986
0.45	4.0492
0.5	4.4970
0.55	4.9490
0.6	5.3908
0.65	5.83096
0.7	6.25490
0.75	6.6268
0.8	6.79368
0.85	5.61134
0.86	4.2250
0.87	2.40890
0.872	2.27096 ....

Table 6.6 contd.

Ca	Flux
0.874	2.0256
0.876	1.63402
0.88	1.4744
0.885	1.1368
0.89	0.5718
0.895	0.29448
0.9	0.1960
0.92	0.04668
0.95	4.7322 E-03
0.97	8.05740 E-04
0.98	3.01610 E-04
0.99	1.04644 E-04
1.00	3.3334 E-05

TABLE 6.7

$\gamma = 45$, $\alpha_T/\alpha = 10$, $\beta = 0.2$, $\phi = 0.01$

Ca	Flux
0.001	8.9982 E-03
0.005	0.04498
0.007	0.062988
0.01	0.089982
0.05	0.44988
0.07	0.62988
0.1	0.89982
0.15	1.3498
0.2	1.7996
0.25	2.2496
0.3	2.6992
0.35	3.1494
0.4	3.59872
0.45	4.0492
0.5	4.49714
0.55	4.9490
0.6	5.398
0.65	5.8456
0.7	6.286
0.75	6.692
0.8	6.8938
0.81	6.8438
0.82	6.7124
0.83	6.4252
0.84	5.7652
0.85	3.68716 ...

Table 6.7 contd.

Ca	Flux
0.855	2.40448
0.86	1.7116
0.87	1.01222
0.873	0.4390
0.877	0.286230
0.88	0.2248
0.89	0.11126
0.892	0.097392
0.895	0.079914
0.897	0.07010
0.9	0.057636
0.92	1.54836 E-02
0.93	7.8598 E-03
0.94	3.90846 E-03
0.95	1.89808 E-03
0.96	8.9808 E-04
0.97	4.13164 E-04
0.98	1.844528 E-04
0.99	7.97568 E-05
1.00	3.3334 E-05

CHAPTER – 7

EFFECT OF CATALYST DEACTIVATION

CHAPTER 7

EFFECT OF CATALYST DEACTIVATION

There are well known reasons why commercial catalysts are liable to lose their activity during the course of reaction. The different types of deactivation are poisoning, sintering, fouling. The problem of catalyst deactivation has been analysed theoretically and good reviews and treatises covering this area are available (Butt et al, 1978; Masamune and Smith, 1966; Forzatti et al, 1984).

Different types of approaches have been employed in the analysis of deactivation of catalyst pellet. In the first time as an explicit parameter is eliminated, whereas in the second deactivation is considered to be dependent on time.

The use of time dependent effectiveness factors has been studied over the past few years. Kam et al (1975) and Kulkarni and Ramachandran (1980) obtained analytical solutions for a single catalyst particle undergoing slow first order self poisoning.

Recently Do and Weiland (1981 a,b) obtained analytical solutions for effectiveness factors for series and parallel fouling in slab, infinite cylinder and sphere geometries by using singular perturbation and integral transform techniques respectively the results compare very well with the numerical solutions of Masamune and Smith (1966).

Here we study parallel and series fouling in bidispersed catalysts using the Galerkin method of quadratures.

7.1 Parallel Fouling

Let us consider catalyst particles of radius r_i which are agglomerated into pellets of radius R. In the particles (micropores) for simplicity we assume a single first order, isothermal, irreversible reaction:

$$A \longrightarrow \text{Products (main reaction)}$$
$$A \longrightarrow \text{Coke (parallel fouling)}$$

At time θ , the residual activity is expressed by the fraction S which is determined by

$$\frac{-\partial S(x, \theta)}{\partial \theta} = C_i S \; ; \quad S\ (\theta = 0) = 1 \qquad (7.1)$$

The reaction rate for the main step is given by $r_A = k_o\ S\ C$ where C is the concentration of A inside the micropore at position X, Y.

By neglecting the accumulation of reactant in the particles as well as in the pellet, we obtain the following mass balance equation for species A in the particle:

Microparticle:

$$\frac{D_{io} d}{X^2 dX} \left[X^2 \quad \frac{dC}{dX} \right] = k S C_i \qquad (7.2)$$

$$C = C_A, \; X = r_i \; ; \; \frac{dC}{dX} = 0, \quad X = 0 \qquad (7.3)$$

The dimensionless equations can be written as

$$\nabla_x^2 C_i = k S C_i r_i^2 / D_{io} = \phi^2 S C_i \qquad (7.4)$$

$$C_i = C_a \; ; \; x = 1, \; \frac{dC_i}{dx} = 0 \qquad (7.5)$$

In the same manner we can write the mass balance equation for the pellet as

Macroparticle:

$$\frac{D_a}{Y^2} \frac{d}{dY} \left[Y^2 \frac{d^2 C_A}{dY} \right] = (-\bar{r}_A) \text{ at average } Y$$

$$= (1-\epsilon) \; k \int_0^1 C_i \, S \, dx^3 \qquad (7.6)$$

with the boundary conditions

$$C_A = C_{AS} \, , \; Y = R \; ; \; \frac{dC_A}{dY} = 0, \; Y = 0 \qquad (7.7)$$

where $(1-\epsilon)$ is the volume of particles per unit volume of pellet. In dimensionless form the equations can be written as

$$\nabla_y^2 C_a = \frac{R^2}{D_a} (-\bar{r}_A) \text{ average at } Y$$

$$= (1-\epsilon) \frac{R^2}{D_a} k \int_0^1 C_i \, S \, dx^3 \qquad (7.8)$$

Further, defining

$$\eta_i = \frac{1}{C_a} \int_0^1 C_i \, S \, dx^3 \qquad (7.9)$$

and

$$\alpha = 3(1-\epsilon) \frac{R^2}{r_i^2} \frac{D_{io}}{D_a} \qquad (7.10)$$

equation 7.8 can be rewritten as

$$\nabla_y^2 C_a = \frac{\alpha}{3} \phi^2 \eta_i C_a = \alpha \left. \frac{dC_i}{dx} \right|_{x=1} \qquad (7.11)$$

with the boundary conditions

$$C_a = 1 \; ; \; y = 1 \qquad (7.12)$$

$$\frac{dC_a}{dy} = 0 \; ; \; y = 0 \qquad (7.13)$$

The activity parameter S can be eliminated from the microparticle equations using the Legendre transformation

$$\Psi_i = \int_0^\theta C_i \, d\theta \qquad (7.14)$$

proposed by Del Borghi et al (1976) and Dudukovic and Lamba (1978). Equation 7.1 on simplification gives

$$S = \exp(-\Psi_i) \qquad (7.15)$$

The microparticle equation can now be written as

$$\nabla_x^2 \Psi_i = \phi^2 \left(1 - \exp(-\Psi_i)\right) \qquad (7.16)$$

With the transformed boundary conditions

$$\Psi_i(1, \theta) = \int_0^{\theta} C_a \, d\theta = \Psi_a \qquad (7.17)$$

$$\frac{d\Psi_i}{dx}(0, \theta) = \theta$$

Also, employing the transformation 7.14 evaluated at the surface of the microparticle, the macroparticle equation 7.11 can be rewritten as

$$\nabla_y^2 \Psi_a = \left.\frac{d\Psi_i}{dx}\right|_{x=1} \qquad (7.18)$$

with the transformed boundary conditions

$$\frac{d\Psi_a}{dy} = 0, \quad y = 0 \qquad (7.19)$$

$$\Psi_a = \theta, \quad y = 1 \qquad (7.20)$$

The derivative $(d\psi_i/dx)_{x=1}$ required in equation 7.18 can be obtained by solving equations 7.16 - 7.17. For this purpose we employ a single point collocation and write the equation in the form

$$F(\psi) = \frac{10.5}{\phi^2}(\psi - \psi_a) + 1 - \exp(-\psi) = 0 \tag{7.21}$$

$$F'(\psi) = \frac{10.5}{\phi^2} + \exp(-\psi) \tag{7.22}$$

where ψ is the value of ψ_i at the collocation point $x = \sqrt{3/7}$. It follows from these equations that $\psi = 0$, for $\psi_a = 0$ and $\psi_a - \psi \longrightarrow 1/10.5$ for $\psi_a \longrightarrow \infty$. Also the derivative $(d\psi_i/dx)_{x=1}$ can be obtained as

$$\left.\frac{d\psi_i}{dx}\right|_{x=1} = \phi^2 \left\{ \frac{7}{10}\left[1-\exp(-\psi)\right] + \frac{3}{10}\left[1-\exp(-\psi_a)\right] \right\} \tag{7.23}$$

Equations 7.21 - 7.23 together give the values of ψ_i and $(d\psi_i/dx)_{x=1}$ for assumed values of ψ_a which can be subsequently used in equation 7.16. This equation can now be solved using the conventional numerical methods or even by collocation. The overall effectiveness factors computed using this procedure are portrayed in Figures 7.2 and 7.3.

A particular difficulty associated with the use of this procedure is the fact that the results obtained are

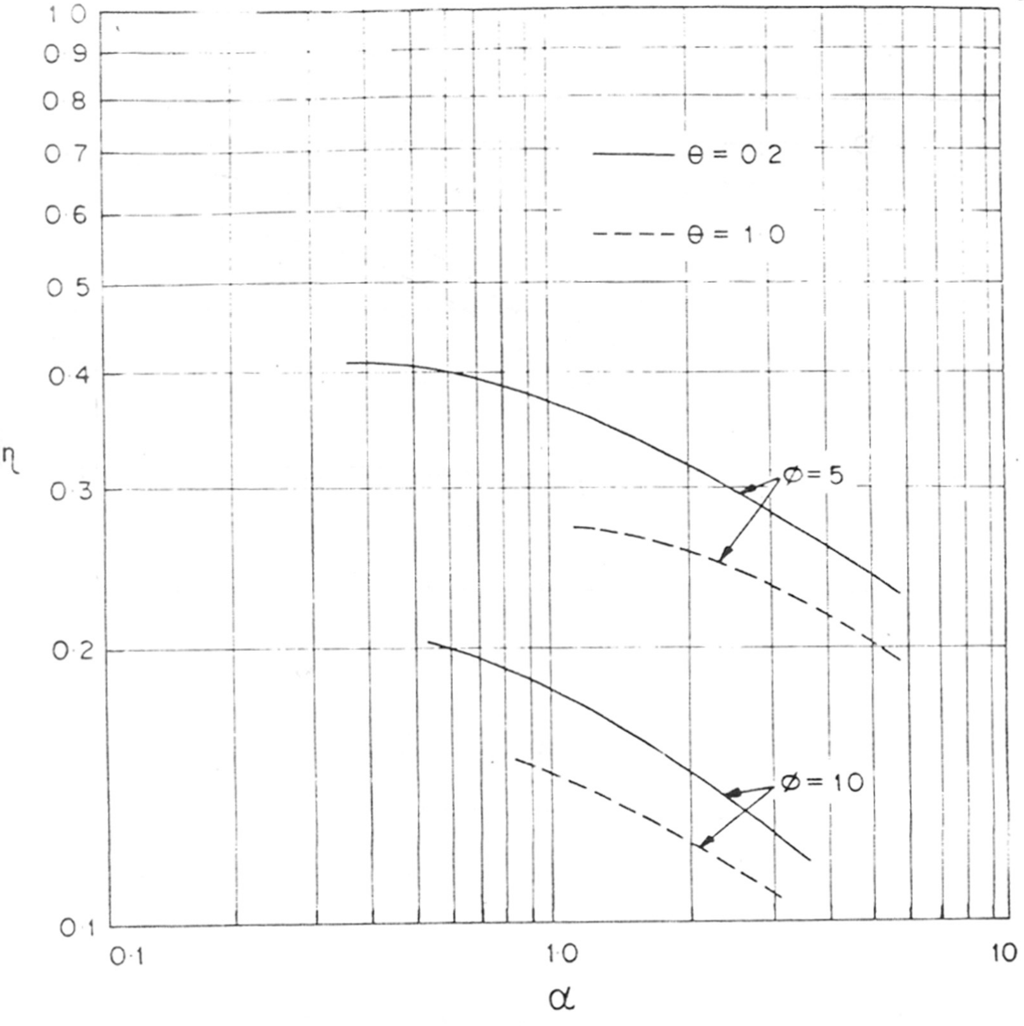

FIG. 7·2: EFFECTIVENESS FACTOR AS A FUNCTION OF α FOR DIFFERENT VALUES OF θ AND ϕ

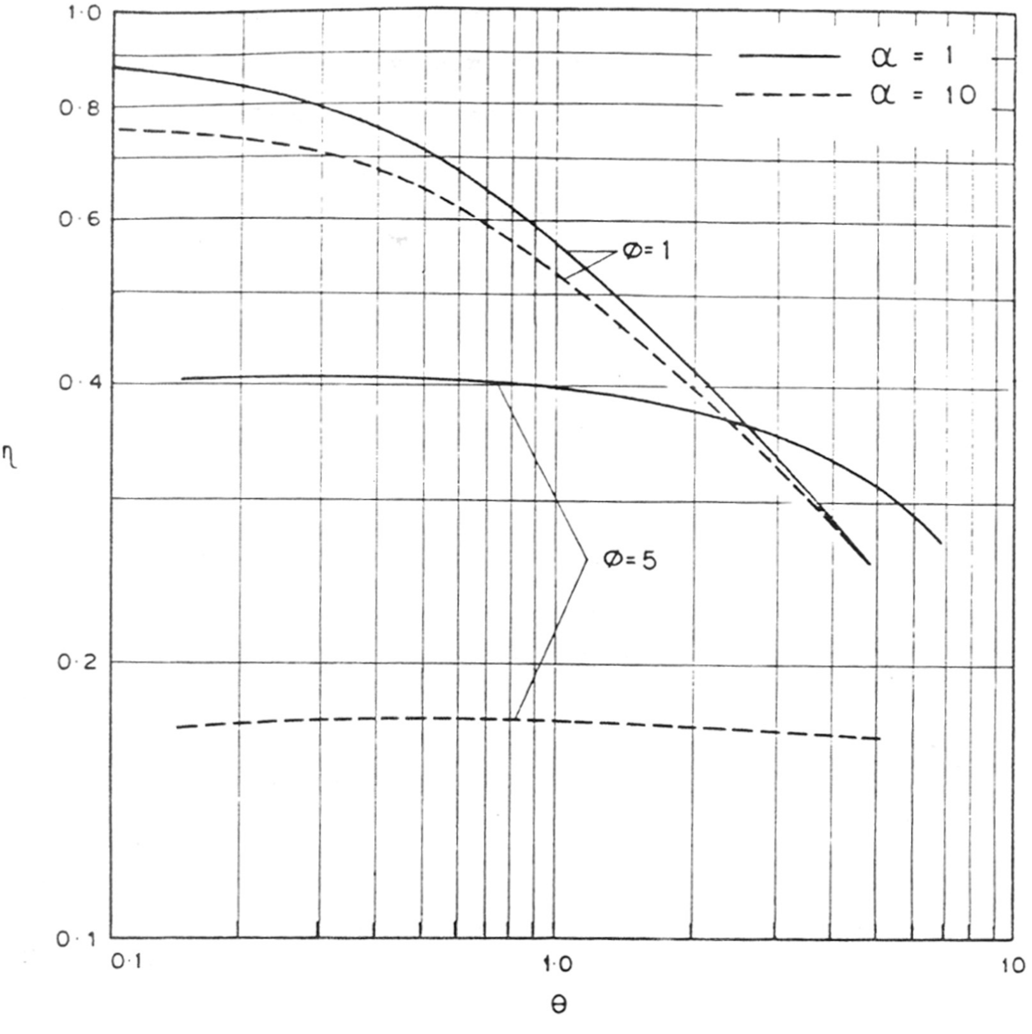

FIG. 7·3: EFFECTIVENESS FACTOR AS A FUNCTION OF DIMENSIONLESS TIME FOR DIFFERENT VALUES OF α AND φ accurate only for low values of ϕ. Also the final estimation of the effectiveness factor is very sensitive to changes in parameter values. To overcome this difficulty it was proposed to simplify the problem by invoking the approximation concerning the variation of macroparticle concentration with time. In view of the relatively weak dependence of C_a on θ, the boundary condition given by equation 7.17 can be modified as

$$\psi_1(1,\theta) = \int_0^{\theta} C_a \, d\theta \simeq C_a\theta = \psi_a \tag{7.24}$$

The set of equations 7.16 - 7.17 with the modified condition 7.24 has now been solved using the polynomial approximation method.

To solve equation 7.16 we employ a polynomial approximation for the ψ_1 profile as

$$\psi_1 = \psi_a + a_1(1-u) + a_2 u(1-u), \quad u = x^2 \tag{7.25}$$

and rewrite equation 7.16 as

$$u\frac{d^2\psi_1}{du^2} + \frac{3}{2}\frac{d\psi_1}{du} = 0.25\phi^2(1-\exp(-\psi_1)) \tag{7.26}$$

and the residual as

$$R_2 = 6(a_2-a_1) - 20a_2u-\phi^2 \left\{1-\exp\left[-\psi_a-a_1(1-u)-a_2u(1-u)\right]\right\}$$

(7.27)

Following the same treatment as described earlier, the resultant equations can then be written as

$$\int_0^1 R_2\ (\underline{a},u)\ (1-u)u^{1/2}\ du=0,\ j=1 \qquad (7.28)$$

$$\int_0^1 R_2\ (\underline{a},u)\ (1-u)u^{3/2}\ du = 0,\ j = 2 \qquad (7.29)$$

Equivalently equations 7.28 - 7.29 can also be written as

$$\int_0^1 F_j(u)\ (1-u)u^{1/2}\ du = \sum_{k=1}^{M} w_k F_j(u_k) = 0 \qquad (7.30)$$

where $F_j(u) = R_2(\underline{a},u)u^{j-1}$, $j=1,2...N$ (here 2) and M may have any value $\geqslant N$. Again choosing u_k 's as the roots of the Jacobi polynomial $p_2(1,1/2)$, equation 7.30 is solved using the Gaussian quadratures to obtain the values of a_1 and a_2. These values of a_1 and a_2 are utilised in the estimation of ψ_i which in terms of transformed variables can be written as

$$\eta_i = \frac{3}{C_a} \int_0^1 x^2\ \frac{d\psi_i}{d\theta}\ \exp(-\psi_i)\ dx \qquad (7.31)$$

It should be noted that the values of a_1 and a_2 calculated using the procedure mentioned above are specific to the values of Θ, ϕ and C_a. In view of the dependence of a_1 and a_2 on Θ, in the process of calculation of η_1 we need to know the variations of a_1 and a_2 with Θ at constant C_a and ϕ. These values of $da_1/d\Theta$ and $da_2/d\Theta$ have been generated by introducing an infinitesimal variation in Θ keeping ϕ and C_a constant and then used to obtain the η_1-C_a variation for one value of ϕ and several values of Θ. One such typical curve for three different values of Θ (= 0.2,1 and 3) for one value of ϕ (ϕ=5) is shown in Figure 7.1. Similar calculations for different values of ϕ have been repeated and the data interpolated to obtain η_1 at any value of C_a at constant Θ and ϕ. This information has been subsequently used in the macroparticle equation which has been solved using Weisz and Hicks' method (1962). The results are presented as $\eta - \alpha$ or $\eta - \Theta$ plots for different values of (Θ,ϕ) or (α,ϕ).

Results and discussion

Figure 7.3 shows a plot of $\eta - \Theta$ for two values of ϕ (= 1,5), each for two values of α (=1,10). It is seen from this figure (curves for ϕ=1,5 ; α=1) that a crossover of curves occurs for the two values of ϕ for the same α. This implies that at lower times a catalyst with no significant diffusional resistance fares well for higher Θ values.

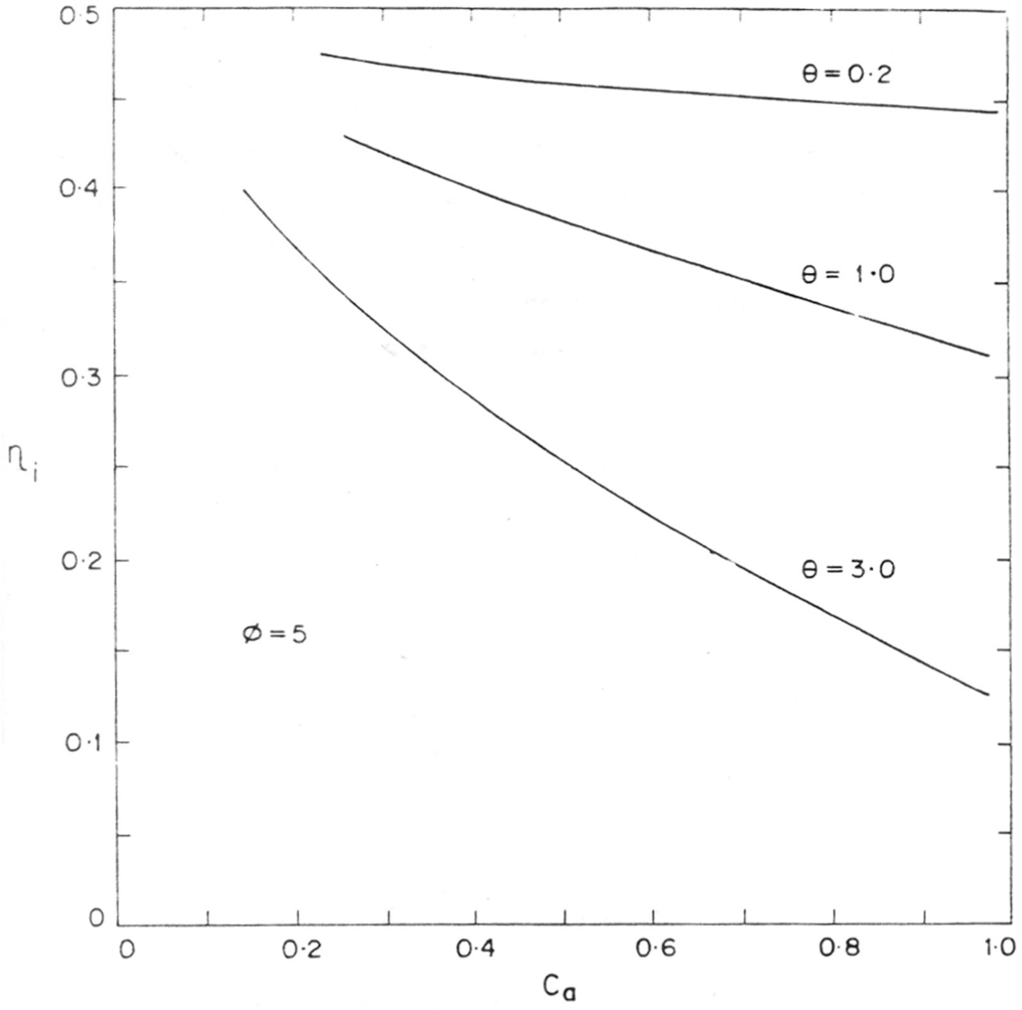

FIG. 7·1: MICROPORE EFFECTIVENESS FACTOR AS A FUNCTION OF MACROPORE CONCENTRATION AT DIFFERENT DIMENSIONLESS TIMES

Also a catalyst with less significant diffusional resistance deactivates faster than one with higher diffusional resistance. It is also seen from this figure that, in general, for any value of ϕ the catalyst has lower effectiveness and deactivates faster with increase in α. Also, the influence of the parameter α is less severe for a catalyst with low diffusional resistance. That is, for low values of ϕ (say $\phi = 1$) the deactivation manifested in the η values and the final time of deactivation is less severely affected with increase in α from 1 to 10. On the other hand, for a catalyst with high diffusional resistance, the influence of an increase in α is felt more severely and both the η and the final time of deactivation get affected considerably. An alternative representation of $\eta - \alpha$ for different values of Θ has already been shown in Figure 7.3.

7.2 Series Fouling

The governing equations for the micro-macroparticle system where a reaction leading to series fouling proceeds ($A \longrightarrow \nu_i B \longrightarrow$ coke) can be written as

Microparticle:

$$\frac{D_{io}\,d}{X^2 dX}\left[X^2 \frac{dC}{dX}\right] = k\,SC \qquad (7.32)$$

$$C = C_A\,, \quad X = r_i\,; \quad \frac{dC}{dX} = 0,\ X = 0 \qquad (7.33)$$

$$\frac{D_{ib}}{X^2}\ \frac{d}{dX}\left[X^2\ \frac{dC'}{dX}\right] = -kS\,C \qquad (7.34)$$

$$C' = C_B\ ,\quad X = r_i\ ;\quad \frac{dC'}{dX} = 0\ ,\ X = 0 \qquad (7.35)$$

The corresponding dimensionless equations are

$$\nabla_x^2\, C_i = \phi^2\, C_i\, S \qquad (7.36)$$

$$C_i = C_a\ ,\quad x = 1\ ;\quad \frac{dC_i}{d\,x} = 0,\ x = 0 \qquad (7.37)$$

$$\nabla_x^2\, C_{ib} = -\,\nu\phi^2\, C_i\, S \qquad (7.38)$$

$$C_{ib} = C_b\ ,\quad x = 1\ ;\quad \frac{dC_{ib}}{dx} = 0\ ,\ x = 0 \qquad (7.39)$$

$$-\,\frac{\partial S}{\partial \theta} = C_{ib}\, S \qquad (7.40)$$

$$S = 1\ ,\quad \theta = 0 \qquad (7.41)$$

Combining equations 7.36 and 7.38, C_{ib} can be eliminated in terms of C_i as

$$C_{ib} = \nu(C_a - C_i) + C_b \qquad (7.42)$$

Employing equation 7.42 in equation 7.40 and using the definition of ψ_i (equation 7.14), and on integration, we obtain

$$S = \exp\left[- \left\{C_b\theta + \nu(\psi_a - \psi_i)\right\}\right] \tag{7.43}$$

Further, assuming a weak dependence of C_a on θ, this equation can be written as

$$S = \exp\left[-(C_b + \nu C_a)\theta + \nu\psi_i\right] \tag{7.44}$$

Employing this definition of S in equation 7.36 the micropore equation can be rewritten in terms of the transformed variable as

$$\nabla_x^2\psi_i = \int_0^\theta \phi^2 \frac{d\psi_i}{d\theta} \exp\left[-(C_b + \nu C_a)\theta + \nu\psi_i\right] d\theta \tag{7.45}$$

By using single point collocation this equation can be rewritten as

$$B_{11}\psi + B_{12}C_a\theta = \int_0^\theta \phi^2 \frac{d\psi}{d\theta} \exp\left[-(C_b + \nu C_a)\theta + \nu\psi\right] d\theta \tag{7.46}$$

Differentiating equation 7.46 and rearranging we obtain

$$\frac{d\psi}{d\,\Theta} = C_a \left[1 + \frac{\phi^2}{B_{12}} \exp\left\{-(C_b + \nu C_a)\Theta + \nu\psi\right\}\right] \quad (7.47)$$

which has to be integrated subject to condition $\psi = 0$ for $\Theta = 0$, using the transformation

$$Z = e^{-(C_b + \nu C_a)\Theta} \; e^{\nu\psi} \quad (7.48)$$

$$\frac{dZ}{d\Theta} = -(C_b + \nu C_a)\,Z + \nu Z \,\frac{d\psi}{d\,\Theta} \quad (7.49)$$

which on further simplification gives

$$d\Theta = -\left[\frac{dZ}{Z\left[C_b + (C_b + \nu C_a)\phi^2/B_{12}Z\right]}\right] + \left[\frac{dZ}{C_b + (C_b + \nu C_a)\phi^2/B_{12}Z}\right]$$

$$(7.50)$$

and on integration leads to

$$\Theta = \frac{1}{b_o} \ln \left[\left\{\frac{(C_b + \nu C_a)\phi^2/B_{12}}{C_b + (C_b + \;\; C_a)\phi^2/B_{12}}\right\} \Big/ \left\{\frac{(C_b + \nu C_a)\phi^2/B_{12}\;Z}{C_b + (C_b + \nu C_a)\phi^2/B_{12}\;Z}\right\}\right]$$

$$+ \frac{1}{(C_b + \nu\,C_a)} \ln \frac{C_b B_{12}/\phi^2 + C_b + \nu\,C_a}{C_b B_{12}/\phi^2 + (C_b + \nu C_a)Z} \quad (7.51)$$

The derivative $d\psi/d\Theta$ and Θ given by equations 7.47 and

7.51 are required in the estimation of the microparticle effectiveness factor which can be written as

$$\eta_i = \frac{3}{C_a} \int_0^1 x^2 \frac{d\psi_i}{d\theta} \exp\left[-(C_b + \nu C_a)\theta + \nu\psi\right] dx \qquad (7.52)$$

or equivalently as

$$\eta_i = 3\left[\frac{w_1 \exp\left[-(C_b + C_a\nu)\theta + \nu\psi\right]}{1 + \phi^2/B_{12} \exp -(C_b + C_a\nu)\theta + \nu\psi} + w_2 \exp(-C_b\theta)\right] \qquad (7.53)$$

In these equations w_1 and w_2 refer to the weight factors and B_{12} the coefficient matrix. It is important to note that C_b appearing in the equation for η_i is also dependent on C_a, the corresponding concentration in the macroparticle. As such this equation will have to be simultaneously solved along with the macroparticle equations.

We now turn to macroparticle equations for species A and B which can be written as

<u>Macroparticle:</u>

$$\frac{D_a}{Y^2} \frac{d}{dY} \cdot \left[Y^2 \frac{dC_A}{dY}\right] = \frac{(1-\epsilon)D_{io}}{r_i} \left.\frac{dC}{dX}\right|_{X=r_i} \qquad (7.54)$$

$$C_A = C_{AS} \;, \quad y = R \;; \qquad \frac{dC_A}{dY} = 0 \;, \quad Y = 0 \qquad (7.55)$$

$$\frac{D_b}{Y^2} \frac{d}{dY} \left[Y^2 \frac{dC_B}{dY} \right] = \frac{(1-\epsilon)}{r_i} D_{io} \left. \frac{dC}{dX} \right|_{X=r_i} \qquad (7.56)$$

$$C_B = C_{BS} \;, \quad Y = R \;; \qquad \frac{dC_B}{dY} = 0 \;, \quad Y = 0 \qquad (7.57)$$

which in the dimensionless form can be written as

$$\nabla_y^2 C_a = \left. \frac{dC_i}{dx} \right|_{x=1} = \frac{\alpha}{3} \phi^2 \eta_i C_a \qquad (7.58)$$

$$C_a = 1, \quad y = 1 \;; \qquad \frac{dC_a}{dy} = 0 \;, \quad y = 0 \qquad (7.59)$$

$$\nabla_y^2 C_b = - \nu' \alpha' \left. \frac{dC_i}{dx} \right|_{x=1} \qquad (7.60)$$

$$C_b = C_{BS} \;, \quad y = 1 ; \qquad \frac{dC_b}{dy} = 0 \;, \quad y = 0 \qquad (7.61)$$

Here $\nu' = \frac{D_{io}}{D_b} \nu_i =$ and $\alpha' = \alpha$

Eliminating C_b in terms of C_a from these equations we obtain the following relation between the concentration of species B at the surface of the microparticle (C_b) and the concentration at the surface of the pellet (C_{BS})

$$C_b = \nu(1 - C_a) + C_{BS} \tag{7.62}$$

Note that C_b is required in equation 7.53 for estimation of the microparticle effectiveness factor.

The macroparticle equation for the species A has now been solved using the polynomial approximation method. The profile for C_a is defined as

$$C_a = 1 + b_1\,(1-t) + b_2 t\,(1-t)\ ;\ t = y^2 \tag{7.63}$$

Substituting equation 7.62 in 7.58 we obtain the residual R_2 as

$$R_2 = -\,2b_2 t + 1.5\,(-b_1 + b_2 - 2b_2 t) - \frac{0.25\alpha\,\phi^2}{3}\,\eta_i C_a \tag{7.64}$$

The residual R_2 is minimised over the volume of the pellet so as to get the best approximation profile. For N=2, this leads to equations 7.28 - 7.29 where R_2 is now defined by equation 7.64. The η_i and C_a required in equation 7.64 are given by equations 7.53 and 7.63. Once b_1 and b_2 are known the overall effectiveness factor is simply obtained as $\eta = -\,18\,(b_1 + b_2)/(\phi^2\alpha)$. The results calculated in terms of the overall effectiveness factor as a function of time θ for different values of ϕ and α are presented in Figure 7.4.

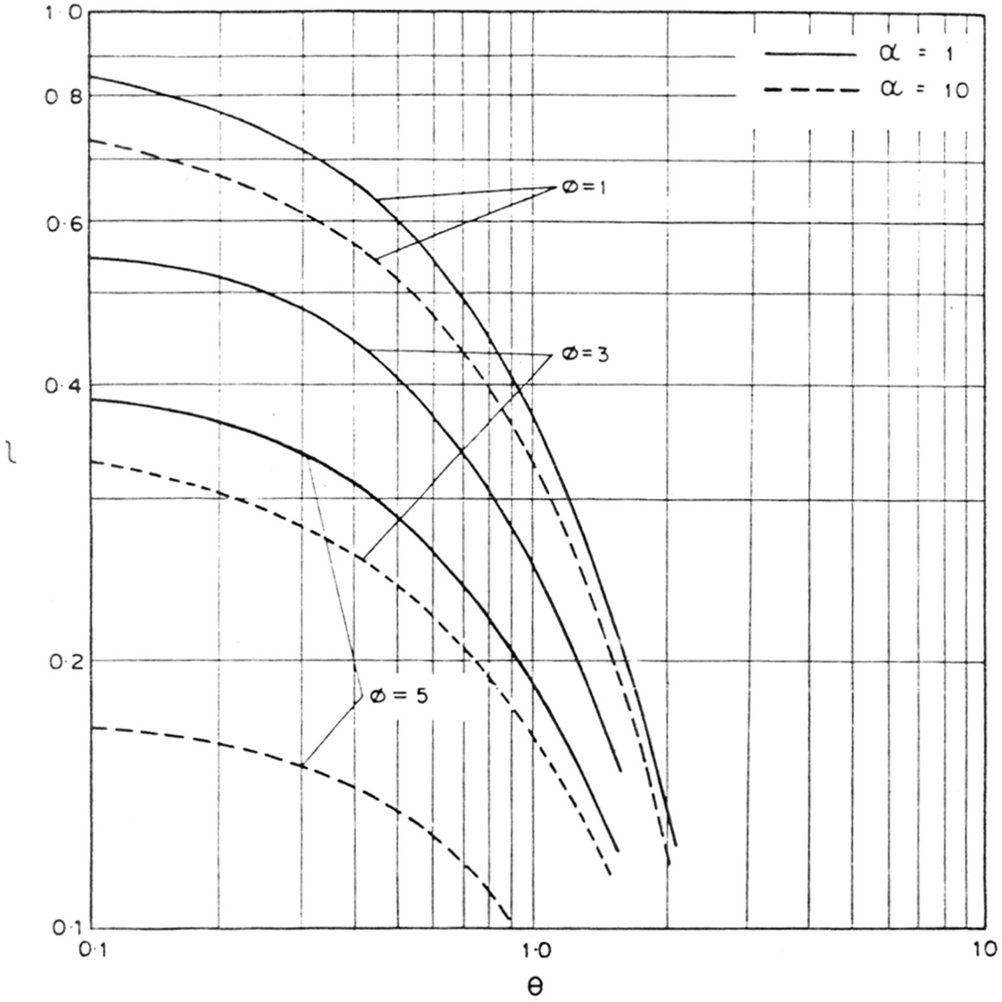

FIG. 7·4: EFFECTIVENESS FACTOR AS A FUNCTION OF θ FOR DIFFERENT VALUES OF α AND Ø

Results and discussion

Typical variations of η as a function of time θ for three different values of ϕ (ϕ=1,3 and 5) for α= 1 and 10 are shown in Figure 7.4. It is seen that for a given value of ϕ the difference between the effectiveness of the catalyst for α= 1 and 10 is highest for the catalyst at shorter times. Also, this difference at any time θ is higher for higher value of ϕ. As time θ increases the difference in general decreases. This decrease in the value of η for α=1 and 10 with θ is more significant for low ϕ than for high ϕ.

The results of this investigation suggest that where series type of fouling occurs, it is preferable to have a catalyst with low diffusional resistance and also low values of α. Thus it is preferable to operate with as small a size of catalyst as possible at low temperatures.

7.3 Conclusions

To summarise, in systems where catalyst deactivation occurs, either due to parallel or series fouling, the study leads to the following conclusions:

(1) For parallel fouling, a catalyst with low ϕ gives better performance at shorter times, while a catalyst with high ϕ fares better at longer times. This also implies that a catalyst with low ϕ deactivates faster than a catalyst

with high ϕ at any value of α.

(2) The catalyst shows lower effectiveness and deactivates faster with increase in α for any value of ϕ.

(3) The parameter α affects the overall value of η and the time for complete deactivation of the catalyst more severely for catalysts with high ϕ than for those with low ϕ. In other words, the effect of bimodal pore dispersion increases with increasing diffusional resistance.

(4) In series fouling, the greatest influence of the parameter α is felt at shorter times. With increase of time, the influence of α diminishes for the same value of ϕ. This is particularly so for catalysts with low ϕ.

(5) The parameter α characterising the micro-macroparticle system has in general a detrimental effect on the effectiveness factor η. It is preferable therefore to operate the system with as low values of α as possible. This clearly suggests the use of small size catalyst particles/pellets.

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NOTATION

$a_i (i=1,...N)$	polynomial constants
A_1	defined by equation 5.21
A_2	defined by equation 5.21
$b_i (i=1,..N)$	polynomial constants
B_1	defined by equation 5.21
B_2	defined by equation 5.21
B_{12}	coefficient matrix for single point collocation
C	concentration of species A in the microparticle
C'	concentration of species B in the macroparticle
C_a	dimensionless concentration of species A in the macroparticle
C_b	dimensionless concentration of species B in the macroparticle
C_A	concentration of species A in the macroparticle
C_B	concentration of species B in the macroparticle
C_i	dimensionless concentration of species A in the microparticle
C_{ib}	dimensionless concentration of species B in the macroparticle
C_{AS}	concentration of species A in the bulk

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C_{BS}	concentration of species B in the bulk
C_1	defined by equation 5.21
C_2	defined by equation 5.21
D_i	microparticle effective diffusivity of species A
D_{io}	temperature dependent part of microparticle effective diffusivity of species A
D_{ib}	microparticle effective diffusivity of species B
D_a	macroparticle effective diffusivity of species A
D_b	macroparticle effective diffusivity of species B
f_1	defined by equation 5.21
f_2	defined by equation 5.21
F_j	defined by equation 4.7
k	rate constant for main reaction
k_a	effective thermal conductivity of macroparticle
k_e	effective thermal conductivity of microparticle
k_f	rate constant for fouling reaction
n	constant or general exponent
p	constant defined in equation 5.1
P_N	Jacobi polynomial

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q	constant defined in equation 5.1
$\bar{r}_A$	average rate of the main reaction on a particle at position Y in the pellet
r_i	radius of the microparticle
R	radius of the macroparticle
R_g	gas constant
R_N	residual
S	activity of particle at position x and at time θ $(x,S) = 1$
t	defined as y^2
T	temperature in the microparticle
T_i	dimensionless temperature in the microparticle
T_s	temperature in the macroparticle
T_a	dimensionless temperature in the macroparticle
T_s^s	temperature at the surface of the catalyst pellet
u	defined as x^2
w_k	weights in the quadrature
x	dimensionless distance variable used in the microparticle
y	dimensionless distance variable used in the macroparticle
X	radial coordinate in the microparticle

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Y	radial coordinate in the catalyst pellet
Z	defined by equation 7.48

Greek symbols

α	parameter in general defined as $3(1-\epsilon)\frac{D_i}{D_a}\frac{R^2}{r_i^2}$
α_T	defined by equation 6.19
β	exothermicity factor defined as $\frac{(-\Delta H)D_i C_{AS}}{k_e T_s^s}$
γ	parameter defined as $E/R_g T_s^s$
η_i	microparticle effectiveness factor
η	macroparticle effectiveness factor
θ	dimensionless time defined as $k_f C_{AS} t$
ν_i	stoichiometric coefficient
ν	parameter defined as $\frac{D_i}{D_a}\nu_i$
ν_1	parameter defined as $(D_{io}/D_b)\nu_i$
ϵ	void fraction of the pellet
ϕ	Thiele modulus in general defined as $r_i\sqrt{k/D_i}$
ϕ_1	modified Thiele modulus defined as $r_i\sqrt{kC_{AS}/D_{io}}$
Ψ_i	cumulative gas concentration defined by equation 7.14
Ψ_a	cumulative gas concentration defined by equation 7.17
Ψ	value of $_i$ at collocation point

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SECTION III

PATTERN FORMATION IN NONLINEAR REACTION-DIFFUSION SYSTEMS

CHAPTER-8

A CASE STUDY OF BIMOLECULAR LANGMUIR-HINSHLWOOD KINETICS

CHAPTER 8

A CASE STUDY OF BIMOLECULAR LANGMUIR-HINSHELWOOD KINETICS

8.1 Introduction

The phenomenological description of several chemically reacting systems is often expressed in terms of the reaction-diffusion equation as

$$\frac{\partial a}{\partial t} = D\nabla_x^2 a - r(a) \qquad (8.1)$$

where ∇^2 is the Laplacian operator, a the concentration of the reactant species, D the diffusion coefficient and $r(a)$, in general, some nonlinear function of the reactant species. Equation 8.1 has been solved for a variety of reaction functions $r(a)$ with appropriate initial and final boundary conditions appropriate to the physical process under investigation. It is now well-accepted that the physical system thus described can possess more than one stationary solution and the particular solution to which the system evolves is determined by the set of initial conditions chosen for the problem. We begin with the analysis in this chapter with the assumption that the homogeneous system $[r(a) = 0]$ described in Equation 8.1

possesses three stationary solutions. We shall refer to each one of these solutions as phases and note that transition from one solution or phase to another solution or phase is possible. Such transition can, for example, be triggered by local fluctuations that are always present in the physical system.

The existence of local diffusion gradients can also bring about a change in the homogeneous solutions of equation 8.1. In fact, in presence of diffusion, under certain sets of operating conditions the two homogeneous states of the system may even coexist. In a truly homogeneous system this phenomenon, of course, cannot arise. We can look at this problem as follows : Let us suppose that we prepare two systems, one in which one steady state prevails, and another in which the second stable state prevails, and bring them in contact with each other at the boundary designated as $x = 0$. It is expected that the boundary separating the two phases will move in one direction or the other depending on the external constraints and one system would completely annihilate the other. One could, however, think of a situation where the velocity of movement of the boundary would be zero, implying coexistence of the two phases.

The necessary condition of the coexistence of the phases is therefore the situation of zero velocity for a given external constraint. An alternative approach to the problem is to consider the process of nucleation of one phase into the other and their relative stabilities. The problem has also been looked at from a different view point by Kobatake (1970) who showed for a particular case the similarity between generalized entropy production in transitions between two stable branches of steady states and the Gibbs free energy in equilibrium phase transitions. Schlogl (1972) considered the reaction-diffusion system and treated coexistence of phases using the analogy of Maxwellian construction. Nicolis _et al_ (1977) considered the onset of instability as a nucleation process and formulated a nonlinear master equation to describe the situation.

The basic models have been applied to model systems such as Schlogl's reaction scheme

$$A + nX \longrightarrow (n+1)X$$

$$X \longrightarrow B$$

which, while simple to analyse from the mathematical view-point, are rarely found in nature. The intention of the present chapter is to apply some of the concepts illustrated for simple systems to more realistic situations. Towards this end we consider a Langmuir-Hinshelwood bimolecular reaction in a CSTR. Several reactions of practical interest conform to such situations and the example considered also exhibits multistationary behaviour under homogeneous conditions. We are interested in demonstrating the coexistence of two of these states for certain sets of external parameters when a local diffusion gradient exists in the system. We also investigate in the present chapter the possible variations that can arise if the diffusion within the system was not isotropic.

The presentation in this section is arranged as follows. The general methodology and the Maxwellian analogy for construction of coexisting states are given. The method is then applied to an important case of bimolecular Langmuir-Hinshelwood kinetics, which analyses the situation in presence of nonisotropic diffusion.

8.2 Coexistence of Stable Solutions

The general conservation equation for reaction-diffusion systems in the presence of external constraints can be written as

$$\frac{\partial a}{\partial t} = D \nabla_x^2 a - F(a, \lambda) \qquad (8.2)$$

where a is the concentration of reactant species, D is the diffusion coefficient, F is the function of variations in concentration due to chemical reaction and λ is the external constraint. It is assumed that the function F is analytic in a and λ.

It is possible in this case that for a certain range of values the system has more than one stationary solution. When the two stable stationary states are brought together at the boundary $x = 0$, the boundary between the phases will move in one direction or another depending on the values of external parameters such as λ. For the two phases to coexist we require the velocity at the boundary to be zero and can be obtained as follows (Nitzan et al, 1975):

By defining a transformation

$$\phi = x - vt \qquad (8.3)$$

where v is a function of x, equation 8.2 may be converted into an ordinary differential equation

$$D \frac{d^2a}{d\phi^2} + v \frac{da}{d\phi} + F(a, \lambda) = 0 \qquad (8.4)$$

This is a nonlinear eigenvalue equation for v at a given λ. Hence coexistence of two states occurs when $v = 0$ at $\lambda = \lambda m$.

The value of λ_m is obtained from

$$D \frac{d^2 a_o}{d\phi^2} + F(a_o , \lambda_m) = 0 \qquad (8.5)$$

If we consider the system of single species with third order kinetics, equation 8.2 can be written as

$$\frac{\partial a}{\partial t} = D \frac{d^2 a}{dx^2} - q\,(a-a_1)\,(a-a_2)\,(a-a_3) \qquad (8.6)$$

Homogeneous steady states for this equation occur at $a = a_1, a_2, a_3$ where a_1, a_2, a_3 are arbitrary functions of .

For a_1 and a_2 to be the only stable states $q > 0$ and $a_2 > a_3 > a_1$.

A new variable y is defined as

$$y = \frac{a - a_1}{a_2 - a_1}$$

Equation 8.6 is rearranged as

$$\frac{\partial a}{\partial t} = D \frac{d^2 a}{dx^2} - q(a_2 - a_1)^2\, y(y-1) \left[y + \frac{(a_3 - a_1)}{(a_2 - a_3)} \right] \qquad (8.7)$$

which is identical to a model studied by Montroll and the solution is given as

$$a(\phi) = a_1+(a_2-a_1)\,(1+\exp(\pm\beta\phi))^{-1} \qquad (8.8)$$

where

$$\beta = \left(\frac{q}{2D}\right)^{1/2} (a_2-a_1) \qquad (8.9)$$

the velocity at the boundary is given as

$$v = \left(\frac{1}{2}\,qD\right)^{1/2} (a_1+a_2-2a_3) \qquad (8.10)$$

Coexistence occurs at $v = 0$ i.e. $a_3 = \frac{1}{2}(a_1+a_2)$ at $\lambda = \lambda_m$.

Another approach for finding the condition of coexistence of phases is given by Schlogl (1972) using Maxwellian construction.

The following reaction scheme was considered

$$\begin{aligned} A + 2X &\longrightarrow 3X \\ B + X &\longrightarrow C \end{aligned} \qquad (8.11)$$

the typical conservation equation for a reaction-diffusion system is given as

$$\frac{\partial a}{\partial t} = D\,\nabla_x^2\,a + r(a) \qquad (8.12)$$

where D, a and ∇^2 have their usual meaning and the rate function r(a) is given by

$$r(a) = -a^3 + 3a^2 - \beta a + \gamma \tag{8.13}$$

It is observed that for certain values of β, γ there exists more than one steady state solution a_1, a_2, a_3 for which $\partial a/\partial t$ vanishes.

At steady state equation 8.13 can be written as

$$\gamma = a^3 - 3a^2 + \beta a = \psi(a) \tag{8.14}$$

At steady state equation 8.12 can be rearranged to form

$$r(a) = \frac{\partial}{\partial a} R(a) \tag{8.15}$$

$$D \nabla_x^2 a = - \frac{\partial}{\partial a} R(a) \tag{8.16}$$

where R is potential field.

For the two phases to coexist, the potentials of the two phases must be the same. Hence

$$R(a_1) = R(a_2) \tag{8.17}$$

$$R(a) - R(a_1) = \int_{a_1}^{a} r(a) \; da \tag{8.18}$$

Using equation 8.13 in 8.18 we get

$$R(a) - R(a_1) = \frac{1}{4} a^4 + a^3 - \frac{\beta}{2} a^2 + \gamma a + \text{const.} \qquad (8.19)$$

This expression has maxima for a equal to a_1 and a_2 . Hence

$$R(a) - R(a_1) = \frac{1}{4} (a-a_1)^2 (a-a_2)^2 \qquad (8.20)$$

Comparing the coefficients of equations 8.19 and 8.20

$$a_1 + a_2 = 2 \qquad (8.21)$$

$$a_1^2 a_2^2 = 4 R(a) \qquad (8.22)$$

On the other hand, comparing the coefficients of equation 8.13 and

$$r(a) = (a-a_1) (a-a_2) (a-a_3) \qquad (8.23)$$

we get

$$a_1 + a_2 + a_3 = 3 \qquad (8.24)$$

$$a_1 a_2 a_3 = \gamma = \psi(a) \qquad (8.25)$$

Thus,

$$a_3 = 1 \qquad (8.26)$$

Using equation 8.26 in equation 8.14

$$\psi(a_3) = \psi(a_2) = \psi(a_1) = \beta - 2 \qquad (2.27)$$

Comparing equations 8.25 and 8.27

$$a_1 a_2 = \beta - 2 \qquad (8.28)$$

Now a_1 and a_2 are the roots of the equation

$$a^2 - 2a + \beta - 2 = 0 \qquad (8.29)$$

Hence

$$a_{1,2} = 1 \pm \sqrt{3 - \beta} \qquad (8.30)$$

To obtain the initial conditions equation 8.16 is multiplied by $\partial a / \partial x$ and integrated with respect to dx, to give

$$\frac{D}{2}\left(\frac{\partial a}{\partial x}\right)^2 + R(a) = R(a_1) \qquad (8.31)$$

From the above equation we get

$$\frac{\partial a}{\partial x} = - \left[\frac{2}{D}\left(R(a_1) - R(a)\right)\right]^{1/2} \qquad (8.32)$$

which leads to

$$\frac{\partial a}{\partial x} = - (2D)^{-1/2} (a - a_1)(a_2 - a) \qquad (8.33)$$

$$x = -(2D)^{1/2} \frac{1}{a_2 - a_1} \ln \frac{a - a_1}{a_2 - a} \qquad (8.34)$$

Hence

$$a = 1 - (1 - \gamma)^{1/2} \tanh \left[\left(\frac{1-\gamma}{2K} \right)^{1/2} x \right] \qquad (8.35)$$

Equation 8.35 represents the concentration profile that one would realise in moving from the state at the coexisting condition to the lower stable state under stationary conditions. It is possible to obtain a complete transient solution to equation 8.12. Thus Magyari (1982), Dehrmann (1982) and Schlogl and Berry (1980) have developed a technique to solve the equation exactly to obtain the complete transient solution. The specific reaction function analysed corresponds to that for Schlogl's reaction scheme and travelling wave solutions are observed.

8.3 Application to Simple Bimolecular Langmuir-Hinshelwood Kinetics

8.3.1 Homogeneous system

Here we analyse a practically more interesting case where the reaction rate is assumed to obey bimolecular Langmuir-Hinshelwood kinetics. Several chemically reacting systems are known to follow such a rate law and typical cases come from a class of hydrogenation and oxidation reactions. It is supposed that a reaction is carried out in a CSTR, the macroscopic equation describing the system being given by

$$\frac{\partial C_A}{\partial t} = F(C_{A_o} - C_A) - V \frac{kC_A}{(1 + KC_A)^2} \qquad (8.36)$$

The dimensionless form of the above equation is written as

$$\frac{\partial a}{\partial t} = 1 - a - \bar{r} = r(a) \qquad (8.37)$$

where $\bar{r} = \dfrac{Da \quad a}{(1+K_A' \, a)^2}$, $Da = \dfrac{kV}{F}$, $K' = KC_{A_o}$

Equation 8.37 can be rearranged and at steady state becomes

$$a^3 + \left(\frac{2-K'}{K'}\right) a^2 + \left(\frac{1-2K' + Da}{K'^2}\right) a - \frac{1}{K'^2} = - r(a) = 0$$

(8.38)

or

$$\frac{1}{K'^2} = a^3 + \frac{2 - K'}{K'} a^2 + \frac{1-2K'+Da}{K'^2} a = \psi(a) \qquad (8.38a)$$

Equation 8.38 for certain sets of values of K' and Da possesses three solutions. For an interval (Da,Da$'$) there exists a critical value of K', $K' > K_c'$ for which $r(a)=0$ gives three solutions; for $K' < K_c'$ only one solution is obtained. Figure 8.1 shows a plot of $r(a)$ vs. a for a particular Da in (Da$'$ Da) for three values of K', $K' < K_c'$, $K' > K_c'$, $K' = K_c'$. As interval (Da$'$ Da) is changed K_c' is changed. The values of a for which $r(a)=0$ as a function of Da for two values of K' are plotted in Figure 8.2.

8.3.2 Spatial inhomogeneity in presence of isotropic diffusion

The homogeneous system in presence of diffusion gradients can be written as

$$\frac{\partial a}{\partial t} = 1 - a - \frac{Da\ a}{(1+K'a)^2} + \frac{D}{F} \nabla_x^2 a \qquad (8.39)$$

or at steady state as

$$\frac{D}{F} \nabla_x^2 a = - \frac{\partial}{\partial x} \left[R(a)\right] = -r(a) \qquad (8.40)$$

where R can be indertified as a potential field. Following the Maxwellian construction as discussed in the previous section, in the multiplicity region the necessary condition

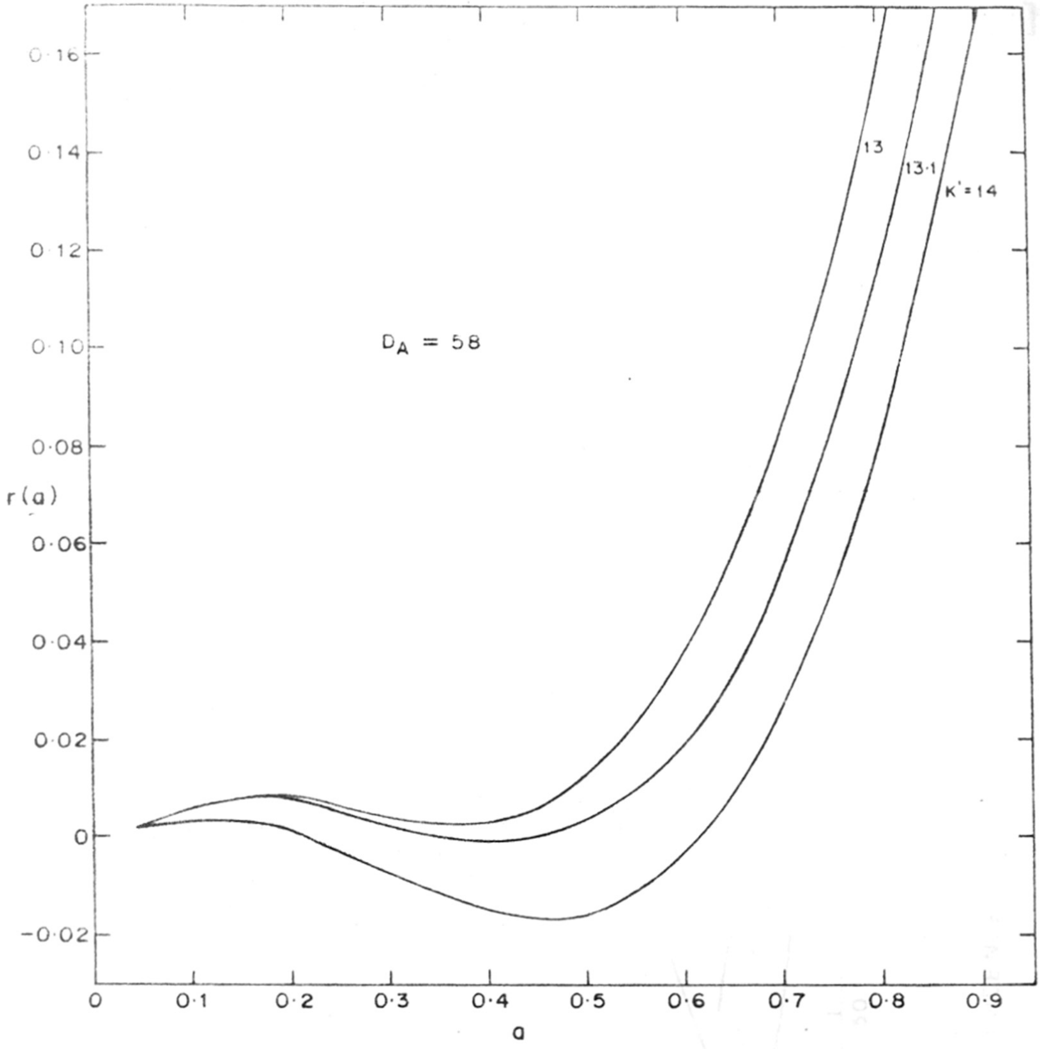

FIG. 8·1. VARIATION OF RATE FUNCTION r(a) WITH CONCENTRATION a

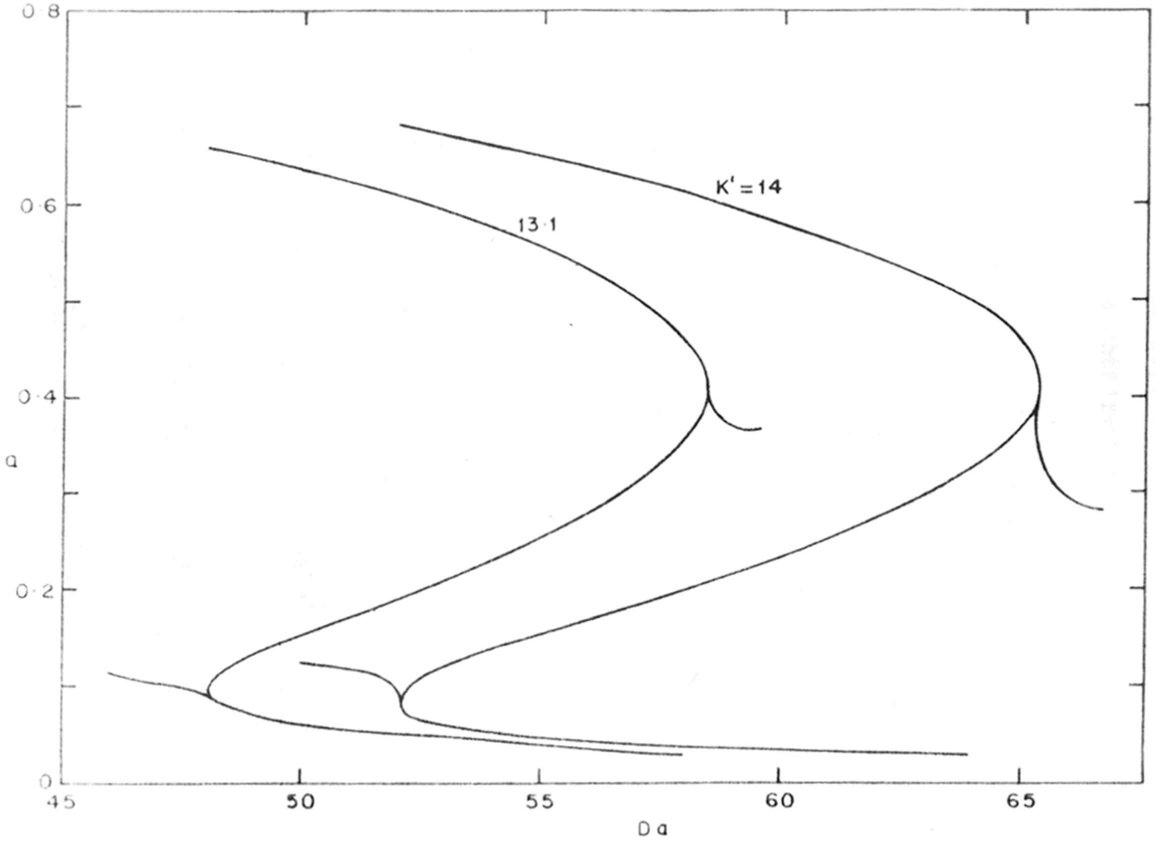

FIG. 8·2. DEPENDENCE OF STATIONARY SOLUTION ON PARAMETER Da for the two phases representing the two solutions (a_1 and a_2) to coexist is obtained as

$$R\,(a_1) = R(a_2) \tag{8.41}$$

with

$$R\,(a) - R\,(a_1) = \int_{a_1}^{a} r(a)\,da \tag{8.42}$$

These relations can be utilised to relate the parameter values (K' and Da) for the coexistence of phases. From the definition of R(a) we get

$$R(a)-R(a_1) = -\frac{a^4}{4} + \left(\frac{2-K'}{K'}\right)\frac{a^3}{3} + \left(\frac{1-2K'+Da}{K'^2}\right)\frac{a^2}{2} - \frac{1}{K'^2} + \text{const.} \tag{8.43}$$

$$= -\frac{1}{4}(a-a_1)^2\,(a-a_2)^2 \tag{8.44}$$

Comparing the coefficients of 8.43 and 8.44 gives

$$\frac{(a_1+a_2)}{2} = \frac{(K'-2)}{3K'} \tag{8.45}$$

$$\frac{(a_1a_2^2) + a_2a_1^2\,)}{2} = \frac{1}{K'^2} \tag{8.46}$$

On the other hand, comparison of coefficients in equation 8.38 and

$$r(a) = -(a-a_1)\,(a-a_2)\,(a-a_3) \qquad (8.47)$$

gives the following relations:

$$a_1 + a_2 + a_3 = \frac{(K'-2)}{K'} \qquad (8.48)$$

$$a_1 a_2 a_3 = \frac{1}{K'^2} = \psi(a) \qquad (8.49)$$

Thus we get, using equations 8.48 and 8.45,

$$a_3 = \frac{K'-2}{3K'} \qquad (8.50)$$

Using equation 8.50 in equation 8.38a

$$\psi(a_3) = \left(\frac{K'-2}{3K'}\right)^3 + \left(\frac{2-K'}{K'}\right)\left(\frac{K'-2}{3K'}\right)^2 + \left(\frac{1-2K'+Da}{K'^2}\right)\left(\frac{K'-2}{3K'}\right) - \frac{1}{K'^2}$$

$$(8.51)$$

It is evident from equation 8.38a that the parameter $\psi(a)$ is constant and equal to $(1/K'^2)$.

$$\psi(a_1) = \psi(a_2) = \psi(a_3) = \text{const} = \frac{1}{K'2} \qquad (8.52)$$

Its value therefore should not depend on the particular state of the system.

Equation 8.51 defines the relation between K' and Da at the coexistence. The equation is cubic in K' and may possess one or three real roots. The coexistence region is plotted in Figure 8.3. It is evident from this figure that one of the roots i.e. (K'), is always negative and hence physically inappropriate. The second roots is nearly always constant while the third root varies with Da as indicated.

We shall now revert to the calculation of the roots. For this purpose substituting the value of a_3 from equation 8.50 into 8.49 we obtain

$$a_1 a_2 = \frac{3}{K'(K' - 2)} \qquad (8.53)$$

and with equation 8.48

$$a^2 - \frac{2}{3}\left(\frac{K'-2}{K'}\right) a + \frac{3}{K'(K' - 2)} = 0 \qquad (8.54)$$

which gives the two roots a_1 and a_2 as

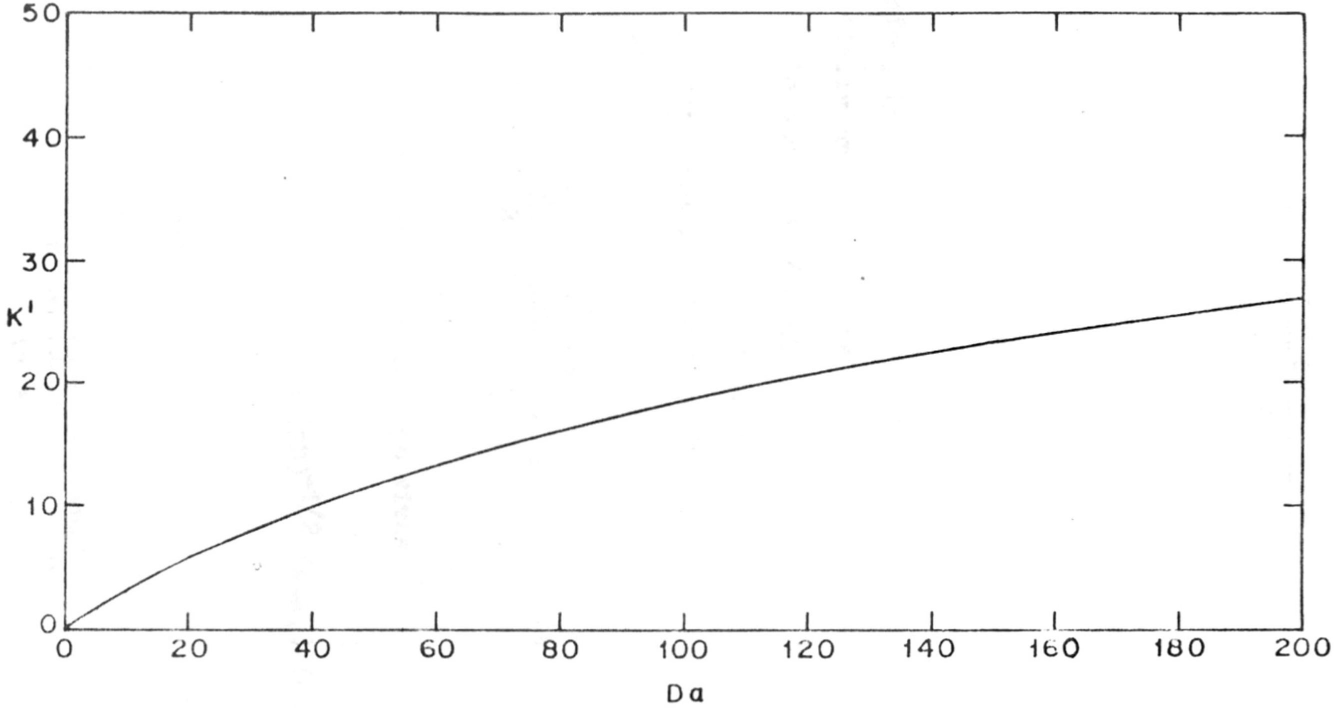

FIG. 8·3. PARAMETER VALUES FOR COEXISTENCE OF STABLE SOLUTIONS

$$a_{1,2} = \frac{-m \pm \sqrt{m^2 - 4n}}{2} \tag{8.55}$$

where $m = -\frac{2}{3} \frac{(K'-2)}{K'}$ and $n = \frac{3}{K'(K'-2)}$

The methodology as outlined above gives, for the values of K' and Da that correspond to the coexistence region, the three roots of the system. For a system initially prepared in such a state coexisting with the unstable state ($a_2=0.3075$), separating the two stable phases we can solve equation 8.39. For this purpose multiplying equation 8.40 by $\partial a/\partial x$ and integrating once we obtain

$$\frac{D}{2}\left(\frac{\partial a}{\partial x}\right)^2 = R(a_1) - R(a) \tag{8.56}$$

Utilizing equation 8.44 in 8.56 gives

$$\frac{\partial a}{\partial x} = -(2D)^{-1/2}(a-a_1)(a_2-a) \tag{8.57}$$

which can be rearranged to obtain

$$a = \frac{a_1+a_2 \exp(p_1)}{(1 + \exp p_1)} \tag{8.58}$$

where $$p_1 = -x(2D)^{-1/2}\,(a_2-a_1)$$

Equation 8.57 provides the necessary relation for obtaining the flux.

8.3.3 Spatial inhomogeneity and nonisotropic diffusion

The derivations detailed as above followed the requirement that diffusion in the system was isotropic. It is of interest to see the effect of variable diffusion. For this purpose we arbitrarily choose a form of diffusivity variation with distance :

$$D = D_o\left[1 + C\ \exp\left(-x^2/l^2\right)\right] \tag{8.59}$$

where C is some arbitrary constant and l represents the spatial correlation length which measures how for down the influence of diffusivity variation prevails. The plots of D vs. x for various values of the correlation length l obtained from Dung and Kozak (1981) are shown in Figure 8.4. Substituting equation 8.59 in 8.40 and rearranging we obtain

$$\left(1 + C\,e^{-x^2/l^2}\right)\frac{d^2a}{dx^2} - \frac{2C\,x}{l^2}\,e^{-x^2/l^2}\,\frac{da}{dx} = \frac{-r(a)}{D_1} \tag{8.60}$$

The equation has to be solved subject to the following conditions:

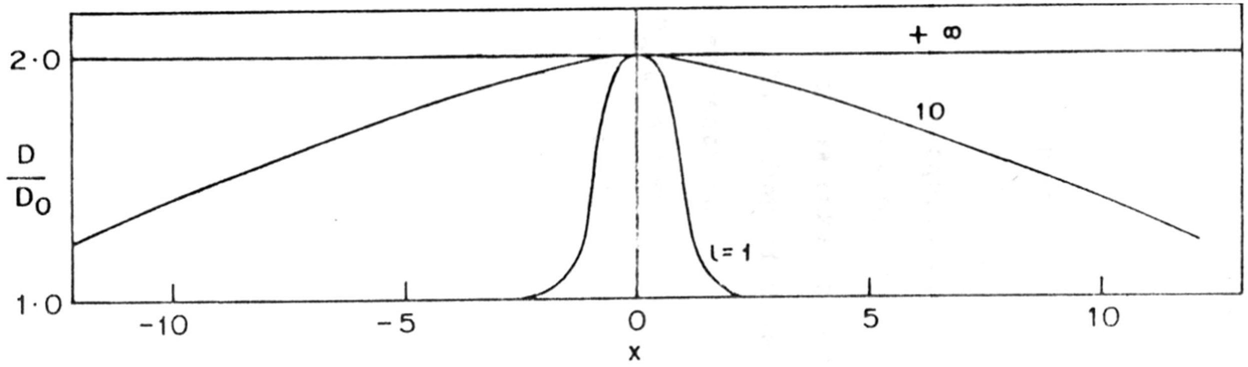

FIG. 8·4. VARIATION OF D VERSUS x FOR VARIOUS VALUES OF CORRELATION LENGTH l

$$a(x=0) = (K'-2) / 3K' ; \quad a(x \to \infty) = \frac{-m - \sqrt{m^2 - 4n}}{2} \qquad (8.61)$$

The relations have been obtained earlier as equation (8.55).

Equation 8.60 represents a boundary value problem with conditions specified at two different locations. It is feasible to convert it into an equivalent initial value problem by defining the flux at $x = 0$. In order to evaluate the slope at the origin we take the asymptotic cases of $l = 0$ and $l \to \infty$. In either of these cases reference to equation 8.59 suggests that D takes a constant value of $D = D_o$ and $D = 2D_o$, assuming that the constant $C = 1$. The slopes calculated using these values of D in equation 8.57 then provide the lower and upper bounds for the initial slope. For any finite value of l, further, equation 8.59 suggests that the slope would always correspond to $l \to \infty$. Thus, for a typical case of $l=0$, the initial slope can be obtained for ($D_o = 5$) as (-2.8361984 E-2), while for $l > 0$ the slope takes the value of (-1.4180992 E-2). Equation 8.60 is then integrated for several values of l with appropriate initial conditions of concentration and slope at the origin. The typical concentration profiles for different values of l are shown in Figure 8.5. We shall now discuss the trends observed in this figure.

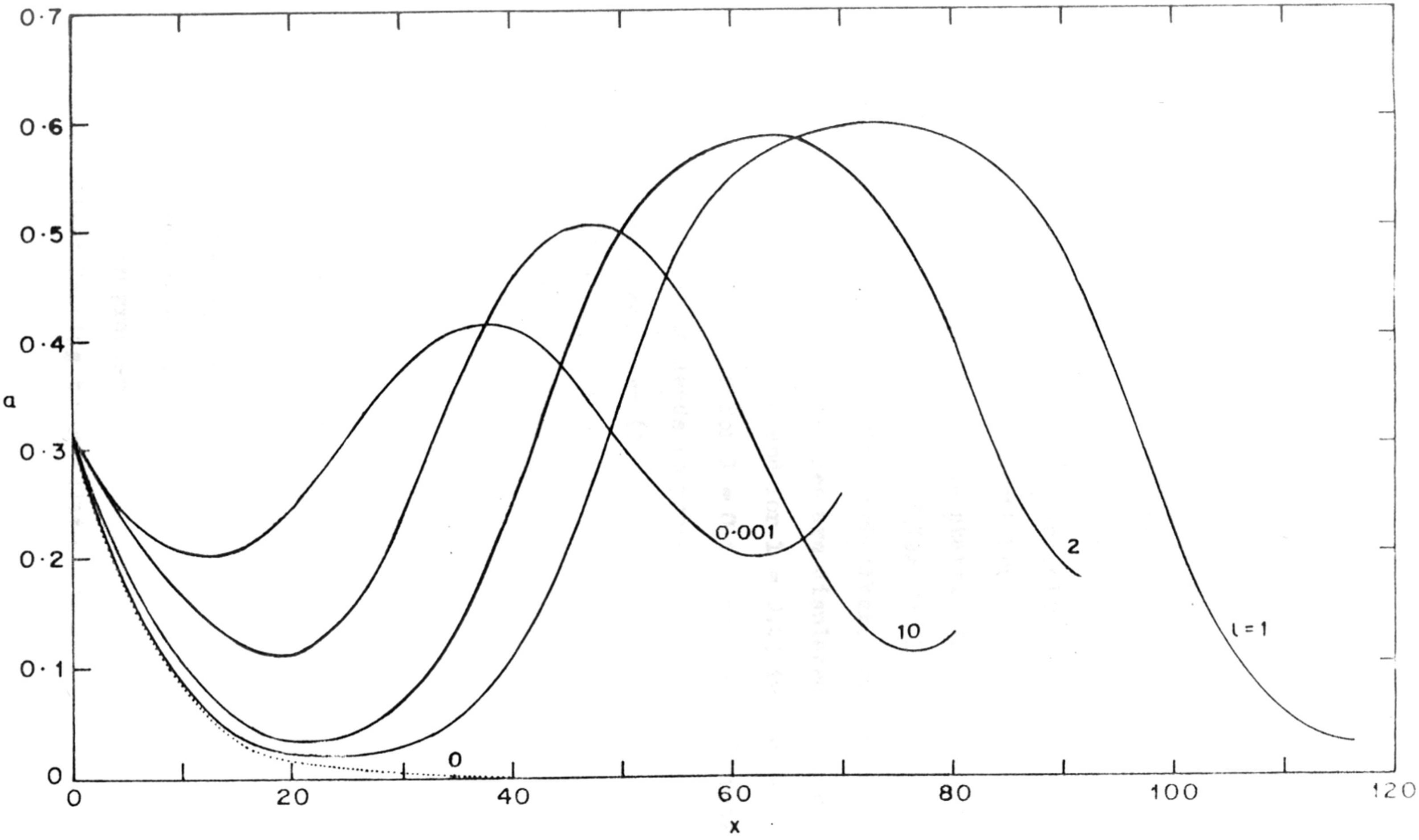

FIG. 8·5. EFFECT OF CORRELATION LENGTH l ON STATIONARY CONCENTRATION PROFILES

8.4 Results and Discussion

The concentration profile for l = 0 smoothly starts from the value at the origin (0.3075) and decreases continuously to finally reach the stable state corresponding to (a_1=8.05 E-3). For even an infinitesimally small value of l , the profile is no longer smooth but starts oscillating even before it reaches the stable state. In fact, for l = 0.001 we observe that the profiles for l = 0.001 and l → ∞ completely coincide with each other. For values of l higher than 0.001 the profiles are displaced towards that corresponding to l = 0 and for l = 0.03 in fact a profile identical to that for l = 0 is realised. Increase of l beyond this value leads to profiles again moving towards the upper boundary (l → ∞) which having reached a certain value of l , the same phenomenon of reversal towards l = 0 profile is realised. It appears thus that, depending on the value of l, the actual profile lies anywhere between the profiles corresponding to l = 0 and l → ∞. In fact, there exist infinite values of l at which the profiles for both l = 0 and l → ∞ can be realised. Infinite values of l for which profiles lie within these bounds can also be realised. It appears thus that, depending on the specific value of l, the transition from one state to another could be smooth as one would realise in the case of a homogeneous diffusion gradient, or the system may generate a spatial pattern leading to oscillatory behaviour. We conclude that the net effect of spatially inhomogeneous diffusion within the system is the formation of spatial patterns within the system.

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NOTATION

a	dimensionless concentration of the species
a_1, a_2, a_3	steady states
a_o	value of a at $v = 0$
C	constant
C_A	concentration of species in the bulk
C_{Ao}	concentration of species in the inlet stream
D	isotropic diffusivity
D_1	parameter defined as D/F
D_o	nonisotropic diffusivity
Da	parameter defined as kV/F
F	flow rate
$F(a, \lambda)$	function of variations in concentration
k	rate constant
K	adsorption constant
K'	parameter defined as KC_{Ao}
l	correlation length
m	defined by equation 8.55
n	defined by equation 8.55
p_1	defined by equation 8.58
q	constant defined in equation 8.6

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r	rate function
$\bar{r}$	defined in equation 8.37
R	defined in equation 8.15
t	time variable
v	velocity at the boundary of two phases
V	volume of the reactor
x	dimensionless distance variable
y	variable defined in equation 8.7

Greek letters

β	constant
γ	constant
λ	external parameter
λ_m	the value of λ at $v = 0$
ϕ	parameter defined by equation 8.3
	defined by equation 8.38a

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