

SOME ASPECTS OF DIFFUSIONAL INTERFERENCE IN CATALYTIC REACTIONS

V. K. JAYARAMAN AND L. K. DORAISWAMY

National Chemical Laboratory, Poona 411 008, India.

ABSTRACT

The aim of the present review is to highlight the implications of the coupling of physical phenomena with chemical reactions occurring in porous catalyst pellets. The usefulness of the concept of effectiveness factors is brought out for simple positive order reactions as well as for reactions involving adsorption of reactants and products. The role of diffusion in altering the selectivity behaviour of different kinds of complex reactions is also analysed. Finally, a brief introductory survey of the dynamic behaviour of a catalyst pellet is presented.

CATALYTIC process constitute a large fraction of all the chemical and petrochemical processes in operation today. To devise any methodology facilitating a rational design of catalytic reactors, information on the intricacies of the catalyst pellet upon which the actual reaction takes place is essential. The utilisable intrinsic activity of a catalyst pellet depends upon various factors, among which the interaction between chemical and physical transport processes is of signal importance and forms the subject matter of the present review. It will be evident from the following sections that under certain circumstances diffusional processes conspire to reduce the activity of a catalyst pellet and falsify the kinetic parameters. Careful analysis of the nature and the effect of these intrusions on the activity, selectivity and dynamic behaviour of catalytic pellets is an essential prerequisite in the operation and control of reactors. Such an analysis also provides broad guidelines for the development and selection of new catalysts.

A number of industrially important reactions are known to operate under conditions of falsified kinetics. A few typical examples are: reduction of nitrobenzene to aniline (an important organic intermediate), hydrogenation of benzene to cyclohexane (an intermediate in the production of nylon), oxidation of sulfur dioxide (in sulfuric acid manufacture), and many important petrochemical reactions.

Several consecutive rate processes occur when a chemical reaction takes place inside a porous catalyst pellet. The reactants must move through the laminar boundary layer surrounding the pellet to the exterior surface of the pellet and then penetrate and diffuse through the porous structure to the active catalytic surface where the reaction occurs. The reaction products must then diffuse through the pores to the external surface and ultimately through the boundary layer into the bulk of the reaction mixture. The heat released during the course of reaction must also follow the same path. These rate processes being finite, the temperature and concentration environments within the pellet are neither uniform nor equal to those at the external surface.

It is customary to gauge the impact of this diffusional disguise by a factor η , normally called the effectiveness factor. An overview of the use of effectiveness factors in analysing various situations encountered in the design and modelling of catalytic reactors is presented in the following sections.

SINGLE REACTION IN A PELLET

Isothermal effectiveness factor

Although industrial catalysts are available in a variety of shapes, it is customary to highlight the physical meaning of the effectiveness factor with one of the three idealized shapes, viz. infinite slab with parallel plane faces, infinite cylinder of

circular cross-section, and sphere. Thus, considering the porous structure to be of spherical shape, a steady state mass balance for an n^{th} order reaction yields

$$D_{eA} \frac{d^2 C_A}{dr^2} + \frac{2}{r} \frac{dC_A}{dr} = k C_A^n \quad [1]$$

where D_{eA} is the effective diffusivity in the pellet, k is the rate constant based on unit catalyst surface and r is the distance parameter. At this stage, it is convenient to define a new parameter ϕ , the Thiele modulus:

$$\phi = r_0 [(k C_{As}^{n-1}) / D_{eA}]^{1/2} \quad [2]$$

where r_0 is the radius of the pellet and C_{As} the concentration of the reactant at the surface of the pellet. For $n=1$, the Thiele modulus becomes independent of concentration.

Equation (1) can be recast as

$$\frac{d^2 C_A}{dr^2} + \frac{2}{r} \frac{dC_A}{dr} = \frac{\phi^2}{r_0^2} C_A \quad [3]$$

The boundary conditions can be defined as
At $r = r_0$ (i.e. at the outside surface of the pellet)

$$C_A = C_{As} \quad [4]$$

At $r = 0$ (i.e. at the centre of the pellet)

$$\frac{dC_A}{dr} = 0 \quad [5]$$

The solution to equation (2) subject to the above boundary conditions can readily be obtained as

$$\frac{C_A}{C_{As}} = \frac{\text{Sin } h(\phi r / R)}{\frac{r}{r_0} \text{Sin } h\phi} \quad [6]$$

This equation gives the concentration profile of the reacting species within the pellet.

As originally realised by Thiele¹ and by Zeldovich² independently, these profiles by themselves are not useful in characterising the diffusional intrusion, and it is necessary to define an effectiveness factor η to visualise readily the implications:

$$\eta = \frac{\text{rate of reaction under diffusional limitations}}{\text{rate of reaction under uniform concentration in the pellet.}}$$

For a spherical pellet η becomes

$$\eta = \frac{3}{\phi} \left(\frac{1}{\tan h\phi} - \frac{1}{\phi} \right) \quad [7]$$

Aris³ has compiled a unique collection of analytical expressions for effectiveness factors for practically all possible shapes of catalysts. These expressions, however complicated, show the same qualitative behaviour of shifting from one asymptote at low ϕ (corresponding to chemical control) to another asymptote for large ϕ (corresponding to diffusion control). A practically useful extension of the concept of the effectiveness factor is the shape generalisation of the Thiele modulus by inclusion of the ratio V_p/S_x (pellet volume/external surface area) in place of the characteristic length (r_0 in equation (2)). This facilitates unification of the η - ϕ curves of all shapes.

Several industrially important reactions involve a change in the number of moles during the course of reaction, and the pressure induced transport occurs in parallel with the diffusive transport. Exact computation of η by using the rigorous dusty gas model was performed by other workers^{4,5}. These calculations indicate that significant pressure gradients may develop during the Knudsen regime. Weekman and Goring⁶ who used a simplified model assuming bulk diffusion as the controlling regime, observed that η decreases with an increase in the number of moles with reaction and conversely increases with the decrease in the number of moles.

Nonisothermal effectiveness factors

When the heat released or adsorbed during the course of reaction is appreciable, thermal diffusivity limitations may cause significant temperature gradients within the pellet. Due to this added complexity, combined heat and mass bal-

ance equations must be solved. For a spherical particle these can be written as

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 D_{eA} \frac{dC_A}{dr} \right) \times R(C, T) \quad [8]$$

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dT}{dr} \right) = (-\Delta H) R(C, T) \quad [9]$$

where $R(C, T)$ is the rate of reaction and ΔH is the enthalpy change due to reaction.

The non-isothermality of the pellet necessitates the introduction of two new parameters: one is the exponent in the Arrhenius rate expression E/RT_s , symbolised by γ and the other, the heat generation function $(-\Delta H D_{eA} C_{As})/(\lambda T_s)$ symbolised by β .

Nondimensionalising equations (8) and (9) and introducing the new parameters the balance equations become

$$\frac{1}{\bar{r}^2} \frac{d}{d\bar{r}} \left(\bar{r}^2 \frac{d\bar{C}_A}{d\bar{r}} \right) = -\phi^2 \bar{C}_A \exp \left[\gamma \left(1 - \frac{1}{\bar{T}} \right) \right] \quad [10]$$

$$\frac{1}{\bar{r}^2} \frac{d}{d\bar{r}} \left(\bar{r}^2 \frac{d\bar{T}}{d\bar{r}} \right) = -\phi^2 \beta \bar{C}_A \exp \left[\gamma \left(1 - \frac{1}{\bar{T}} \right) \right] \quad [11]$$

where

$$\bar{C}_A = C_A/C_{As}, \quad \bar{T} = T/T_s, \text{ and } \bar{r} = r/r_0, \quad [12]$$

These equations are evidently nonlinear. Approximate solutions in closed form can be obtained by employing different mathematical techniques. A representative graph for $\gamma = 20$ is depicted in figure 1 for a first order nonisothermal reaction. This curve represents a fairly typical value of operating variables, viz. an activation energy of 24000 cal/g mole and a reaction temperature of 600°K. The figure shows an interesting feature: for $\beta > 0$, the effec-

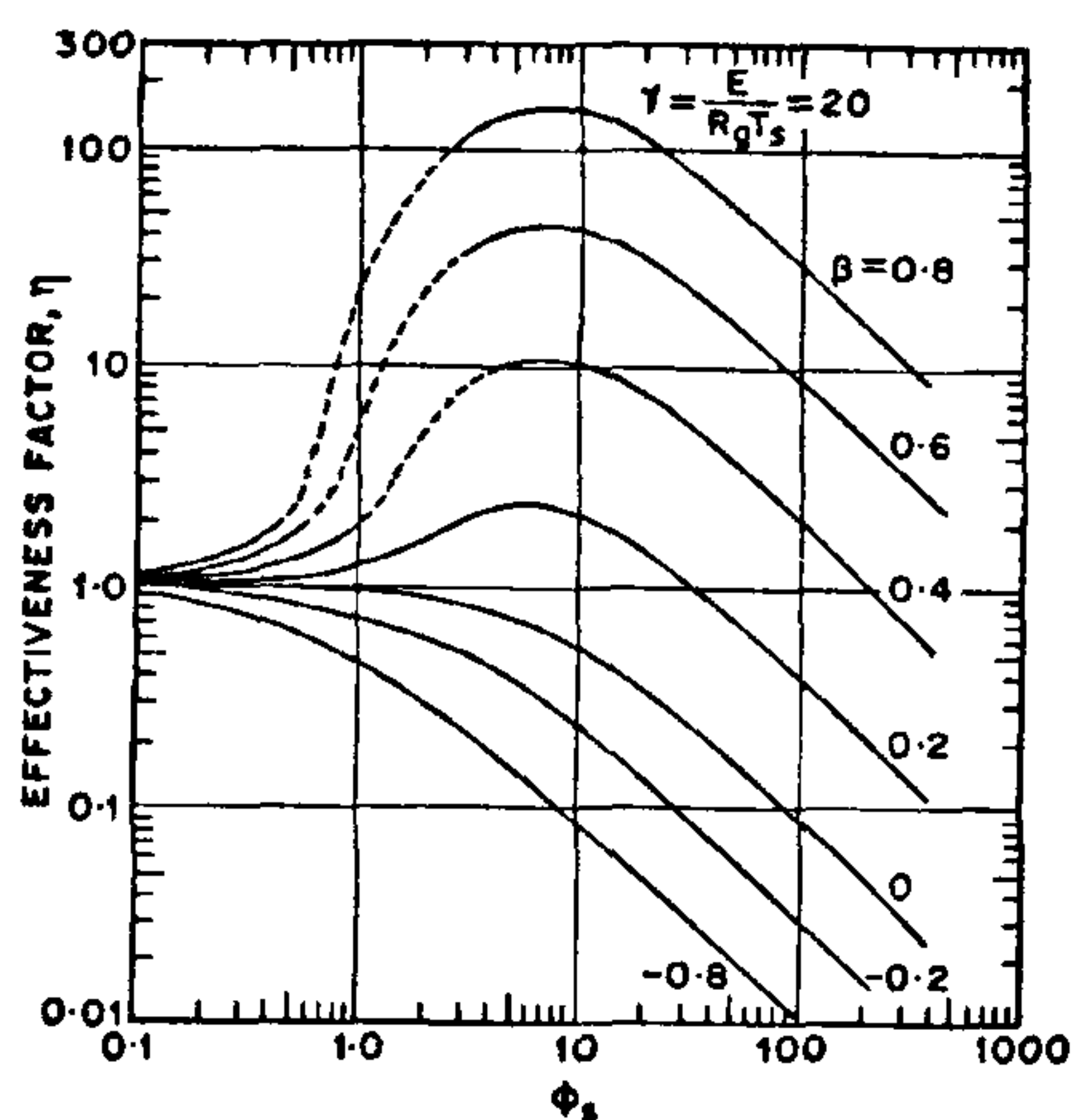


Figure 1. Effectiveness factor η as a function of ϕ_s for first order nonisothermal reaction.

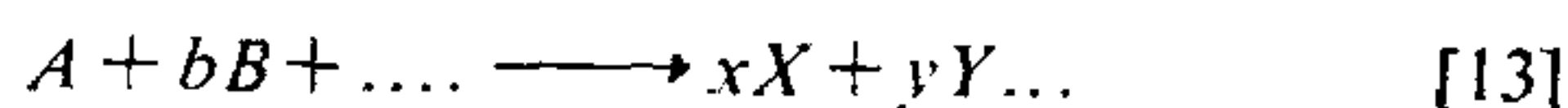
tiveness factor exceeds unity. The reason for this occurrence is that the temperature gradients developed within the pellet overcompensate the reduction in the rate caused by the concentration gradient. The other strikingly odd feature is that for large values of β and a narrow range of Thiele modulus, the value of η is nonuniquely determined. In other words, three different values of η correspond to the same set of values of ϕ , β and γ , thereby showing multiplicity of steady states. This is a case of physiochemical instability. At present, considerable interest is centered on this aspect of pellet behaviour and a more detailed analysis is presented in a subsequent section. Experimental observations of the occurrence of steady state multiplicity by others^{7,8} have demonstrated that this phenomenon is not merely an academic curiosity but must adequately be taken care of in design calculations.

For pellets consisting of a network of macropores, from which the micropores branch out, inclusion of one more parameter α (apart from the Thiele modulus ϕ) is necessary to characterise their behaviour. This factor represents the ratio of diffusivities in the micro and macropores⁹⁻¹⁴.

LANGMUIR-HINSHELWOOD-HOUGEN-WATSON (LHHW) KINETICS

The analyses presented in the previous sections apply to a single reactant with a simple power law type expression for the rate of reaction. In reality, the reactions occurring on a solid surface follow a sequence of steps like the adsorption of the reactant on to the surface, surface reaction, and desorption of the product from the surface. Thus the rate expression will contain additional terms to characterise the actual sequence. The most useful analysis leading to graphical display of results, in terms of easily measurable nondimensional parameters was first carried out by Roberts and co-workers¹⁵⁻¹⁷

The general chemical equation for describing the reaction may be written as



with the rate given by

$$kp_A / (1 + K_A p_A + \sum_i k_i p_i) \quad [14]$$

where K_A, K_B, \dots and p_A, p_B, \dots are adsorption equilibrium constants and the partial pressures respectively, and index i refers to any product or reactant other than A .

For type I kinetics (in which B is not present) a new parameter K is defined such that the terms in the denominator $[k_A p_A + \sum_i k_i p_i]$ can be put in the more tractable form $(1 + K p_A)$, where

$$K = [k_A - D_{eA} \sum_i (k_i \nu_i / D_{ei})] / \omega \quad [15]$$

and

$$\omega = 1 + \sum_i K_i [p_i + (p_A \nu_i D_{eA} / D_{ei})]$$

ν_i is stoichiometric coefficient and includes all species other than A .

The final results obtained can be plotted in the usual form of $\eta - \phi$ curves (see figure 2) and the effect of adsorption can be brought out by a series of curves bounded by the zero order asymptotic curve at $k p_A \rightarrow \infty$ on one side and first order asymptotic curve on the other side.

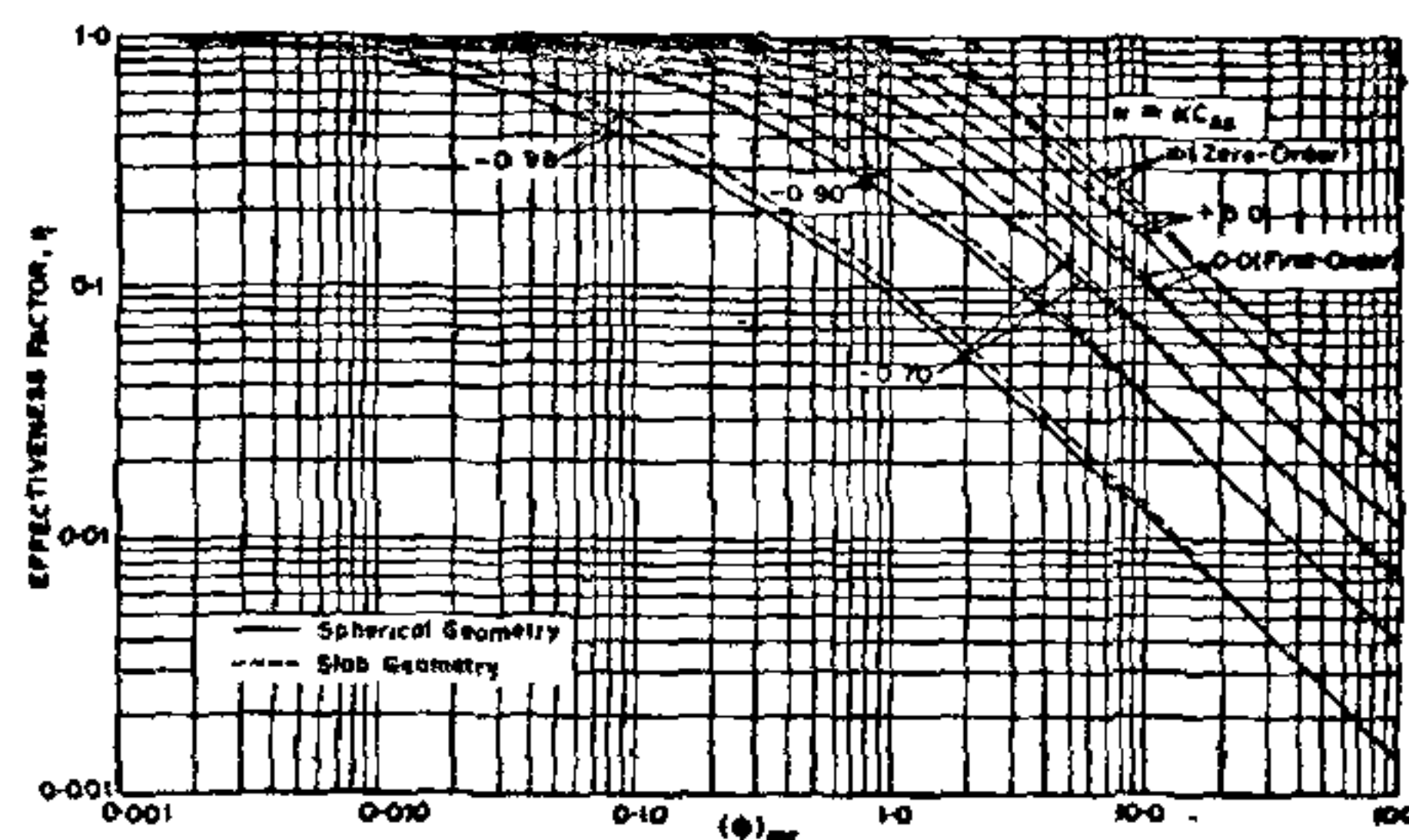


Figure 2. Effectiveness factor plots for various values of the parameter Kc_{As} (Type I-LHHW kinetics).

Where a second reactant is involved (type II) an additional parameter

$$E = \left(\frac{-D_{eB} p_{Bs}}{D_{eA} p_{As}} \right) - 1$$

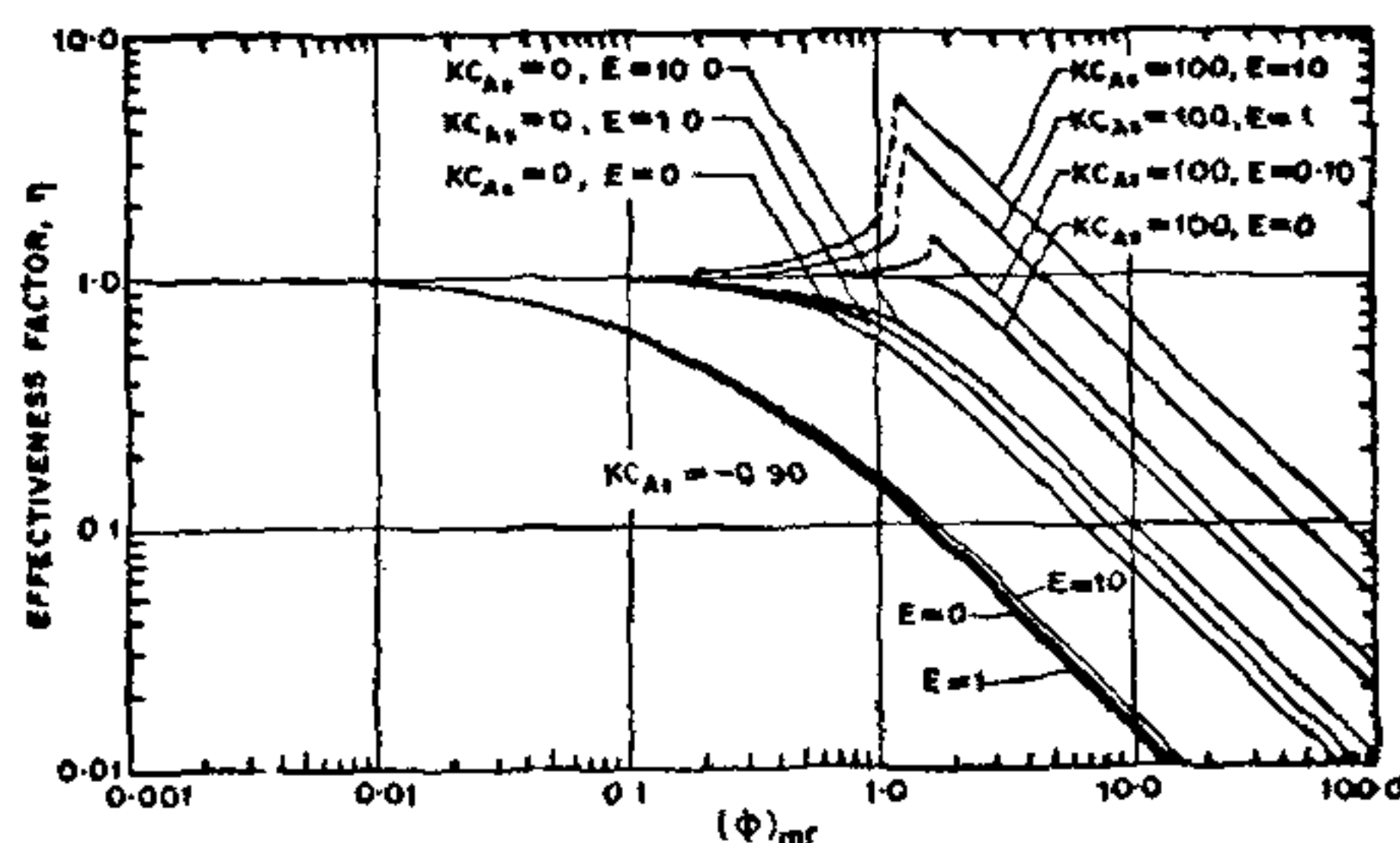


Figure 3. Effectiveness factor plots for different combinations of E and Kc_{As} (Type II-LHHW kinetics).

is defined to provide a quantitative measure of its stoichiometric presence. Figure 3 shows a representative graph of $\eta - \phi$ for type II kinetics. Here again it can be noticed that η exceeds unity for certain parameter values and multiple solutions are possible as in the case of nonisothermal first order reactions. This occurs due to the rate equation possessing a maximum under certain conditions.

An explicit algebraic expression has been developed by Rajadhyaksha *et al*²² for a common class of LHHW kinetics and general order kinetics. This relates the effectiveness factor to the kinetic, adsorption, and transport parameters under nonisothermal conditions. This can directly be used in fixed bed reactor calculations

to take into account the influence of adsorption and intraparticle processes. A few other such examples are also available³

FALSIFICATION OF KINETIC PARAMETERS

Apart from drastically changing the activity-selectivity behaviour, diffusional limitations pose several difficulties in the interpretation of experimental kinetic data. Due to the existence of finite concentration and temperature gradients, the kinetics can no more be expressed by the intrinsic behaviour alone but the influence by transport parameters should also be taken into consideration. In other words, the pellet exhibits kinetics falsified by transport processes. This masking of the kinetics has been referred to as "disguised kinetics" by Wei¹⁹ and Carberry²⁰ has examined the implications of this disguise in determining the operating regime of a process. Rajadhyaksha and Doraiswamy²¹ have presented a comprehensive treatment of the subject.

Falsification of activation energy

The intrinsic activation energy of a chemical reaction can be expressed as

$$E = -R_g \frac{d \ln k}{d(1/T)} \quad [16]$$

In the presence of intraparticle diffusion this becomes

$$E_a = -R_g \frac{d(\ln \eta k)}{d(1/T)} \quad [17]$$

where E_a is the apparent activation energy. Equation (17) can be written as

$$E_a = E - R_g \frac{d \ln \eta}{d(1/T)} \quad [18]$$

or

$$E_a = E \left(1 + \frac{1}{2} \frac{d \ln \eta}{d \ln \phi} \right) \quad [19]$$

For a first order reaction in a slab

$$\eta = \tan h \phi / \phi \quad [20]$$

Hence,

$$E \left[\frac{1}{2} + \phi \left(\frac{1 - \tan h^2 \phi}{2 \tan h \phi} \right) \right] \quad [21]$$

The implications of this equation can readily be understood when the temperature is increased, *i.e.* when transition occurs from kinetic to pore diffusion regime, the apparent activation energy falls to $E/2$.

Falsification of order of reaction

In the case of non-first order kinetics, pore diffusion exercises a two fold influence; it alters activation energy as well as the order of reaction. From first principles, it can easily be shown that $n_a = (n + 1)/2$ under strong pore diffusional control. In the intermediate regime, however, n_a will depend on the temperature and the E_a will vary both with temperature and with concentration.

For a more exhaustive exposition readers can refer to the review of Rajadhyaksha and Doraiswamy²² where various aspects of the falsification of kinetic parameters have been outlined. These falsifications have a profound influence, and it becomes imperative for the designer to account for them, in formulating the pertinent kinetics. Several experimental techniques have been developed and criteria proposed to detect the extent of falsification and to ensure the absence of diffusional effects^{3 23-27}

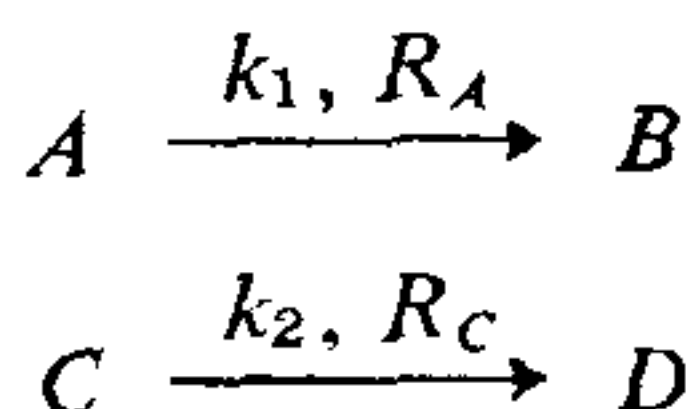
DIFFUSIONAL DISGUISE OF THE SELECTIVITY OF CATALYST PELLETS

We have already seen that diffusional limitations may considerably affect the activity of the pellet and as a result the conversion may be lowered. In simple reactions, we have a fortunate situation—other important design parameters can be adjusted to compensate for this decrease. However, in the case of multipath reactions, the effect of these transport limitations being different for different reaction steps, no such counter balancing measures are normally feasible. Thus it is absolutely essential to analyse carefully the

effects of these intrusions and to incorporate them in the design calculations (see references^{17,27-30}).

We shall consider three broad types of complex reactions: (1) independent, (2) parallel, and (3) consecutive.

(1) Independent reactions



It is convenient to define a differential selectivity as

$$\Delta = \frac{R_A}{R_A + R_C} = \frac{1}{1 + S/s} \quad [22]$$

where s is the intrinsic selectivity k_1/k_2 and $S = C_C/C_A$.

In the presence of intraphase transport limitations the differential selectivity becomes

$$\Delta_{\text{diff}} = \frac{R_A}{R_A + R_C} = \frac{1}{1 + \eta_2 k_2 C_C / \eta_1 k_1 C_A} \quad [23]$$

Under strong diffusional limitation for isothermal conditions for flat plate geometry and for nearly equal diffusivities of A and C equation (23) becomes

$$\frac{\Delta_{\text{diff}}}{\Delta} = \frac{1 + S/s}{1 + (S/s)^{1/2}} \quad [24]$$

Thus the value of $\Delta_{\text{diff}}/\Delta$, depends on whether s is greater than or less than unity. This is illustrated in figure 4. For intrinsic selectivities greater than unity, $\Delta_{\text{diff}}/\Delta < 1$ but not very much so, this is particularly true for small values of S . For s less than unity, $\Delta_{\text{diff}}/\Delta$ is considerably enhanced in the presence of strong diffusional limitations.

(2) Parallel reactions

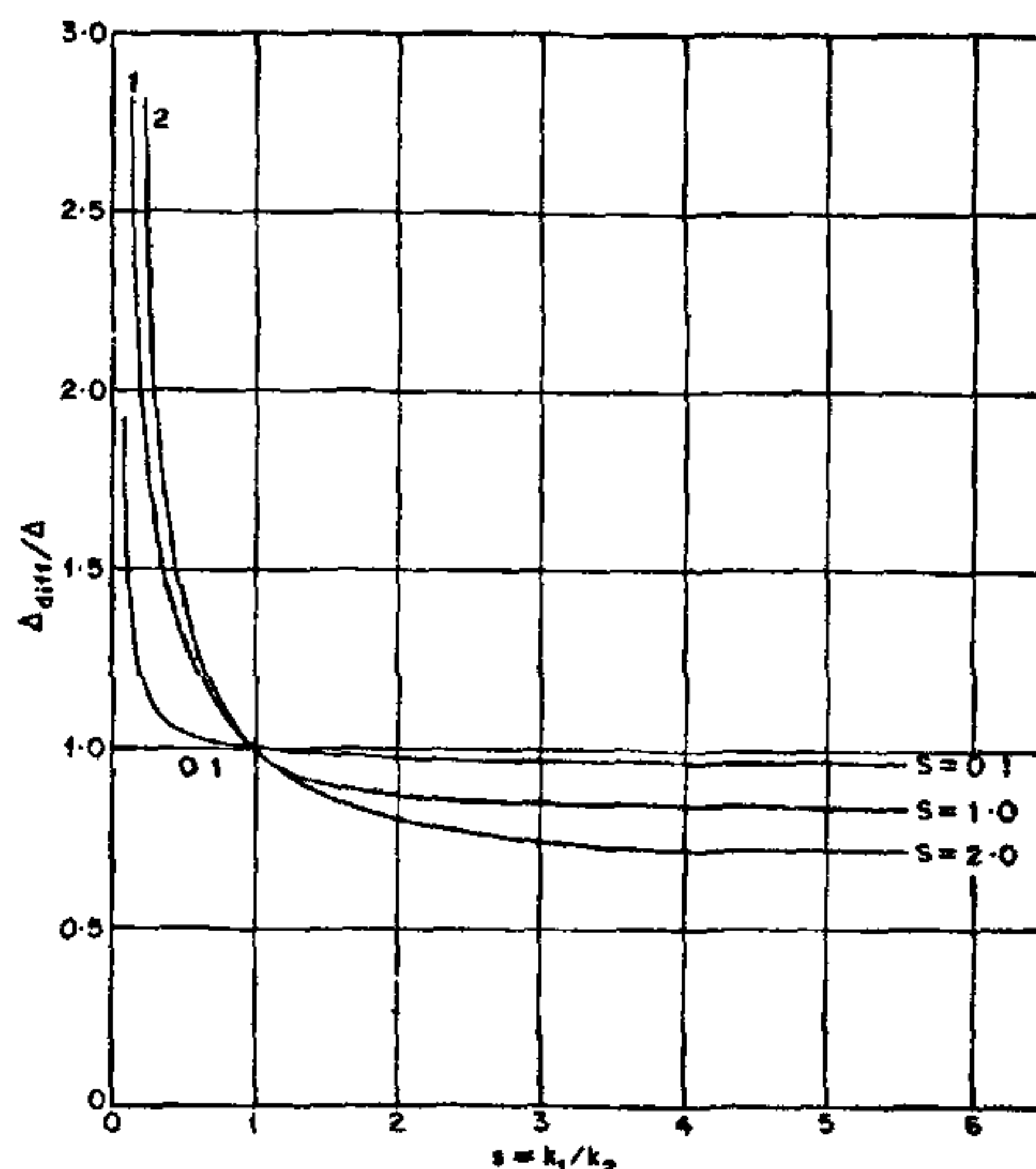
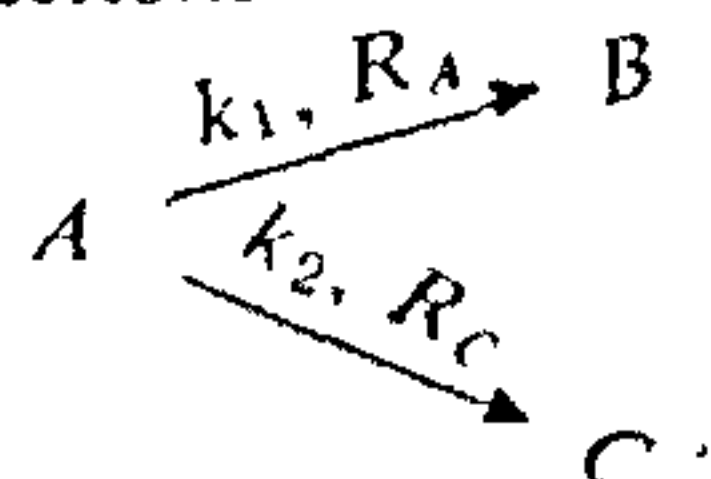


Figure 4. Influence of diffusion on selectivity for an independent reaction scheme.

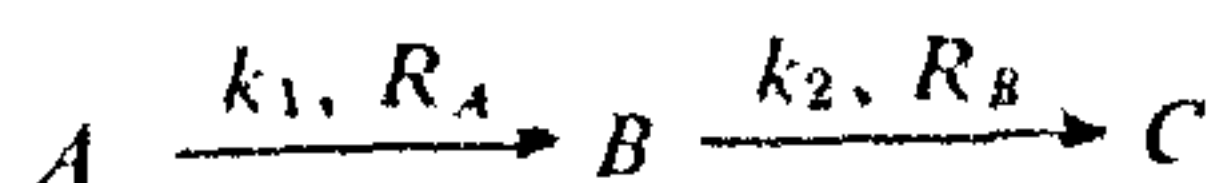
For this scheme since a common reactant is involved (*i.e.* $\eta_1 = \eta_2$) for equal order kinetics there can be no influence of pore diffusion on selectivity. If, on the other hand, reaction (1) were of first order and (2) of second order, then the second reaction would be curtailed to a larger extent inside the pores because of decreased concentration and as a consequence selectivity will increase. The effect of diffusion here, is similar to the effect of pressure, the reaction with the higher order being curtailed to a greater extent with reduction in pressure.

A few other useful generalisations with respect to the effect of reaction order are:

(1) The influence of intraparticle diffusion, on selectivity increases as the difference between the two reaction orders increases.

(2) If the desired product is formed in the lower order reaction, selectivity is enhanced due to intraparticle diffusion. Since, as pointed out earlier in this section, lowering the pressure or diluting the feed has the same effect as a diffusional retardation, operation of such a reaction at reduced pressure will lead to higher selectivity.

(3) Series reactions



In this case the influence of diffusion is far more complicated than in either of the two previous cases. Defining point selectivity, as the ratio of the rate of production of intermediate to the rate of consumption of reactant, under diffusional limitation, Δ becomes

$$\Delta_{\text{diff}} = \frac{s D_{eB} \frac{d\bar{C}_B}{d\bar{r}}}{D_{eA} \frac{d\bar{C}_A}{d\bar{r}}} \quad [25]$$

It can be seen from equation (25) that Δ_{diff} varies with the degree of conversion as represented by s ; so to obtain the overall picture we should compare the behaviour of diffusionally limited and nonlimited cases as reaction proceeds. Thus, equation (25) can be integrated over a range of conversions to give

$$f_B = \frac{s}{s-1} [(1-f_A)^\Omega - (1-f_A)] \quad [26]$$

with

$$\Omega = \frac{1}{\sqrt{s}}$$

where f_B is the fraction of A initially reacted to B and f_A is the total fraction of A reacted.

In a similar fashion, an expression for f_B is easily derived under no diffusional limitation as

$$f_B = \frac{s}{s-1} [(1-f_A)^\Omega - (1-f_A)] \quad [27]$$

where the factor $\Omega = 1/s$ and not $1/\sqrt{s}$ as in equation (26).

Both equations are of the same form and represent respectively the overall selectivity under intrinsic surface reaction conditions and under conditions where pore diffusion is operative. The difference lies only in the definition of Ω .

A comparison of these equations is made in figure 5 for a representative value of $s = 3$. It is evident that the maximum yield of B obtainable when a porous catalyst is operating under diffusional intrusion is only about one-half of that obtainable if the effectiveness factor were unity.

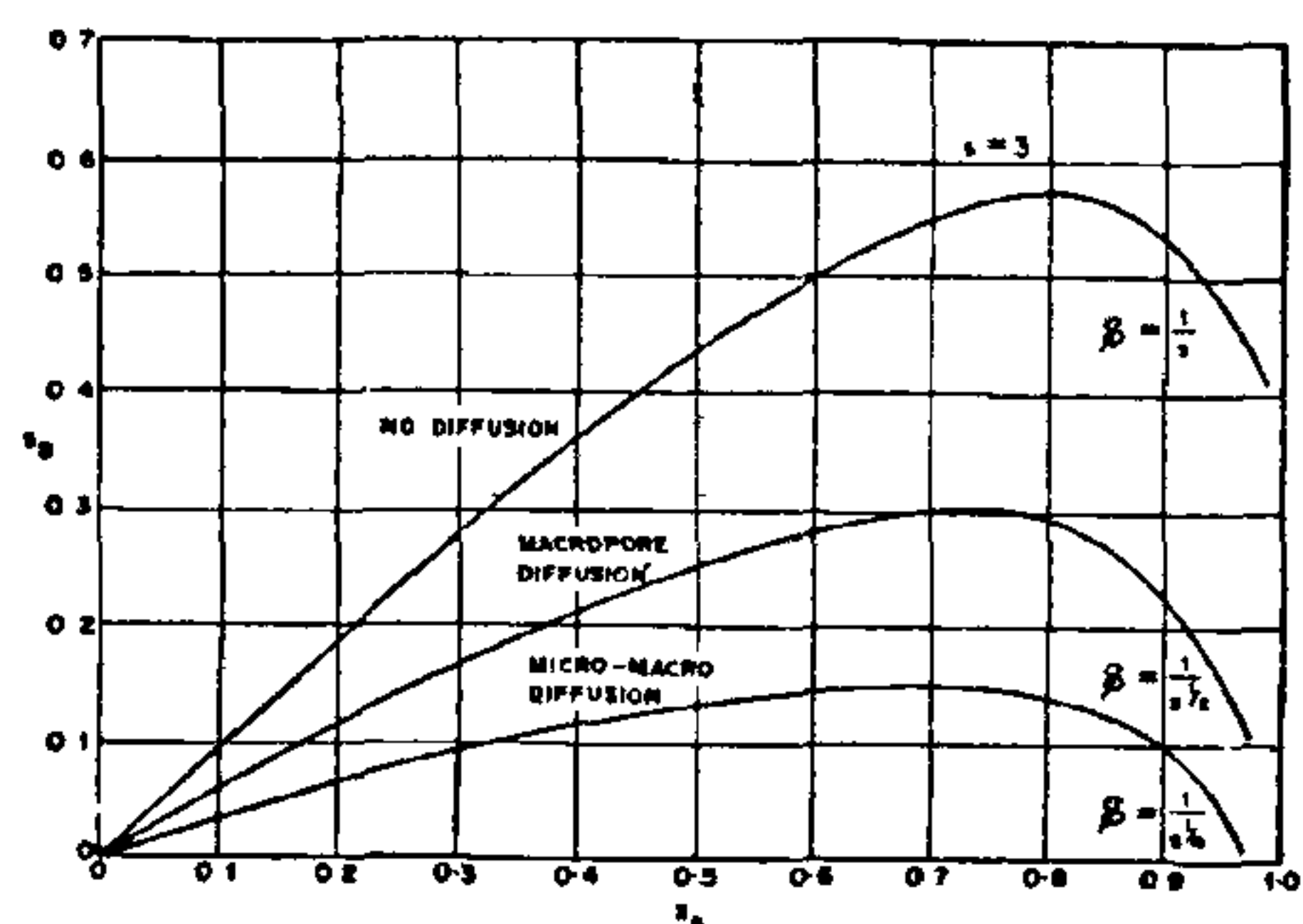


Figure 5. Conversion to intermediate B as a function of total conversion for a series reaction scheme.

It must be pointed out here that for series reactions, although the effectiveness factor continues to drop as the Thiele modulus is increased, the observed selectivity becomes independent of the Thiele modulus for $\phi > 3$ and $\eta < 0.3$. Thus the decrease in selectivity as discussed above occurs surprisingly at effectiveness factors between 1 and 0.3. Hence, if a series reaction is carried out on pellets with effectiveness between 1 and 0.3 it should be possible to increase the yield of the desired intermediate substantially, by subdividing the catalyst or altering the pore structure such that the effective diffusivity is enhanced.

Nonisothermal networks

As sufficient temperature gradients can exist within a pellet for exothermic reactions on supported catalysts (the supports are usually poor conductors of heat) the yield in complex reactions is altered under these conditions not only by diffusion of mass but also of heat. We shall first consider this effect in a system of parallel reactions, and then proceed to the more important case of consecutive reactions.

Parallel reactions: Ostergard³¹ has solved the governing mass and heat transport equations and presented numerical solutions for a few specific values of β and E_1/E_2 . The following conclusions can be drawn from his data.

1) The effect of E_1/E_2 in the range 1.1–1.4 on the effectiveness factor is less than 10%.

2) Under significant transport limitations the yield increases sharply with the increase in the

heat generation parameter β , i.e. under diffusional limitation the effect of β is more pronounced.

3) If the activation energy of the desired reaction is higher than that for the wasteful reaction [i.e. $E_2/E_1 > 1$] the yield is enhanced under transport limitation.

Consecutive reactions: It has already been seen that the effectiveness factors greater than unity are possible in simple exothermic reactions proceeding within a pellet under nonisothermal conditions. In a complex consecutive reaction scheme, however, nonisothermicity of the pellet generally leads to lower yield of the desired intermediates.

The heat and mass balance equations for a consecutive exothermic network scheme constitute a set of highly nonlinear differential equations. Elaborate computer solutions to these

have been obtained by Butt³² and some of the pertinent results are described below.

Clearly, when $\beta_2 = 0$ the heat effect will be due only to the first reaction, when $\beta_1 = 0$ the second reaction alone contributes to nonisothermicity, and when $\beta_1 = \beta_2 = 0$, the system becomes isothermal. Representative plots of η vs $(\phi)_2$ for specific values of β_1 and β_2 and $s = 1.4, 8, 12$ and $\gamma_1 = \gamma_2 = 20$ are shown in figure 6.

Evidently a multitude of such plots can be prepared. A significant feature of these plots is that the second reaction greatly influences the nature of these curves. When the first reaction is endothermic and the second exothermic, the curve follows the course of an endothermic reaction till the overall effect becomes exothermic, and then it follows the course of an exothermic reaction.

It would now be instructive to compare the yield under nonisothermal diffusional limitation with the following three isothermal cases: no diffusion, diffusional limitation in a monodispersed system, and diffusional limitation in a bidispersed system. This is illustrated in figure 7 where the yield is plotted as a function of C_{B_1}/C_{A_1} for $s = 4$. It may be noted that the annihilation of yield caused by nonisothermicity is far greater than in any other case.

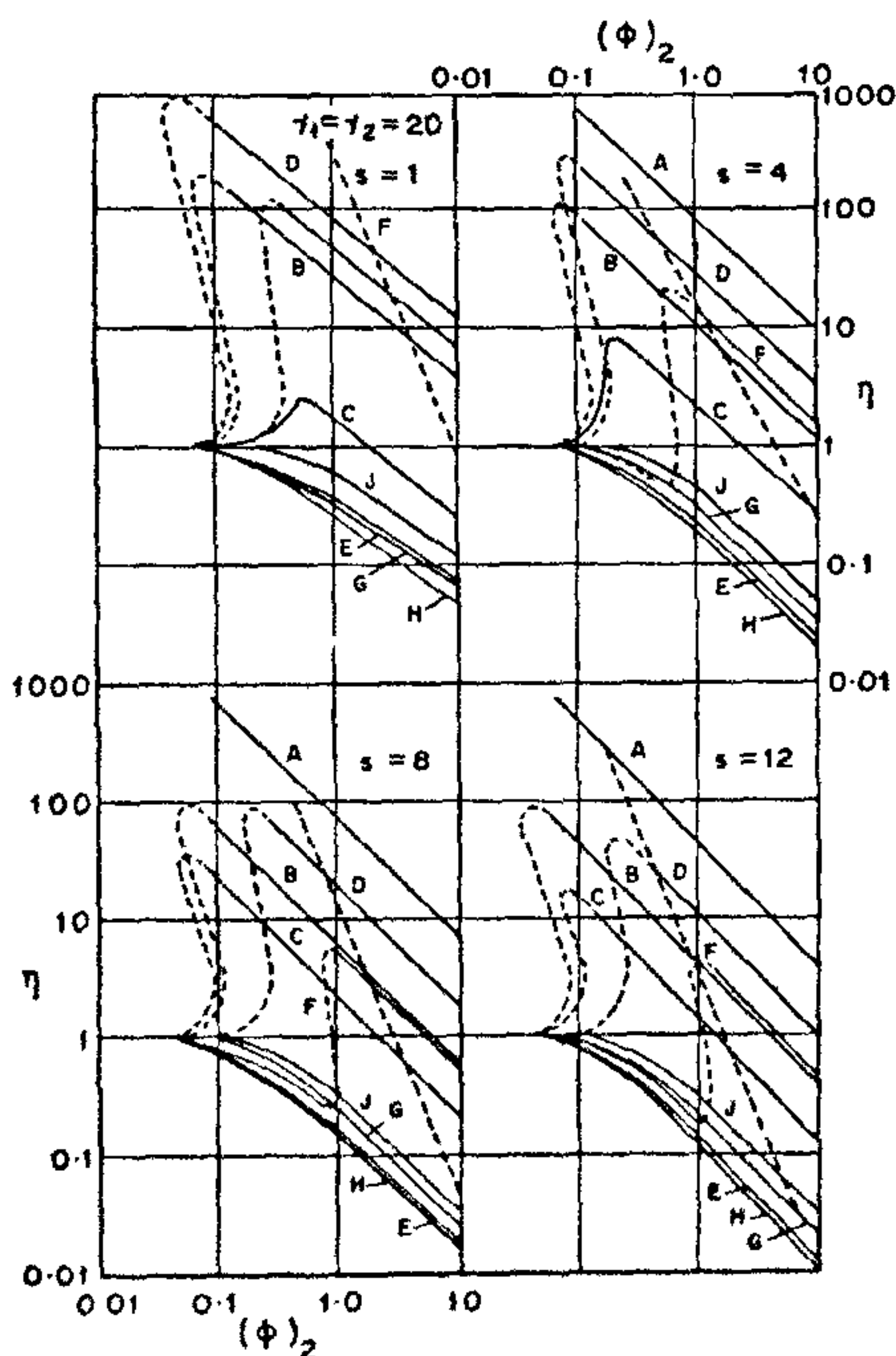


Figure 6. Effectiveness factor as a function of the Thiele modulus for a nonisothermal consecutive scheme for various values of the selectivity ratio (Butt, 1966)³².

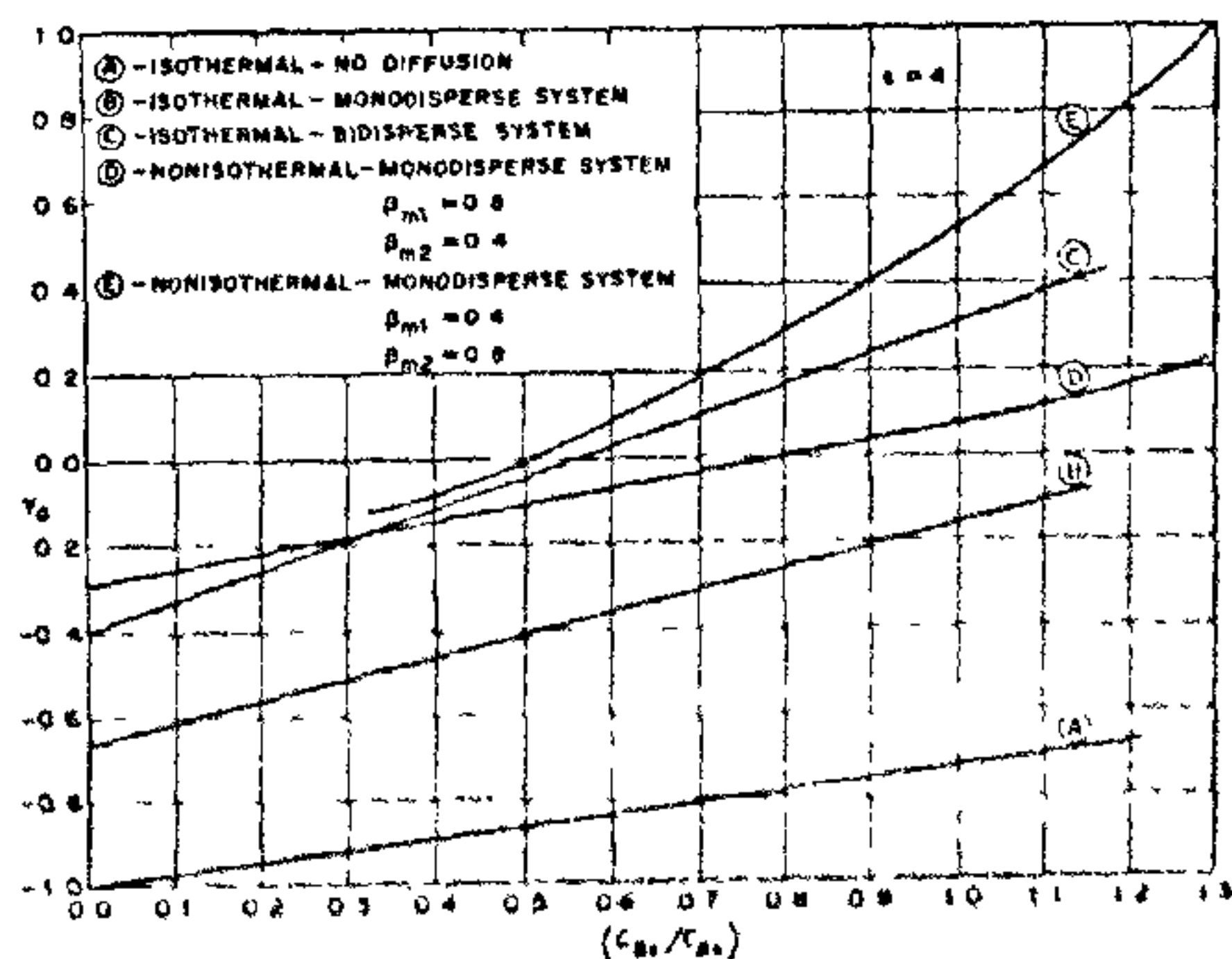


Figure 7. Point yield as a function of the ratio C_{B_1}/C_{A_1} for a nonisothermal consecutive scheme for various diffusion models.

MULTIPLICITY, STABILITY AND DYNAMICS OF CATALYST PELLETS

We have already seen that the superposition of diffusional processes over rate processes may lead to multiplicity of steady states. The fact that such catalytic reaction systems, though exposed to constant operating conditions, can exhibit sustained oscillatory states, arouses suspicion besides interest, for the physical meaning becomes obscure in the absence of rigorous

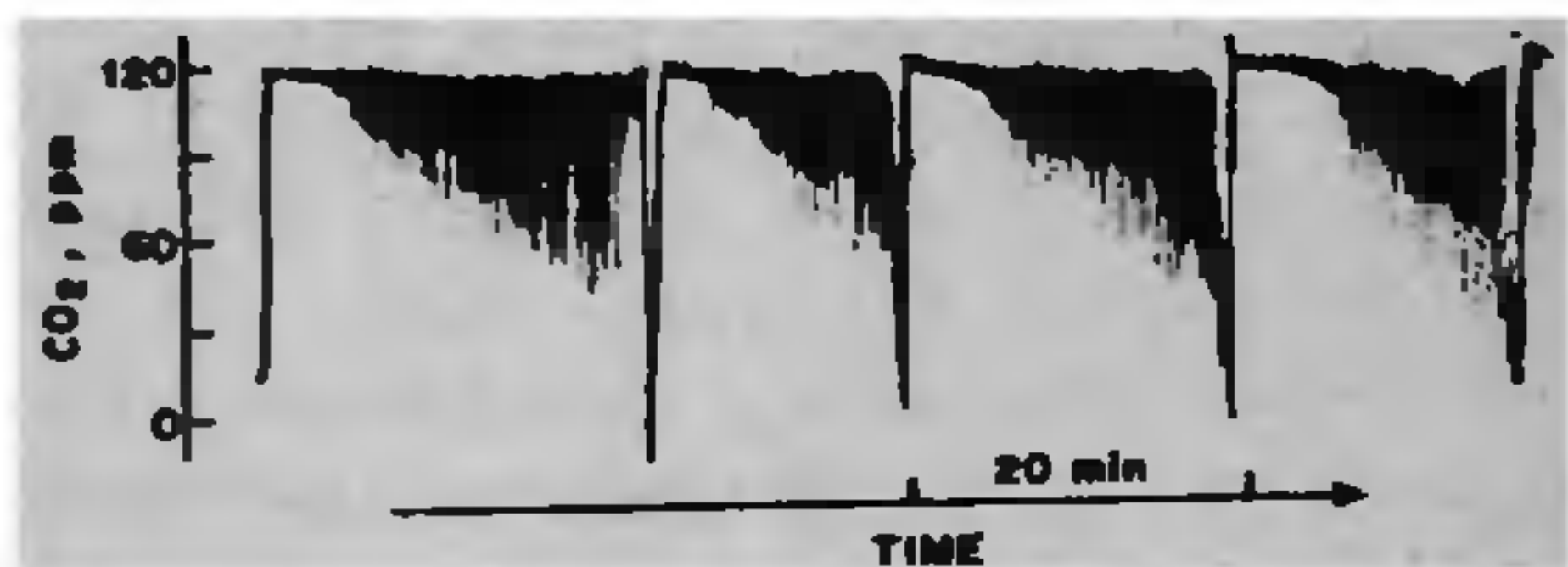


Figure 8. Example of complex cycle behaviour oxidation of CO in a single/porous pellet.

mathematical tools. The very likelihood of their occurrences was questioned until recently when a vast number of experimental results were published verifying theoretical predictions. One such example of complex cyclic behaviour is the oxidation of CO in a single pellet^{33,34}. This is illustrated in figure 8. Excellent reviews on this subject covering a variety of reacting systems are available^{3,35-39}. Further discussion will be restricted to introductory aspects of the subject with specific reference to catalyst pellets. The following definitions are commonly used for the mathematical description of the concepts:

1) **Local stability of the steady state:** A steady state is defined to be locally stable if infinitesimal deviations from the steady state, converge to zero. In other words, if the system after being subjected to certain perturbations, returns to the original state, it is locally stable.

2) **A steady state is defined to be globally stable** if finite deviations from the steady state remain in a neighbourhood of the state as time tends to infinity.

3) **Multiplicity of steady states:** Multiplicity of steady states is the number of different sets of state variables at which the time change of all state variables is identically zero.

4) **Parametric sensitivity:** It shows whether small changes in a parameter have large effects on the equilibrium state. A steady state is not considered stable if it has high sensitivities with respect to change of those parameters, affected by small perturbations. Parametric sensitivity is widely used in fixed-bed reactor design²¹.

For stability analysis, the heat and mass balance equations must be written in transient form. Nonisothermal equations are highly nonlinear due to the exponential temperature dependence of the rate constant. Liyapunov has proved that if a set of nonlinear differential equations is linearised about the steady state, these linearised equations offer sufficient information regarding the behaviour of the system, in the neighbourhood of that steady state. (This is valid under the condition that the real part of the eigen values of the linearised matrix is zero or negative. It follows that these linearised equations are sufficient to determine the local stability of the system. A steady state deemed to be stable by such an analysis may or may not be globally stable. Even a steady state shown to be unstable by linearised analysis may or may not lead to sustained oscillations. Sustained oscillatory states being caused by nonlinear effects, a precise description of these states requires numerical solution of the governing nonlinear equations. The global numerical analysis will also supply the information regarding the attainability of a specific steady state of the system starting from any particular set of initial conditions.

For detailed analyses concerning the dynamic behaviour of catalyst pellets, readers may refer ref. nos. 3, 15, 16, 40-46. Some important basic findings of these analyses are:

1) The steady state multiplicity and the associated instability are usually induced by some feedback mechanism, the feedback being caused either through species or energy. For example, axial dispersion of material and energy is one of the important feedback mechanisms in chemical reactors. Feedback can also be generated by the creation or destruction of active sites on a catalyst.

2) The number of steady states obtainable by intraparticle gradients alone is restricted to three.

3) For certain parameter values the interaction between external and internal gradients may produce two separate regions of multiple steady states. Also, overlapping of these regions may occur producing more than three steady states. For the case of a spherical catalytic surface, theoretical analyses have indicated possible existence of infinite number of steady states.

4) Under special circumstances asymmetric profiles can exist within the pellet.

5) Forced unsteady state operation can profoundly improve conversion and selectivity.

6) Interaction between active 'patches' on a catalyst can produce unstable operation, including chaotic oscillations.

7) Oxidation reactions in general can produce instability through the very nature of adsorption, without assistance from the kinetic-diffusion behaviour of the reaction system.

1. Thiele, E. W., *Ind. Engg. Chem.*, 1939, **31**, 916.
2. Zeldovitch, Ya. B., *Acta Physicochim.*, U.S.S.R., 1939, **10**, 583.
3. Aris, R., "*The Mathematical Theory of Diffusion and Reaction in Permeable Catalysts*", Clarendon Press, Oxford, 1975.
4. Abed, R. and Rinker, R. C., *AIChE J.*, 1973, **19**, 618.
5. Apecetche, M. A., Gonzales, M. G., Williams, R. G. G. and Cunningham, R. E., *J. Catal.*, 1973, **29**, 241.
6. Weekman, V. W. and Goring, R. L., *J. Catal.*, 1965, **4**, 260.
7. Furusawa, T. and Kunii, D., *J. Chem. Eng. Jpn.*, 1974, **4**, 274.
8. Wicke, E., Beusch, H. and Fieguth, P., *Adv. Chem. Ser.*, 1972, **109**, 615.
9. Hashimoto, N., Moffat, A. J. and Smith, J. M., *AIChE J.*, 1976, **22**, 944.
10. Jayaraman, V. K., Kulkarni, B. D. and Doraiswamy, L. K., *AIChE J.*, 1982 (in press).
11. Kulkarni, B. D., Jayaraman, V. K. and Doraiswamy, L. K., *Chem. Eng. Sci.*, 1981, **36**, 943.
12. Mingle, J. O. and Smith, J. M., *AIChE J.*, 1961, **7**, 243.
13. Ors, N. and Dogu, T., *AIChE J.*, 1979, **25**, 723.
14. Uyanik, O., "*Effect of micropores on gaseous diffusion in bidisperse porous catalysts*", M.S. Thesis, Middle East Tech., Univ., Ankara, Turkey, 1977.
15. Roberts, G. W. and Satterfield, C. N., *I&EC Fundam.*, 1965, **4**, 288.
16. Roberts, G. W. and Satterfield, C. N., *I&EC Fundam.*, 1966, **5**, 317.
17. Roberts, G. W., *Chem. Eng. Sci.*, 1972, **27**, 1409.
18. Rajadhyaksha, R. A., Vasudeva, K. and Doraiswamy, L. K., *J. Catal.*, 1976, **41**, 610.
19. Wei, J., *Chem. Eng. Sci.*, 1965, **20**, 729.
20. Carberry, J. J., *Catal. Rev.*, 1969, **3**, 61.
21. Rajadhyaksha, R. A., Vasudeva, K. and Doraiswamy, L. K., *Chem. Eng. Sci.*, 1975, **30**, 1399.
22. Rajadhyaksha, R. A. and Doraiswamy, L. K., *Catal. Rev. Sci., Engg.*, 1976, **13**, 209.
23. Koros, K. M. and Nowak, E. J., *Chem. Engg. Sci.*, 1967, **22**, 470.
24. Mears, D. E., *IEC Proc. Des. Dev.*, 1971, **10**, 541.
25. Tajbl, D. G. and Doraiswamy, L. K., *Catal. Rev. Sci. Engg.*, 1974, **10**, 177.
26. Wagner, C., *Chem. Tech.*, (Berlin), 1945, **18**, 1.
27. Weisz, P. B. and Prater, C. D., *Adv. Catal.*, 1954, **6**, 143.
28. van der Vusse, J. G., *Chem. Engg. Sci.*, 1966, **21**, 1239.
29. Wirges, H. P. and Rahse, W., *Chem. Eng. Sci.*, 1975, **30**, 647.
30. Wheeler, A., *Adv. Catal.*, 1951, **3**, 249.
31. Ostergard, K., Paper presented at the 3rd Cong. Catal., North Holland, Amsterdam, 1965.
32. Butt, J. B., *Chem. Eng. Sci.*, 1966, **21**, 275.
33. Beusch, H., Fieguth, P. and Wicke, E., *Adv. Chem. Ser.*, 1972, **44**, 445.
34. Hugo, P., *Ber. Bunsenges, Phys. Chem.*, 1970, **74**, 121.
35. Furusawa, T. and Kunii, D., *J. Chem. Eng. Jpn.*, 1974, **4**, 274.
36. Nicolis, G. and Portnow, J., *Chem. Rev.*, 1973, **73**, 3650.
37. Schmitz, R. A., *Adv. Chem. Ser.*, 1975, **148**, 154.
38. Gilles, E. D., "*Paper presented at the 4th International Symposium on Chemical Reaction Engineering*", Heidelberg, 1976.
39. Endo, I., Furusawa, T. and Matsuyama, H., *Catal. Rev. Sci. Engg.*, 1978, **18**, 297.
40. Binder, M. S. and Calvelo, A., *Chem. Eng. Sci.*, 1974, **29**, 1909.
41. Eigenberger, G., "*Paper presented at the 4th International Symposium on Chemical Reaction Engineering*" Heidelberg, 1976.

42. Hlavacek, V., Kubicek, M. and Marek, J. *Catal.*, 1969, 15, 31.
43. Hlavacek, V., Kubicek, M. and Marek, M., *J. Catal.*, 1969, 15, 171.
44. Horak, J. and Jiracek, F., "Paper presented at the 2nd International Symposium on Chemical Reaction Engineering", Amsterdam, 1972.
45. Pikios, C. A. and Luss, D., *Chem. Eng. Sci.*, 1977, 32, 191.
46. Wei, J., *Ind. Eng. Chem.*, 1966, 38, 58.
47. Carberry, J. J., *AIChE J.*, 1962, 8, 557.
48. Mason, E. A. and Evans, R. B., *J. Chem. Ed.*, 1969, 46, 358.
49. Scheintuch, M. and Schmitz, R. A., *Catal. Rev. Sci. Eng.*, 1977, 15, 107.
50. Wakao, N. and Smith, J. M., *Chem. Eng. Sci.*, 1969, 46, 358.

ANNOUNCEMENT

AWARDS UNDER ISCA YOUNG SCIENTISTS PROGRAMME

ISCA introduced the programme for the benefit of young scientists from the 68th Session of the Science Congress held in January, 1981. The programme enables the young scientists to present their proposed research work with opportunities to exchange ideas in the relevant scientific problems with their counterparts and specialists. The details of the programme are given below:

- (i) Only ISCA members are eligible for consideration for the Award;
- (ii) The upper age limit for the Award is 30 years as on January 1 of the session;
- (iii) The papers to be presented for consideration shall have to be under single authorship. Preference shall be given for independent work. One copy of the full paper alongwith three copies of its abstract (in 100 words) shall have to reach the office of the General Secretary (Headquarters) not later than August 16 preceding the session. Full name designation and address alongwith the date of birth (duly supported by attested copy of the certificated to be attached) and the section where it is desired to be presented shall have to be clearly indicated on the top of the first page of the full paper and on the top of all the three copies of the abstracts.
- (iv) The papers/abstracts will be scrutinised and the scientists will be required to present their papers in respective sections. The Sectional Presidents and Recorders with the help of three members of the concerned Sectional Committee (specialists) shall recommend suitable papers after their presentations during the session. From the names suggested by the sections, final selection will be made by a committee specially constituted by the General President.
- (v) The Awards will be announced by the General President at the meeting of the General Committee when the Certificate of Merit and the Cash Award of Rs. 500/- will be handed over to the recipient with the citation. A further amount of Rs. 2,500/- towards incidentals, etc. will be sent to the Awardees later from the Headquarters of the Association. The total number of Awards are twenty; and
- (vi) The Awardees will be provided with the admissible travelling and daily allowance by the ISCA (second class concessional bothways rail fare + daily allowance of Rs. 20/- for eight days from 2nd to 9th January).

INDIAN SCIENCE CONGRESS ASSOCIATION
14, Dr. Biresw Guha Street,
Calcutta 700 017.