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II EFFECT OF CATALYST POISONING ON SELECTIVITY —— A MODELLESS APPROACH

III SELECTIVITY OPTIMISATION FOR COMPLEX NON-LINEAR REACTION SCHEMES

IV REACTOR SIMULATION FOR THE HYDROGEN FLOURIDE REACTION——FLOURSPAR + SULPHURIC ACID ⟶ PRODUCTS.

A Thesis
Submitted to the Faculty of Graduate Studies Through the
Department of Chemical Engineering in Partial Fulfilment
of the Requirements for the Degree of
Doctor of Philosophy at the
University of Windsor

by

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Windsor, Ontario
1968

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APPROVED BY:

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PART I

"Because of past studies chemical engineers are prone to accept, as a general rule the previous conclusion, that different theoretical models predict almost the same reaction effects on overall mass transfer rate.................. . The selection of a correct model is indeed very important..."

C.J. Huang and C.H. Kuo
A.I.Ch.E.J. 11, 901
(1965) in a discussion
on the effects of
diffusivities.

HYDRODYNAMIC MODEL SELECTION FOR COUNTER DIFFUSING SYSTEMS——A SELECTIVITY STUDY IN MASS TRANSFER WITH NON-LINEAR CHEMICAL KINETICS.

ABSTRACT

A two step non-linear complex reaction scheme $2M1 \longrightarrow 2M2 \longrightarrow M3$ has been used to establish the need for a careful selection of a mass transfer model for counter diffusing systems. By comparing the Penetration Theory and Film Theory selectivity parameters, it is shown that the two fluid-mechanical models do not predict the same results. It is also shown that the deviations between the results predicted by the two models do not appear to be directly related to increasing complexity in the reaction kinectics. In addition, the effect of reaction order on the selectivity parameter, has been examined by varying the order of the second step reaction.

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CHAPTER I

INTRODUCTION

The solution to the problem of predicting the effect of a liquid phase chemical reaction on gas absorption or vice versa, has been attempted by proposing a hydrodynamic model of the gas-liquid interface and the liquid flow pattern. Amongst the various models suggested, the so called film theory model postulated by Nernst (25), Lewis and Whitman (24) and the penetration-surface renewal theory model proposed by Higbie (14), Kishineveskii (17) and Danckwerts (9), are the two that are most commonly used. When the diffusion coefficients of various reacting species are the same, the results predicted by the film theory and the laminar and turbulent boundary layer theories are found to be in remarkable agreement with each other. This interesting fact has been pointed out by Brian and Beaverstock (4), Kishineveskii and Armash (18), Astarita (1), and a few others. Basing their conclusions on the results available in the literature, Brian et al (4) concluded, " This insensitivity to the fluid mechanical models used suggests that the theoratical predictions will be good approximations even for physical systems which depart considerably from the idealised models." In a similar vein, Astarita (1) stated that in most cases the mass transfer model invoked has little influence on the predicted ratio of the mass transfer coefficient with chemical reaction to the physical mass transfer coefficient. Conclusions of this nature, have led in the past to a rather indiscriminate selection of models for the prediction of the transfer coefficient ratio $\left[\frac{\text{mass transfer with chemical reaction}}{\text{mass transfer without chemical reaction}}\right]$ in heterogeneous fluid-fluid systems. It is to be noted that the conclusion regarding the insensitivity of predicted results to the hydrodynamic model used, is of fundamental importance; but, it has been arrived at on the basis of results obtained from studies dealing with relatively simple systems in which, the products of chemical reaction can never cross the phase boundary. The lone exception is the work of Szekely and Bridgewater (31). On the basis of their investigations of a linear kinetic system with a volatile intermediate, they questioned this alleged insensitivity of predicted results to the model selected. It was decided therefore, to undertake a detailed study with a view to determine, whether or not, the predicted transfer coefficient ratio is always insensitive to the hydrodynamic models used. In order to do so, it was proposed to compare the film and penetration model selectivity of an intermediate, M_2, formed during a complex reaction described below:

$$2M1 + [\beta] \xrightarrow{k_1} 2M2 \qquad (i)$$

$$2M2 + [\beta] \xrightarrow{k_2} M3 \qquad (ii)$$

$$-\left[\frac{dC_{M1}}{d\tau}\right] = 2k_1 \left[C^{n}_{M1}\right] [\beta] \qquad (iii)$$

$$-\left[\frac{dC_{M2}}{d\tau}\right] = 2k_2 \left[C^{m}_{M2}\right] [\beta] - 2k_1 \left[C^{n}_{M1}\right] [\beta] \qquad (iv)$$

The component M1 diffuses from a fluid 'α' into another fluid 'β' where it reacts to form an intermediate M2. It is further assumed that M2 can either react to form M3 or diffuse back into fluid 'α'. The stipulation that M2 can diffuse back across the interface makes this study different from the ones conducted thus far. According to Bridgewater (5) systems of this type are encountered in the liquid phase oxidation of hydrocarbons by absorbed oxygen. As mentioned before, the commonly used index for comparing various hydrodynamic models is the transfer coefficient ratio; but, in this case it was decided to use an equivalent parameter - the Selectivity.

CHAPTER II

REVIEW OF LITERATURE

Peaceman (27), in 1951, compared the film and penetration theory solutions for several kinds of chemical reactions and found that these solutions were in close agreement with each other, as long as the diffusion coefficients of the various reacting species did not differ significantly from each other. Similar results were reported later by Danckwerts and Kennedy (11). The reactions treated by these authors however, were one-step reactions. Brian and Beaverstock (4), analysed a two step reaction of the type:

$$\text{A (gas)} \rightleftharpoons \text{A (liquid)}$$

Liquid Phase:

$$\text{A} + \text{C (already in liquid)} \longrightarrow \text{B (nonvolatile)}$$
$$\text{B} + \text{C} \longrightarrow \text{D (nonvolatile)},$$

and found that if the diffusion coefficients for various components were similar, the results from the penetration theory and film theory would not differ significantly. The components, 'B','C' and 'D' were assumed to be nonvolatile and thus could not cross the liquid-gas phase boundary.

Huang and Kuo (15), using the film and penetration - surface renewal theories, derived equations for the ratio of interphase mass transfer accompanied by a first order reversible reaction. They found that when the diffusivities of the reactants and the products are nearly equal, the effect of chemical reaction on the overall mass transfer ratio is insensitive to the model adopted for calculations. Kishineveskii et al (18) and Astarita (1) reached similar conclusions from their analys$\overset{e}{\text{i}}$s. It must be emphasized again that in all these studies, the products of the chemical reaction could not cross the phase boundary.

Szekely and Bridgewater (31) investigated the fluid - fluid system,

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C \tag{1}$$

$$-\frac{dC_A}{d\tau} = k_1 C_A \tag{2}$$

$$-\frac{dC_B}{d\tau} = k_2 C_B - k_1 C_A \tag{3}$$

in which, both A and B are volatile (A diffuses from a fluid α into fluid β, where it reacts to form B, which in turn can either diffuse back into α or can get converted to C). Because the product of reaction 'B' could cross the phase boundary, it was possible to compare the transfer coefficient ratio for 'B' instead of 'A'. Szekely et al (31) found that the selectivity of the intermediate B, as calculated by the film and penetration - surface renewal models, differed by as much as 22%. The difference in the results obtained by Szekely et al (31) and Brian et al (4), can be attributed to the different assumptions made in these studies concerning the nature of the intermediate 'B'. Thus, whereas in Brian et al's (4) investigation, 'B' could not cross the phase boundary, in Szekely et al's (31) investigation, 'B' could diffuse through the fluid - fluid phase boundary.

In reporting their results, Szekely et al (31) conjectured that other counter diffusing fluid - fluid systems involving more complicated kinetics would display the effect of hydrodynamic patterns more severely. Since the kinetic scheme they investigated involved only first order reactions, the resulting equations for both the film theory model and the penetration models were linear and hence quite easy to solve.

Useful as Szekely et al's (31) results are, their conclusions have the following shortcomings:

i. Linear reactions are an exception rather than a rule in actual chemical engineering practice, and Szekely et al's (31) conclusions are certainly not applicable to cases of nonlinear kinetics. They could only make conjectures regarding the effects of " more complicated kinetics".

ii. Szekely et al (31) have investigated only one case and it can be thought of as an isolated example rather than as a general conclusion.

It is obvious that in order to show the relative importance of model selection for the prediction of the transfer coefficient ratio in a counter diffusing heterogeneous fluid - fluid system, it is necessary to undertake a much more extensive investigation. This study was primarily undertaken with that purpose in mind. Its major objectives are listed below:

i. To establish the relative importance of model selection for heterogeneous counter diffusing fluid - fluid systems with nonlinear kinetics; that is, to quantitatively establish the sensitivity of predicted transfer coefficient ratio to the hydrodynamic model used.

ii. To check Szekely et al's (31) conjectures about the effect of more complicated kinetics on the sensitivity of predictions to the hydrodynamic model used.

CHAPTER III

THEORETICAL MODEL OF THE SYSTEM

The system considered is one in which a fluid species M1 . present in a fluid medium 'α', diffuses into a fluid 'β',

$$M1(\text{ fluid } \alpha\ ) \rightleftharpoons M1(\text{ fluid } \beta\ )$$

where it reacts with the fluid 'β',

$$2M1 + [\beta] \longrightarrow 2M2 .$$

The fluid component M2 then either diffuses back into the medium 'α' or undergoes another irreversible reaction :

$$2M2 + [\beta] \longrightarrow M3 .$$

In this analysis M1 and M2 were treated as gases, whereas β was assumed to be a liquid. However, this treatment is equally valid for liquid - liquid systems. It was assumed that β was in such an excess that its concentration could be considered constant. As Danckwerts (10) and Carberry (7) have shown, absorption into liquids can generally be regarded as an isothermal process. Physical and chemical properties of the system were assumed to be constant. It was also assumed that the diffusive fluxes of species M1 and M2 did not interact. Some further simplifying assumptions that were made in the course of this study are listed below :

i. The diffusion coefficients of M1 and M2 are equal. This assumption is realistic in light of the fact that in most cases the diffusivity in a given medium depends only very slightly on the solute concentration.

ii. There is no resistance to mass transfer in the gas phase. Thus the concentration of species M1 at the gas liquid interface, corresponds to the equilibrium partial pressure of M1 in the bulk gas phase. This assumption does not in any way limit the scope of the problem. The equilibrium assumption is also made for species M2.

iii. The back pressure of the species M2 in the gas phase is zero. This assumption was made for the sake of simplicity and standardisation.

iv. No appreciable change in volume takes place as a result of the chemical reaction.

v. Fluxes of M1 and M2 from the gas phase towards the liquid phase are positive.

The assumptions listed above apply equally well to gas liquid contacting, in packed towers, in wetted wall columns, and to gas absorption into stagnant liquids.

For the system under investigation, selectivity was defined as the ratio of the rate of formation of the intermediate M2, to the rate of depletion of the reactant M1. Selectivity defined in this way is equivalent to the ratio of the surface flux of M2 to that of the surface flux of M1. This definition has been used both by Butt (6) and Bridgewater (5).

CHAPTER IV

DIFFUSION EQUATION

A. General Diffusion Equation

For a reacting species i, the mass balance over a moving small element of liquid, near the gas liquid interface, is described by the partial differential equation :

$$\nabla(D_i \nabla C_i) = \nabla(UC_i) + \frac{\delta C_i}{\delta t} + r \qquad (4)$$

Molecular Transport = Convection + Accumulation

+ Reaction Rate.

The Lagrangian System of Coordinates is used for the derivation of this equation.

The diffusion equation as written above is of very little practical value and is generally simplified by making one or more of the following assumptions :

i. D_i , the diffusivity is constant. This assumption is a good approximation except in the case of polymer solutions, where D_i is strongly dependent on the concentration of various species.

ii. The velocity U is constant over the moving small element of the fluid under consideration.

Equation (4) can therefore be written as

$$D_i \Delta C_i = U.\nabla C_i + \frac{\delta C_i}{\delta t} + r \qquad (5)$$

iii. Each liquid element moves as a single whole with a constant velocity, like a plug in a plug flow reactor. It is implied that there is no motion in a direction perpendicular to the interface, or U=0. With U=0, equation (5) is reduced to

$$D_i \Delta C_i = \frac{\delta C_i}{\delta t} + r \qquad (6)$$

Equation (6) is a mathematical statement of the penetration - surface renewal model.

iv. The concentration profile of a species i in the element is independent of time. This assumption leads to the statement of the so-called film theory model. Thus,

$$D_i \Delta C_i = r \qquad (7)$$

v. Equations (6) and (7) can be further simplified by assuming that the radius of curvature of the gas liquid interface is very large in comparison to the depth of the diffusion / penetration layer, and thus the diffusion process is one-dimensional. According to Levich (23), this condition is almost always fulfilled in real cases. In Cartesian Coordinates, equations (6) and (7) can accordingly be written as

$$D_i \frac{\delta^2 C_i}{\delta x^2} = \frac{\delta C_i}{\delta t} + r \qquad (8)$$

$$D_i \frac{d^2 C_i}{dx^2} = r \qquad (9)$$

B. Mathematical Statement of Penetration Theory

Equation (8) is a statement of mass balance over a small element of liquid in contact with the interface. This equation has been derived under the assumption of a zero velocity gradient in a direction normal to the interface. If the chemical reaction term is dropped, equation (8) can be written as

$$D_i \frac{\delta^2 C_i}{\delta x^2} = \frac{\delta C_i}{\delta t} \qquad (10)$$

If the element of liquid under consideration can be assumed to have :

i. the characteristics of a plug of an infinite depth moving as a whole with a constant velocity, or can be treated as a stagnant element of infinite depth i.e.:

$$0 \leq x \leq \infty \qquad (11a)$$

ii. a uniform initial concentration C_i^o :

$$C_i = C_i^o \; ; \quad t = 0 \quad 0 < x \leq \infty$$
$$C_i = C_i^o \; ; \quad t \geq 0 \quad x \rightarrow \infty \qquad (11b)$$

iii. an interfacial concentration C_i^* :

$$C_i = C_i^* \; ; \quad t \geq 0 \quad x = 0 \qquad (11cc)$$

then, the flux X(t) at exposure time t and at the interface can be expressed as

$$X(t) \equiv - D_i \left(\frac{\delta C_i}{\delta x} \right)_{x=0} = (C_i^* - C_i^o) \sqrt{\frac{D_i}{\pi t}} \qquad (12)$$

The **derivation** of equation (12) is described in Appendix IA.

The average flux, $\tilde{X}(t^*)$, for an exposure or penetration time of t^* is given as

$$\tilde{X}(t^*) = \frac{\int_0^{t^*} -\left(D_i \frac{\delta C_i}{\delta x}\right)_{x=0} dt}{\int_0^{t^*} dt} \tag{13}$$

$$\tilde{X}(t^*) = \frac{\sqrt{D_i}\,(C_i^* - C_i^o) \int_0^{t^*} \frac{dt}{\sqrt{\pi t}}}{\int_0^{t^*} dt} = 2(C_i^* - C_i^o)\sqrt{\frac{D_i}{\pi t^*}} \tag{14}$$

In accepted chemical engineering terminology

$$\tilde{X}(t^*) = K_{Lp}^o\,(C_i^* - C_i^o) \tag{15}$$

where, $$K_{Lp}^o = 2\sqrt{\frac{D_i}{\pi t^*}} \tag{15a}$$

K_{Lp}^o is the penetration theory liquid phase mass transfer coefficient without chemical reaction.

Equation (12) has been derived with the help of assumptions (11). These assumptions are very stringent and are strictly true in rare cases only. Under the conditions imposed by assumptions (11), equation (12) can have only very limited applicability. Danckwerts (9) has listed the conditions under which equation (12) can be applied as a close approximation to :

i. liquid layers of restricted depth, and
ii. liquid moving parallel to the surface with a velocity that varies with depth.

The necessary condition for (i) is that the time of exposure should be so short that the depth of penetration is less than the depth of the liquid; for (ii), it must be so short that the depth of penetration is less than the depth at which the velocity is appreciably different from that at the surface. By the term depth of penetration is meant the distance from the interface over which C_i is appreciably different from C_i^o. Danckwerts (9) has arbitrarily defined the penetration depth as the distance from the interface at which the rise in concentration is 1/100 that at the surface.

Equation (12) has been extensively used for describing mass transfer for situations comparable to conditions (i) and (ii). The resulting models are of great help in understanding the phenomena occuring in industrial equipment. Thus, Brian et al (3), have described the phenomena of mass transfer in a packed absorption column by assuming that the liquid flows down over a piece of absorber packing in slug laminar flow. Absorption is thought to take place by unsteady molecular diffusion and accumulation within a slug of liquid as it flows down the packing and is exposed to the gas phase for a given contact time interval. The liquid is assumed to be instantaneously and completely mixed in flowing from one piece of packing to the other, and to be free of velocity gradients and turbulence near enough to the surface to affect the transport process adjacent to the gas liquid interface. Thus, each new contact time interval is begun in each slug with a flat concentration profile for all components. The contact time between successive mixing points is so short that the absorbed species never penetrates deeply enough to approach the wall of the piece of packing. Therefore, the liquid depth can be taken as infinite for the sake of mathematical simplicity. The descriptions for spray and bubble absorbers as well as for wetted wall columns that satisfy considerations (i) and/or (ii), have been given by Higbie (14).

C. System Equations According to the Penetration Theory

1. Chemical Rate Equations :

$$\mathrm{M1\ (gas)} \rightleftharpoons \mathrm{M1\ (liquid)} \tag{16}$$

Liquid Phase:

$$2\mathrm{M1} + \beta \xrightarrow[r_1]{k_1} 2\mathrm{M2} \tag{17}$$

$$\mathrm{M2\ (liquid)} \rightleftharpoons \mathrm{M2\ (gas)} \tag{18}$$

Liquid Phase:

$$2\mathrm{M2} + \beta \xrightarrow[r_2]{k_2} \mathrm{M3} \tag{19}$$

The rate equation for step (17) is,

$$-\frac{dC_{M1}}{d\tau} = 2k_1 \left(C^{n}_{M1} \right) [\beta] \tag{20}$$

and for the step (19) is,

$$-\frac{dC_{M2}}{d\tau} = 2k_2\ (C_{M2}^{m})\,[\beta] - 2k_1\ (C_{M1}^{n})\,[\beta] \tag{21}$$

If β is present in large excess, its concentration can be assumed to be constant. Thus equations (20) and (21) can be written as

$$-\frac{dC_{M1}}{d\tau} = 2k_1\ C_{M1}^{n} \tag{22}$$

$$-\frac{dC_{M2}}{d\tau} = 2k_2\ C_{M2}^{m} - 2k_1\ C_{M1}^{n} \tag{23}$$

2. Mass Balance Equations :

For the reacting system described by equations (16 - 23), the following mass balance can be written:

$$D_{M1}\ \frac{\delta^2 C_{M1}}{\delta x^2} = \frac{\delta C_{M1}}{\delta t} + 2k_1 C_{M1}^{n} \tag{24}$$

$$D_{M2}\ \frac{\delta^2 C_{M2}}{\delta x^2} = \frac{\delta C_{M2}}{\delta t} + 2\left(k_2 C_{M2}^{m} - k_1 C_{M1}^{n}\right) \tag{25}$$

The appropriate initial and boundary conditions are as follows :

$t = 0 \quad 0 < x \leq \infty \quad C_{M1} = 0$ (26a)

$t \geq 0 \quad x = 0 \quad C_{M1} = C_{M1}^{*}$? (26b)

$t \geq 0 \quad x \to \infty \quad C_{M1} \to 0$, bounded (26cc)

$t = 0 \quad 0 < x \leq \infty \quad C_{M2} = 0$ (27a)

$t \geq 0 \quad x = 0 \quad C_{M2} = 0$ (27b)

$$t \geq 0 \qquad x \rightarrow \infty \qquad C_{M2} \rightarrow 0 \text{ bounded.} \tag{27cc}$$

In equations (24 - 27) 't' refers to the instantaneous time in the life of a liquid element. The boundary conditions (26) and (27), are mathematical statements of the underlying assumptions of the penetration theory.

Boundary conditions (26a, 27a) were chosen for convenience only. Any other bulk concentration can be used. The boundary condition (27b) states that though 'M2' can diffuse back into the gas, its concentration at the interface is zero. This numerical value was chosen for convenience. It should be noted that this boundary condition is different from the normally assumed condition ($\frac{\delta C_{M2}}{\delta x}$)$_{x=o}$ = 0 (which express the nonvolatility of the species M2).

The equations (24 - 27) were non-dimensionalised to :

$$\frac{\delta^2 a}{\delta y^2} = \frac{\delta a}{\delta \theta} + a^n \tag{28}$$

$$\frac{\delta^2 b}{\delta y^2} = \nu \frac{\delta b}{\delta \theta} + \nu \lambda b^m - \nu a^n \tag{29}$$

$$\theta = 0 \qquad 0 < y \leq \infty \qquad a = 0 \tag{30a}$$

$$\theta \geq 0 \qquad y = 0 \qquad a = 1 \tag{30b}$$

$$\theta \geq 0 \qquad y \rightarrow \infty \qquad a \rightarrow 0 \text{ bounded.} \tag{30cc}$$

$$\theta = 0 \qquad 0 < y \leq \infty \qquad b = 0 \qquad (31a)$$

$$\theta \geq 0 \qquad y = 0 \qquad b = 0 \qquad (31b)$$

$$\theta \geq 0 \qquad y \rightarrow \infty \qquad b \rightarrow 0 \text{ bounded.} \qquad (31cc)$$

The transformations used to obtained these dimensionless equations are listed under the mass transfer section of the nomenclature (Page 100).

3. Reaction Diffusion Modulus :

Equations (24 - 27) have to be solved with a view to determining the average value of the expression

$$\left[\frac{-D_{M2}\left(\frac{\delta C_{M2}}{\delta x}\right)_{x=o}}{-D_{M1}\left(\frac{C_{M1}}{\delta x}\right)_{x=0}}\right]$$

, over a predetermined period of time. One index of this predetermined time that is often used in mass transfer literature is the reaction diffusion modulus ψ_p derived by making a suitable substitution for t in the expression for K^o_{Lip}

$$K^o_{Lip} = 2\sqrt{D_i/\pi t} \qquad (15a)$$

In this case, $t = \theta/(2k_1 \overset{*}{C}{}^{n-1}_{M1})$ is chosen. (See the transformation used for non dimensionlising t).

$$K^o_{LM1p} = 2\sqrt{\frac{2D_{M1}k_1\overset{*}{C}{}^{n-1}_{M1}}{\pi\theta}} \qquad (32)$$

$$\frac{\pi\,\theta}{4} = \frac{2D_{M1}k_1\overset{*}{C}{}^{n-1}_{M1}}{K^o{}_{LM1p}} = \psi^2_p \qquad (33)$$

$$\theta = \frac{4\psi_p^2}{\pi} \tag{34}$$

where $\psi_p = \sqrt{2D_{M1}k_1 C_{M1}^{*n-1} / K^o_{LM1p}}$ (35)

The definition of selectivity 'σ_{BAp}' leads to

$$\sigma_{BAp} = \left[\frac{\text{Average of } - D_{M2}\left(\frac{\delta C_{M2}}{\delta x}\right)_{x=o}}{\text{Average of } - D_{M1}\left(\frac{\delta C_{M1}}{\delta x}\right)_{x=o}}\right] \text{ over a}$$

predetermined value of the exposure time 't'.

$$\sigma_{BAp} = \frac{\frac{1}{\nu}\int_0^t (- \delta C_{M2}/\delta x)_{x=0}\, dt}{\int_0^t (- \delta C_{M1}/\delta x)_{x=o}\, dt} \tag{36}$$

In non dimensional terms

$$\sigma_{BAp} = \frac{\frac{1}{\nu}\int_0^\theta (- \delta b/\delta y)_{y=o} d\theta}{\int_0^\theta (- \delta a/\delta y)_{y=0}\, d\theta} \tag{37}$$

For $\nu = 1$, equation (37) is some times written as,

$$\sigma_{BAp} = \frac{\sqrt{\pi/4\theta}\int_0^\theta (- \delta b/\delta y)_{y=o} d\theta}{\sqrt{\pi/4\theta}\int_0^\theta (- \delta a/\delta y)_{y=o} d\theta} \tag{37a}$$

In this form,

$$\overset{\sigma}{BA}_p = \left[\frac{\text{Mass Transfer Coefficient with chemical reaction}}{\text{Mass Transfer Coefficient without chemical reaction}}\text{ for M2}\right] \Big/ \left[\frac{\text{Mass Transfer Coefficient with chemical reaction}}{\text{Mass Transfer Coefficient without chemical reaction}}\text{ for M1}\right] \qquad (37b)$$

D. Solution of Penetration Model System Equations

In order to evaluate $\overset{\sigma}{AB}p$ (equation 37) for various values of θ (or corresponding values of ψ_p), it is necessary to solve equations (28) and (29) along with the initial and boundary conditions (30) and (31). Closed solutions for these equations, except for the case $m = n = 1$, are not known. For mathematical simplicity and because of limitation on computer time, only the following cases were considered : 2

1. $\nu = 1$, $m = 1$, $\overset{**}{n} = 1$
2. $\nu = 1$, $m = 1.5$, $n = 1$
3. $\nu = 1$, $m = 2$, $n = 1$.

Detailed description of the methods used in solving these special cases of equations (28) and (29), follow on the succeeding pages.

** $n = 1$ was chosen because of limitation on computer time. The numerical methods described on the following pages apply equally well to cases where $n \neq 1$.

1. $\nu = 1$, $m=1$, $n=1$.

Equations (28) and (29), with initial and boundary conditions (30) and (31), were solved with the help of the Laplace Transform Tables (28), the step by step procedure is given in Appendix (IA). Szekely et al (31) give the final solution as

$$a = \frac{1}{2}\left[e^{-y}\operatorname{erfc}\left(\frac{y}{2\sqrt{\theta}} - \sqrt{\theta}\right) + e^{y}\operatorname{erfc}\left(\frac{y}{2\sqrt{\theta}} + \sqrt{\theta}\right)\right] \tag{38}$$

$$b = \left(\frac{1}{1-\lambda}\right)\left(\left[e^{-y\sqrt{\lambda}}\operatorname{erfc}\left(\frac{y}{2\sqrt{\theta}} - \sqrt{\lambda\theta}\right) + e^{y\sqrt{\lambda}}\operatorname{erfc}\left(\frac{y}{2\sqrt{\theta}} + \sqrt{\lambda\theta}\right)\right] - \left[e^{-y}\operatorname{erfc}\left(\frac{y}{2\sqrt{\theta}} - \sqrt{\theta}\right) + e^{y}\operatorname{erfc}\left(\frac{y}{2\sqrt{\theta}} + \sqrt{\theta}\right)\right]\right) \tag{39}$$

and

$$\int_0^{\theta}\left(-\frac{\delta a}{\delta y}\right)_{y=0} d\theta = \left[\left(\theta + \frac{1}{2}\right)\operatorname{erf}\sqrt{\theta} + \sqrt{\frac{\theta}{\pi}}\, e^{-\theta}\right] \tag{40}$$

$$\int_0^{\theta}\left(-\frac{\delta b}{\delta y}\right)_{y=0} d\theta = -\left(\frac{1}{1-\lambda}\right)\left\{\left(\theta + \frac{1}{2}\right)\operatorname{erf}\sqrt{\theta} + \sqrt{\frac{\theta}{\pi}}\, e^{-\theta} - \left[\left(\theta\sqrt{\lambda} + \frac{1}{2\sqrt{\lambda}}\right)\operatorname{erf}\left(\sqrt{\lambda\theta}\right) + \sqrt{\theta/\pi}\; e^{-\lambda\theta}\right]\right\} \tag{41}$$

$$\overset{\sigma}{B}Ap = - \left(\frac{1}{1-\lambda}\right)\left\{1-\frac{\left[\left(\frac{4}{\pi}\psi_p^2\sqrt{\lambda} + \frac{1}{2\sqrt{\lambda}}\right)\mathrm{erf}\left(2\psi_p\sqrt{\frac{\lambda}{\pi}}\right) + \frac{2\psi_p}{\pi}\, e^{-(4/\pi)\,\lambda\psi_p^2}\right]}{\left[\left(\frac{4}{\pi}\psi_p^2 + \frac{1}{2}\right)\mathrm{erf}\left(\frac{2\psi_p}{\sqrt{\pi}}\right) + \frac{2\psi_p}{\pi}\, e^{-(4/\pi)\psi_p^2}\right]}\right\} \tag{42}$$

2 and 3. General Procedure for Numerical Solutions

For n=1, and $\nu=1$, equation (29) can be written as,

$$\frac{\delta^2 b}{\delta y^2} = \frac{\delta b}{\delta\theta} + \lambda b^m - \frac{1}{2}\left[e^{-y}\mathrm{erfc}\left(\frac{y}{2\sqrt{\theta}} - \sqrt{\theta}\right) + e^{y}\mathrm{erfc}\left(\frac{y}{2\sqrt{\theta}} + \sqrt{\theta}\right)\right] \tag{43}$$

An analytic solution of equation (43), is not known for when $m \neq 1$. However, numerical techniques employing finite difference methods are available. Out of the two types of finite difference schemes, explicit and implicit, an implicit scheme was chosen. This was done because implicit schemes are inherently stable for all values of $\Delta\theta/\Delta y^2 > 0$ (see equation 17C Appendix C). On the other hand explicit schemes are easier to operate, though they are time consuming because of stability condition $\Delta\theta/\Delta y^2 \leq 1/2$ (see equation 13C Appendix C). The boundary condition (31C) is always a problem in numerical calculations as it involves the division of a semi-infinite length into a finite number of mesh divisions. As mentioned by Secor et al (29) this difficulty can be dealt with in several ways. A practical infinity can be defined and the region $0 \leq y \leq \infty_{\text{practical}}$ can be divided into a uniform mesh. This approach results in a coarse grid in the region of interest (close to the interface i.e. $y = 0$) and results in a corresponding lack of accuracy. However, by using a non-uniform mesh (fine mesh in the region of rapid change and a coarse grid far away from the surface), or a very fine mesh, this difficulty can be overcome. The latter method is time consuming; whereas lack of precise knowledge about the location of the regions of rapid change makes the method of non-uniform grids unworkable.

The space "$0 \leq y \leq \infty$, $0 \leq \theta$" was therefore mapped onto a semi-infinite (in θ) rectangle "$0 \leq z \leq 1$, $0 \leq \theta$", by the transformation

$$y = \frac{cz}{1-z} \qquad (44).$$

Thus at $y=0$, $z=0$ and at $y=\infty$, $z=1$. The constant, c is used to distribute the grid according to the experimenter's needs. A larger c means a finer grid near the interface and a coarser grid at the other end of the space coordinate. A proper value of c can be selected only after experimentation. A value of $c = 0.98$ was chosen, after comparing the analytical and numerical results for the case of $m = 1$.

Equation (43) can be rewritten as:

$$\frac{\delta}{\delta y}\left(\frac{\delta b}{\delta z}\frac{dz}{dy}\right) = \frac{\delta b}{\delta\theta} + \lambda b^{m} - \frac{1}{2}\left[e^{-cz/(1-z)}\operatorname{erfc}\left(\frac{cz}{(1-z)2\sqrt{\theta}} - \sqrt{\theta}\right) + e^{\frac{cz}{1-z}}\operatorname{erfc}\left(\frac{cz}{(1-z)2\sqrt{\theta}} + \sqrt{\theta}\right)\right] \tag{45}$$

$$\frac{\delta b}{\delta z}\frac{dz}{dy} = \frac{\delta b}{\delta z}\,\frac{(1-z)^{2}}{c} \tag{46}$$

$$\frac{\delta}{\delta y}\left(\frac{\delta b}{\delta z}\frac{dz}{dy}\right) = \frac{\delta}{\delta z}\,\frac{dz}{dy}\left(\frac{\delta b}{\delta z}\frac{dz}{dy}\right) = \frac{\delta^{2} b}{\delta z^{2}}\left(\frac{dz}{dy}\right)^{2} + \frac{\delta b}{\delta z}\,\frac{dz}{dy}\,\frac{\delta}{\delta z}\left(\frac{dz}{dy}\right) \tag{47}$$

Equation (47) leads to,

$$\frac{\delta^{2} b}{\delta y^{2}} = \frac{\delta^{2} b}{\delta z^{2}}\,\frac{(1-z)^{4}}{c^{2}} - \frac{\delta b}{\delta z}\left(\frac{2(1-z)^{3}}{c^{2}}\right) \tag{48}$$

With these transformations, equation (43) is changed to,

$$\frac{\delta b}{\delta\theta} = a - \lambda b^{m} - \frac{2\delta b}{\delta z}\,\frac{(1-z)^{3}}{c^{2}} + \frac{\delta^{2} b}{\delta z^{2}}\,\frac{(1-z)^{4}}{c^{2}} \tag{49}$$

where,

$$a = \frac{1}{2}\left[e^{-cz/(1-z)}\operatorname{erfc}\left(\frac{cz}{(1-z)2\sqrt{\theta}} - \sqrt{\theta}\right) + e^{cz/(1-z)}\operatorname{erfc}\left(\frac{cz}{(1-z)2\sqrt{\theta}} + \sqrt{\theta}\right)\right],$$

with the boundary and the initial conditions:

$\theta \geq 0$ $\quad$ $z = 0$ $\quad$ $b=0$ (50a)

$\theta = 0$ $\quad$ $0 > z \geq 1$ $\quad$ $b=0$ (50b)

$$\theta \geq 0 \qquad z \longrightarrow 1 \qquad b = 0 \tag{50cc}$$

The implicit finite difference approximation for the equation (49) can be written as,

$$\frac{b_{i,j+1} - b_{i,j}}{\Delta\theta} = a_{i,j+1} - \lambda b^{m}_{i,j} - \frac{2\left(b_{i+1,j+1} - b_{i,j+1}\right)}{\Delta z}\,\frac{(1 - \Delta z(i-1))^{3}}{c^{2}} + \left(\frac{b_{i+1,j+1} - 2b_{i,j+1} + b_{i-1,j+1}}{\Delta z^{2}}\right)\left(\frac{(1-(i-1)\,\Delta z)^{4}}{c^{2}}\right),$$

$$i=1,2,\ldots N-1$$

$$j=1,2,\ldots M-1 \tag{51a}$$

where,

$$a_{i,j+1} = \frac{1}{2}\left\{ e^{-c(\,(i-1)\Delta z)/(1-(i-1)\Delta z)}\,\mathrm{erfc}\left(\frac{c(i-1)\Delta z}{(1-(i-1)\Delta z)2\sqrt{j\Delta\theta}} - \sqrt{j\Delta\theta}\right) + e^{c(\,(i-1)\Delta z)/(1-(i-1)\Delta z)}\,\mathrm{erfc}\left(\frac{c(i-1)\Delta z}{(1-(i-1)\Delta z)2\sqrt{j\Delta\theta}} + \sqrt{j\Delta\theta}\right)\right\},$$

$$i=2,3,\ldots N-1$$

$$j=1,2,\ldots M-1$$

(51b).

The equations (50a, 50b, 50cc), in the form useful for digital computations, are:

$$b_{(1,j)} = 0.0 \qquad j = 1,2,\ldots \quad M \tag{52a}$$

$$b_{(i,1)} = 0.0 \qquad i = 1,2,\ldots \quad N \tag{52b}$$

$$b_{(N,j)} = 0.0 \qquad j = 1,2,\ldots \quad M \tag{52cc}$$

where,

$$M = \frac{\Delta\theta}{\theta} + 1 \tag{53}$$

$$N = \frac{1}{\Delta z} + 1 \tag{54}$$

The following values of $\Delta\theta$ and Δz were used:

$\theta < 0.02 \qquad \Delta\theta = 0.0001$

$\theta > 0.02 \qquad \Delta\theta = 0.018$

$\Delta z = 0.02$

Equation (51a) can be written as,

$$\begin{aligned} & b_{i+1,j+1}\left[\frac{2(1-(i-1)\Delta z)^3\Delta\theta}{\Delta z c^2} - \frac{(1-(i-1)\Delta z)^4\Delta\theta}{\Delta z^2 c^2}\right] \\ & \quad + b_{i,j+1}\left[1-\frac{2(1-(i-1)\Delta z)^3\Delta\theta}{\Delta z\ c^2} + \frac{2(1-(i-1)\Delta z)^4\Delta\theta}{\Delta z^2 c^2}\right] \\ & \quad + (-1)b_{i-1,j+1}\left[\frac{(1-(i-1)\Delta z)^4\Delta\theta}{\Delta z^2 c^2}\right] \\ & \quad = \Delta\theta a_{i,j+1} - \Delta\theta\lambda b^m_{i,j} + b_{i,j} \quad , \end{aligned}$$

$$i = 2,3,\ldots \quad N-1$$

$$J = 1,2,3,\ldots \quad M-1 \qquad (55)$$

Equation (55) has the following triangular form,

$$S_{B2p}b_{2,j+1} + S_{C2p}b_{3,j+1} = S_{D2p}$$

$$S_{A3p}b_{2,j+1} + S_{B3p}b_{3,j+1} + S_{C3p}b_{4,j+1} = S_{D3p}$$

$$S_{A4p}b_{3,j+1} + S_{B4p}b_{4,j+1} + S_{C4p}b_{5,j+1} = S_{D3p}$$

$$\underline{\qquad\qquad} \quad \underline{\qquad\qquad} \quad \underline{\qquad\qquad} \qquad \underline{\qquad}$$

$$S_{AN-2p}b_{N-3,j+1} + S_{BN-2p}b_{N-2,j+1} + S_{CN-2p}b_{N-1,j+1} = S_{DN-2}$$

$$S_{AN-1p}b_{N-2,j+1} + S_{BN-1p}b_{N-1,j+1} = S_{DN-1p}$$

(56)

where,

$$S_{A2p} = 0$$

$$S_{Aip} = -\frac{(1-(i-1)\Delta z)^4\Delta\theta}{\Delta z^2 c^2}$$

$$i = 3,4,\ldots N-1 \qquad (57a)$$

$$S_{Bip} = 1 - \frac{2(1-(i-1)\Delta z)^3\Delta\theta}{\Delta z\ c^2} + \frac{2(1-(i-1)\Delta z)^4\Delta\theta}{\Delta z^2 c^2}$$

$$i = 2,3,\ldots N-1 \qquad (57b)$$

$$S_{Cip} = \frac{2(1-(i-1)\Delta z)^3\Delta\theta}{\Delta z c^2} - \frac{(1-(i-1)\Delta z)^4\Delta\theta}{\Delta z^2 c^2}$$

$$i = 2,3,\ldots \quad N-2$$

$$S_{CN-1p} = 0 \qquad (57cc)$$

$$S_{Dip} = \Delta\theta a_{i,j+1} - \Delta\theta\lambda b^{m}_{i,j} + b_{i,j}$$

$$i = 2,3,\ldots \quad N-1$$

$$j = 1,2,\ldots \quad M-1$$

$$\text{and } m = 1.5,2\ldots \qquad (57d)$$

Equations (56), and hence, (55), can be solved by Gaussian elimination to obtain the values of b on the line j + 1 (for details of the method, see Appendix D).

Douglas (12) has shown that the round-off error for this numerical method is less than the discretisation error for the usual choice of Δz and $\Delta\theta$. It is to be noted that the term, (λb^{m}) was evaluated on the line 'j' instead of 'j + 1'. This was suggested by Lees (22), who showed that equally accurate results can be obtained if terms such as, (b^{m}), are evaluated on the line 'j' instead of the line 'j + 1'. This modification of the usual implicit finite difference scheme, however, results in a linear **triangular** system of equations, instead of the non linear ones that would result if (b^{m}) was evaluated on the line 'j + 1'. Lees (22) has indicated that there would be a five to six fold reduction in machine time as a consequence of this modification. As an experimental check, the results for $(b^{m}_{i,j})$, were compared with the results for, $(b_{i,j+1})(b^{m-1}_{i,j})$. No significant improvement was found and all further calculations, were therefore done for $(b^{m}_{i,j})$. As a test of convergence for the solution, calculations were repeated with half the normal values of time and space increments. The improvement was found to be less than 1%. In order to calculate σ_{BAp} according to equation (37), the values of the term

$\int_0^\theta \left(-\frac{\delta b}{\delta y}\right)_{y=0} d\theta$ and $\int_0^\theta \left(-\frac{\delta a}{\delta y}\right)_{y=0} d\theta$ are needed.

$\int_0^\theta \left(-\frac{\delta a}{\delta y}\right)_{y=0} d\theta$, was found by using equation (40), whereas

$\int_0^\theta \left(-\frac{\delta b}{\delta y}\right)_{y=0} d\theta$, was evaluated as follows:-

$$\int_0^\theta \left(-\frac{\delta b}{\delta y}\right)_{y=0} d\theta = \int_0^\theta \left(-\frac{\delta b}{\delta z}\right)\left(\frac{(1-z)^2}{c}\right)_{z=0} d\theta = \frac{1}{c}\int_0^\theta \left(-\frac{\delta b}{\delta z}\right)_{z=0} \tag{58}$$

The integration for (58), was done by Simpson's rule. (see Appendix A).

Knowing,

$\int_0^\theta \left(-\frac{\delta a}{\delta y}\right)_{y=0} d\theta$ and $\int_0^\theta \left(-\frac{\delta b}{\delta y}\right)_{y=0} d\theta$, σ_{BAp} was calculated for various values of m, λ, and ψ_p (or the corresponding θ). The results are tabulated in Tables (1-24).

E. Quantitative Aspects of the Film Theory:

The Nernst (25), Lewis and Whitman (24) film theory, although earlier in its origin, can be treated as a special case of Higbie's (14) penetration theory, if it is assumed that the small element of liquid referred to in Higbie's model attains its final concentration profile instantaneously. This amounts to a stagnant film of thickness, δ_f , next to the gas liquid interface. A similar film can be visualised on the gas side of the interface. The other assumptions of Higbie's theory are retained. In the context of the film theory, the assumptions made can be stated as:

i. Outside the two films, the concentration of reactants in the bulk of the two phases is uniform.

ii. The velocity profile in the film is flat. This corresponds to the penetration theory assumption of zero velocity gradient in a direction normal to the interface. Stagnant liquids and liquids moving under laminar flow conditions approximate this situation closely.

iii. The resistence to mass transfer is totally within the film, wherein molecular transport takes place by Fick's law.

If the term 'r' is neglected in the equation (9), the resulting equation can be written as

$$D_i \frac{d^2 C_i}{dx^2} = 0$$

$$C_i = \overset{*}{C}_i \;;\; x=0$$

$$C_i = \overset{o}{C}_i \;;\; x=\delta_f$$

$$\tilde{X} = X = \left(-D_i \frac{dC_i}{dx}\right)_{x=0} = \frac{D_i}{\delta_f}\left(\overset{*}{C}_i - \overset{o}{C}_i\right) = \overset{o}{K}_{Lf}\left(\overset{*}{C}_i - \overset{o}{C}_i\right) \quad (60),$$

where, $\overset{o}{K}_{Lf} = D_i/\delta_f$ (61)

$\overset{o}{K}_{Lf}$ is the liquid side mass transfer coefficient without chemical reaction.

F. System Equations for Film Theory:

Equations (16-23) which describe the chemical processes occuring in the gas liquid system are valid for the film theory as well. The mass balance equations for the film theory are however different. These will now be enumerated:

1. Mass Balance Equations According to the Film Theory

For a reacting species i

$$D_{M1} \frac{d^2 C_{M1}}{dx^2} = 2k_1 C_{M1}^n \quad (62)$$

$$D_{M2} \frac{d^2 C_{M2}}{dx^2} = 2k_2 C_{M2}^m - 2k_1 C_{M1}^n \quad (63)$$

The boundary conditions chosen are

$$x = 0 \qquad C_{M1} = C^{*}_{M1} \qquad (64a)$$

$$x = \delta_f \qquad C_{M1} = 0 \qquad (64b)$$

$$x = 0 \qquad C_{M2} = 0 \qquad (65a)$$

$$x = \delta_f \qquad C_{M2} = 0 \qquad (65b)$$

$$x \geq \delta_f \qquad a = b = 0 \qquad (65cc)$$

Boundary conditions (65a) is a suitable boundary condition for a volatile substance. The value ($x = 0 \quad C_{M2} = 0$) for (65a) was chosen for convenience. These boundary conditons match the boundary conditions for the penetration model. Equations (62-65) can be non dimensionalised to

$$\frac{d^2 a}{dy^2} = \psi_f^2 a^n \qquad (66)$$

$$\frac{d^2 b}{dy^2} = \nu \lambda \psi_f^2 b^m - \nu \psi_f^2 a^n \qquad (67)$$

$$y = 0 \qquad a = 1 \qquad (68a)$$

$$y = 1 \qquad a = 0 \qquad (68b)$$

$$y = 0 \qquad b = 0 \qquad (69a)$$

$$y = 1 \qquad b = 0 \qquad (69b)$$

The selectivity σ_{BA} according to film theory is defined as

$$\sigma_{BAf} = \frac{-D_{M2}\left.\frac{dC_{M2}}{dx}\right|_{x=0}}{-D_{M1}\left.\frac{dC_{M1}}{dx}\right|_{x=0}} \qquad (70)$$

In non-dimensional form,

$$\sigma_{BAf} = \frac{1}{\nu}\,\frac{(-db/dy)_{y=0}}{(-da/dy)_{y=0}} \qquad (71)$$

For $\nu = 1$, equation (71) can also be written as

$$\sigma_{BAf} = \left(\frac{\text{mass transfer coefficient with chemical reaction}}{\text{mass transfer coefficient without chemical reaction}}\ \text{for M2}\right) \Bigg/ \left(\frac{\text{mass transfer coefficient with chemical reaction}}{\text{mass transfer coefficient without chemical reaction}}\ \text{for M1}\right) \qquad (71a)$$

G. Solution of Film Model System Equations

Like the penetration model equations, equations (66-69) can be solved analytically only for the special case of m = n = 1. Solutions for cases corresponding to (a, b, c) of the penetration theory were attempted.

1. $\nu = 1$, $m = n = 1$

The solution of equations (66, 68a,b) is,

$$a = \frac{\operatorname{Sinh}(\psi_f - \psi_f y)}{\operatorname{Sinh}\psi_f}, \quad \left(\frac{da}{dy}\right)_{y=0} = -\frac{\psi_f \operatorname{Cosh}\psi_f}{\operatorname{Sinh}\psi_f} \qquad (72)$$

$$b = \left(\frac{1}{1-\lambda}\right)\left[\mathrm{Cosh}\left(y\psi_f\sqrt{\lambda}\right) - \frac{\mathrm{Sinh}\left(y\psi_f\sqrt{\lambda}\right)}{\tanh\left(\psi_f\sqrt{\lambda}\right)} - \frac{\mathrm{Sinh}\left(\psi_f - \psi_f y\right)}{\mathrm{Sinh}\ \psi_f}\right] \quad (73)$$

$$\sigma_{BAf} = \left\{\frac{-D_{M2}\frac{dC_{M2}}{dx}}{-D_{M1}\frac{dC_{M1}}{dx}}\right\} = \frac{\left(-db/dy\right)_{y=0}}{\left(-da/dy\right)_{y=0}}$$

$$\sigma_{BAf} = -\left(\frac{1}{1-\lambda}\right)\left(1 - \frac{\sqrt{\lambda}\ \tanh\psi_f}{\tanh\psi_f\sqrt{\lambda}}\right) \quad (74).$$

2. and 3. Numerical Solutions for $\nu = 1, n_* = 1, \ m = 1.5, 2.0$

Like it's counterpart in the penetration equation, equation (67) when written as,

$$\frac{d^2b}{dy^2} = \lambda\psi_f^2 b^m - \frac{\psi_f^2\,\mathrm{Sinh}\ \psi_f - \psi_f y}{\mathrm{Sinh}\ \psi_f} \quad (75),$$

has not been solved analytically for the boundary conditions (69a and 69b) unless m = 1. As equation (75), (69a and 69b) pose a two point non linear boundary value **problem ; they** cannot be solved by any of the usual numerical techniques involving superposition of two solutions. The Quasilinearisation technique due to Bellman (2) and Kalaba (16) was selected. This technique coupled with the fourth order Runge-Kutta integration method has been used by Lee (20) for the solution of the axial diffusion model

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$n_* = 1$ was adopted to save computer time. Quasilinearisation can take care of any n≠ 1.

tubular reactor problem, and by Lee (20) and Lapidus et al (19) for optimisation and control problems. Instead of directly solving the non linear differential equation, the solution, when it exists, is obtained as a limit of a sequence of functions representing solutions of linear differential equations. Quasilinearisation provides a technique for the construction of this monotone sequence of functions which converge to the solution of the non linear equation. This representation is achieved by the use of the 'maximum operation' . The linear differential equations, whose solutions constitute the elements of the monotone sequence, can be easily solved with the help of the principle of superposition. The progress towards convergence is quadratic in the sense that each iteration doubles the number of digits of accuracy. The method is briefly outlined in the Appendix (E) and its application to equation (75) is given in the following pages.

a. Quasilinearisation

The right hand side of equation (75) is a continuous function of b and y for all $y \in D(0 \leq y \leq 1)$. It is twice differentiable with respect to b over the domain of interest and has a bounded second partial derivative with respect to b. It is also clear that this expression is a strictly convex function of b over the domain D. Moreover $b = 0$ over B, the boundary of domain D. It follows therefore, (see Appendix E) that the solution of equation (75) can be obtained as the least upperbound of the sequence generated by the recursion relations

$$L\left[b_o(y)\right] = \lambda\psi_f^2\left(v_o(y)\right)^m - \frac{\psi_f^2 \operatorname{Sinh}\left(\psi_f - \psi_f y\right)}{\operatorname{Sinh}\psi_f} + \left(b_o(y) - v_o(y)\right)\left(m\lambda\, \psi_f^2 v_o^{m-1}(y)\right) \qquad (76)$$

where,

$$L\left[\quad\right] = \frac{d^2}{dy^2}\left[\,\right] \qquad (77)$$

$$L\left[b_1(y)\right] = \psi_f^2 \lambda b_o^m(y) - \frac{\psi_f^2 \operatorname{Sinh}\left(\psi_f - \psi_f y\right)}{\operatorname{Sinh}\psi_f} + \left(b_1(y) - b_o(y)\right)\left(m\lambda\, \psi_f^2 b_o^{m-1}(y)\right) \qquad (78)$$

and,

$$L\left[b_{n+1}(y)\right] = \psi_f^2 \lambda b_n^m(y) - \frac{\psi^2 \operatorname{Sinh}\left(\psi_f - \psi_f y\right)}{\operatorname{Sinh}\psi_f} + \left(b_{n+1}(y) - b_n(y)\right)\left(m\lambda\psi_f^2 b_n^{m-1}(y)\right)$$

$$m = 1.5,\ 2 \qquad (79)$$

The boundary conditions for both (76) and (78) are

$b_n(0) = 0 \qquad b_n(1) = 0$

$n = 0, 1, \ldots n$

$v_o(0) = 0 \qquad v_o(1) = 0 \qquad (80)$

Equation (76) and (79), with boundary conditions (80) are second order linear differential equations with variable coefficients. In order to start the generation of the sequence, all that is needed is a guess at the function $v_o(y)$. From a knowledege of the physical situation, and for the purpose of computational convenience, $v_o(y)$ was assumed to be

$$0 = v_o(y);\ 0 \leq y \leq 1 \quad (81)$$

With the assumption stated in equation (81), equation (76) can be solved analytically to give $b_o(y); 0 \leq y \leq 1$. Two methods——the fourth order Runge-Kutta technique and the finite difference formulations ——are available for the solution of equation (78) and similar equations that follow. Since $b_o(y)$ is found analytically it is possible to store values of $b_o(y), 0 \leq y \leq 1$, in the computer memory, but the same is not true for $b_1(y)$. Values of $b_1(y)$ can be calculated and stored at discrete intervals of Δy only. If the Runge-Kutta integration procedure is adopted for the evaluation of $b_2(y)$, the step size has to be increased to $2\Delta y$, as the values of $b_1(y)$ at points halfway between $b_1(y)$ and $b_1(y + \Delta y)$ are required. Thus, if no interpolation polynomial is used, each iteration doubles the step size for a Runge-Kutta integration method. Therefore, without interpolation in five iterations, an eighty division mesh is reduced to a ten division mesh. This can introduce gross errors. Other stability problems commonly associated with marching integration techniques also reduce the efficacy of the Runge-Kutta method. During computations for this problem, for example, it was found that for $\lambda \geq 0.1$, the Runge-Kutta technique yielded unstable results for m = 1.5 and 2. Despite these difficulties encountered in the use of the Runge-Kutta method, the marching technique has been used by Bellman (2), Kalaba (16), and Lee (20).

Sylvester et al (30) were the first to use the finite difference scheme in conjunction with quasilinearisation. Lee (21) has recently solved his old axial diffusion model tubular reactor problem using the finite difference method. The finite difference formulation being less accurate than the Runge-Kutta techniques, it (the finite difference scheme) must use a smaller step size for integration. This in turn results in the use of more computer time. Equations (76-80) can be described in the finite difference form as follows:

$$\frac{b_{o(i-1)} - 2b_{o(i)} + b_{o(i-1)}}{\Delta y^2} = \lambda\psi^2\left(v_{o(i)}\right)^m - \frac{\psi_f^2 \mathrm{Sinh}\left(\psi_f - \psi_f(i-1)\,\Delta y\right)}{\mathrm{Sinh}\,\psi_f} + \left(b_{o(i)} - v_{o(i)}\right)\left(m\lambda\psi_f^2 v_{o(i)}^{m-1}\right),$$

$$i = 2,3,\ldots \quad N-1 \qquad (82)$$

$$b_{o(1)}=0 \;;\quad b_{o(N)}=0 \quad \text{and} \quad N=\frac{1}{\Delta y}+1 \qquad (82a)$$

Equation (82) can also be written as

$$b_{o(i-1)}-\left(2+\Delta y^2 m\lambda\ \psi_f^2 v_{o(i)}^{m-1}\right)b_{o(i)}+b_{o(i+1)} = (1-m)\left(\Delta y^2\lambda\ \psi_f^2 v_{o(i)}^m\right)-\frac{\Delta y^2\psi_f^2 \mathrm{Sinh}\left(\psi_f-\psi_f(i-1)\Delta v\right)}{\mathrm{Sinh}\,\psi_f}$$

$$i=2,3,\ldots \quad N-1 \qquad (83),$$

$$\frac{b_{1(i-1)} - 2b_{1(i)} + b_{1(i+1)}}{\Delta y^2} = \lambda\psi_f^2 b_{o(i)}^m - \frac{\psi_f^2 \mathrm{Sinh}\left(\psi_f - \psi_f(i-1)\Delta y\right)}{\mathrm{Sinh}\,\psi_f} + \left(b_{1(i)}-b_{o(i)}\right)\left(m\lambda\ \psi_f^2 b_{o(i)}^{m-1}\right),$$

$$i=2,3,\ldots \quad N-1 \qquad (84)$$

$$b_{1(1)} = b_{1(N)} = b_{o(1)} = b_{o(N)} = 0 \tag{84a}$$

and,

$$\frac{b_{n+1(i-1)} - 2b_{n+1(i)} + b_{n+1(i+1)}}{\Delta y^2} = \psi_f^2 \lambda b_{n(i)}^m - \frac{\psi^2 \operatorname{Sinh}\left(\psi_f - \psi_f (i-1)\Delta y\right)}{\operatorname{Sinh} \psi_f}$$

$$+ \left(b_{n+1(i)} - b_{n(i)}\right)\left(m\lambda \; \psi_f^2 b_{n(i)}^{m-1}\right)$$

$$i = 2, 3, \ldots \qquad N-1 \tag{85}$$

$$b_{n+1(1)} = b_{n+1(N)} = b_{n(1)} = b_{n(N)} = 0 \tag{85a}$$

Equation (85) can also be written as

$$b_{n+1(i-1)} - \left(2 + \Delta y^2 m\lambda \psi_f^2 b_{n(i)}^{m-1}\right) b_{n+1(i)} + b_{n+1(i+1)}$$

$$= (1-m)\left(\Delta y^2 \psi_f^2 \lambda \; b_{n(i)}^m\right) - \frac{\Delta y^2 \psi_f^2 \operatorname{Sinh}\left(\psi_f - \psi_f (i-1)\,\Delta y\right)}{\operatorname{Sinh} \psi_f},$$

$$i = 2, 3, \ldots \qquad N-1 \tag{86}$$

Equations (83, 84, and 86), along with the boundary conditions (82a, 84a, and 85a), represent a triangular system of equations of the form:

$$\begin{array}{llllr}
S_{B2f}b_{n(2)} & + S_{C2f}b_{n(3)} & & & = S_{D2f} \\
S_{A3f}b_{n(2)} & + S_{B3f}b_{n(3)} & + S_{C3f}b_{n(4)} & & = S_{D3f} \\
 & S_{A4f}b_{n(3)} & + S_{B4f}b_{n(4)} & + S_{C4f}b_{n(5)} & = S_{D4f} \\
 & \text{———} & \text{———} & \text{———} & \text{——} \\
S_{A(N-2)f}b_{n(N-3)} & + S_{B(N-2)f}b_{n(N-2)} & + S_{C(N-2)f}b_{n(N-1)} & & = S_{D(N-2)f} \\
 & S_{A(N-1)f}b_{n(N-2)} & + S_{B(N-1)f}b_{n(N-1)} & & = S_{D(N-1)f}
\end{array} \qquad (87)$$

with,

$$S_{Aif} = 1, \qquad i = 3,4,\ldots \quad n-1 \qquad (88)$$

$$S_{Bif} = -\left(2 + \Delta y^2 m\lambda\psi_f^2 b_{n(i)}^{m-1}\right), \qquad i = 2,3,\ldots \; N-1 \qquad (89)$$

$$S_{Cif} = 1, \qquad i = 2,3,\ldots \quad N-2 \qquad (90)$$

$$S_{Dif} = (1-m)\left(\Delta y^2\psi_f^2\lambda b_{n(i)}^m\right) - \frac{\Delta y^2\psi_f^2 \operatorname{Sinh}\left(\psi_f - \psi_f(i-1)\Delta y\right)}{\operatorname{Sinh}\psi_f},$$

$$i = 2,3,\ldots \qquad N-1 \qquad (91)$$

These equations can be solved by Gaussian elimination (see Appendix D). In calculating the concentration profile of 'b', the interval $0 \leq y \leq 1$ was divided into two-hundred parts. For $\lambda \leq 10^2$, with seven iterations ($n = 6$), five digit accuracy could be obtained. For $10^2 < \lambda \leq 10^4$, in order to obtain the same accuracy, ten iterations were needed. Experiments were made with $\Delta y = .0025$, but no improvement in accuracy could be made. Knowing $(da/_{dy})y = 0$, and the concentration profile of 'b', σ_{BAf} can be easily calculated for various values of m, λ and ψ. The results are presented in tables (1-24).

CHAPTER V

RESULTS

TABLE I

Reaction M1 $\longrightarrow$ M2 is of 1.0 order and M2 $\longrightarrow$ M3 is also of 1.0 order.

ψ (the reaction diffusion modulus) = 0.100000E+00

θ (the time)= 0.127272E-01

λ	FILM MODEL σ_{BAf}	PENETRATION MODEL σ_{BAp}	RATIO $\sigma_{BAf}/\sigma_{BAp}$
0.100000E-05	-0.331990E-02	-0.421910E-02	0.786873E+00
0.100000E-03	-0.327012E-02	-0.421902E-02	0.775091E+00
0.100000E-01	-0.331848E-02	-0.421919E-02	0.786521E+00
0.100000E+03	-0.311793E-02	-0.376804E-02	0.827467E+00
0.100000E+05	-0.896769E-03	-0.899782E-03	0.996651E+00

TABLE II

Reaction M1 ⟶ M2 is of 1.0 order and M2 ⟶ M3 is also of 1.0 order.

ψ (the reaction diffusion modulus) = 0.931358E+00

θ (the time) = 0.110400E+01

λ	FILM MODEL σ_{BAf}	PENETRATION MODEL σ_{BAp}	RATIO $\sigma_{BAf}/\sigma_{BAp}$
0.100000E-05	-0.214832E+00	-0.249920E+00	0.859602E+00
0.100000E-03	-0.214874E+00	-0.249917E+00	0.859780E+00
0.100000E-01	-0.214760E+00	-0.249659E+00	0.860212E+00
0.100000E+03	-0.637602E-01	-0.607834E-01	0.104897E+01
0.100000E+05	-0.721298E-02	-0.688693E-02	0.104734E+01

TABLE III

Reaction M1 $\longrightarrow$ M2 is of 1.0 order and M2 $\longrightarrow$ M3 is also of 1.0 order.

ψ (the reaction diffusion modulus) = 0.100000E+01

θ (the time) = 0.127272E+01

λ	FILM MODEL	PENETRATION MODEL	RATIO
	σ_{BAf}	σ_{BAp}	$\sigma_{BAf}/\sigma_{BAp}$
0.100000E-05	-0.238367E+00	-0.274760E+00	0.867546E+00
0.100000E-03	-0.238403E+00	-0.274757E+00	0.867686E+00
0.100000E-01	-0.238251E+00	-0.274431E+00	0.868162E+00
0.100000E+03	-0.668276E-01	-0.634432E-01	0.105334E+01
0.100000E+05	-0.751669E-02	-0.715339E-02	0.105078E+01

TABLE IV

Reaction M1 → M2 is of 1.0 order and M2 → M3 is also of 1.0 order.

ψ (the reaction diffusion modulus) = 0.200000E+01

θ (the time) = 0.509090E+01

λ	FILM MODEL σ_{BAf}	PENETRATION MODEL σ_{BAp}	RATIO $\sigma_{BAf}/\sigma_{BAp}$
0.100000E-05	-0.517973E+00	-0.544707E+00	0.950921E+00
0.100000E-03	-0.517972E+00	-0.544684E+00	0.950959E+00
0.100000E-01	-0.516743E+00	-0.542444E+00	0.952620E+00
0.100000E+03	-0.872755E-01	-0.819676E-01	0.106475E+01
0.100000E+05	-0.954122E-02	-0.900683E-02	0.105933E+01

TABLE V

Reaction M1 → M2 is of 1.0 order and M2 → M3 is also of 1.0 order.

ψ (the reaction diffusion modulus) = 0.206439E+01

θ (the time) = 0.542400E+01

λ	FILM MODEL	PENETRATION MODEL	RATIO
	σ_{BAf}	σ_{BAp}	$\sigma_{BAf}/\sigma_{BAp}$
0.100000E-05	-0.530950E+00	-0.556475E+00	0.954130E+00
0.100000E-03	-0.530934E+00	-0.556451E+00	0.954143E+00
0.100000E-01	-0.529600E+00	-0.554040E+00	0.955887E+00
0.100000E+03	-0.877076E-01	-0.824698E-01	0.106351E+01
0.100000E+05	-0.958401E-02	-0.905706E-02	0.105818E+01

TABLE VI

Reaction M1 ⟶ M2 is of 1.0 order and M2 ⟶ M3 is also of 1.0 order.

ψ (the reaction diffusion modulus) = 0.582766E+01

θ (the time) = 0.432240E+02

λ	FILM MODEL	PENETRATION MODEL	RATIO
	σ_{BAf}	σ_{BAp}	$\sigma_{BAf}/\sigma_{BAp}$
0.100000E-05	-0.828405E+00	-0.830365E+00	0.997639E+00
0.100000E-03	-0.828296E+00	-0.830205E+00	0.997700E+00
0.100000E-01	-0.817584E+00	-0.815028E+00	0.100313E+01
0.100000E+03	-0.909073E-01	-0.897655E-01	0.101271E+01
0.100000E+05	-0.990081E-02	-0.978663E-02	0.101666E+01

TABLE VII

Reaction M1 $\longrightarrow$ M2 is of 1.0 order and M2 $\longrightarrow$ M3 is also of 1.0 order.

ψ (the reaction diffusion modulus) = 0.600000E+01

θ (the time) = 0.458181E+02

λ	FILM MODEL	PENETRATION MODEL	RATIO
	σ_{BAf}	σ_{BAp}	$\sigma_{BAf}/\sigma_{BAp}$
0.100000E-05	-0.833334E+00	-0.835130E+00	0.997849E+00
0.100000E-03	-0.833218E+00	-0.834964E+00	0.997909E+00
0.100000E-01	-0.822019E+00	-0.819185E+00	0.100345E+01
0.100000E+03	-0.909078E-01	-0.898295E-01	0.101200E+01
0.100000E+05	-0.990086E-02	-0.979303E-02	0.101101E+01

TABLE VIII

Reaction M1 → M2 is of 1.0 order and M2 → M3 is also of 1.0 order.

ψ (the reaction diffusion modulus) = 0.100000E+02

θ (the time) = 0.127272E+03

λ	FILM MODEL	PENETRATION MODEL	RATIO
	σ_{BAf}	σ_{BAp}	$\sigma_{BAf}/\sigma_{BAp}$
0.100000E-05	-0.899997E+00	-0.900388E+00	0.999566E+00
0.100000E-03	-0.894756E+00	-0.900059E+00	0.994108E+00
0.100000E-01	-0.877471E+00	-0.871367E+00	0.100700E+01
0.100000E+03	-0.909090E-01	-0.905177E-01	0.100432E+01
0.100000E+05	-0.990098E-02	-0.986185E-02	0.100396E+01

TABLE IX

Reaction M1 → M2 is of 1.0 order and M2 → M3 is of 1.5 order.

ψ (the reaction diffusion modulus) = 0.118923E+00

θ (the time) = 0.180000E-01

λ	FILM MODEL	PENETRATION MODEL	RATIO
	σ_{BAf}	σ_{BAp}	$\sigma_{BAf}/\sigma_{BAp}$
0.100000E-05	-0.465200E-02	-0.502903E-02	0.925028E+00
0.100000E-03	-0.465200E-02	-0.502903E-02	0.925028E+00
0.100000E-01	-0.465200E-02	-0.502902E-02	0.925029E+00
0.100000E+01	-0.465206E-02	-0.502860E-02	0.925119E+00
0.100000E+03	-0.464096E-02	-0.498702E-02	0.930608E+00
0.100000E+05	-0.387170E-02	-0.324587E-02	0.119280+01

TABLE X

Reaction M1 ⟶ M2 is of 1.0 order and M2 ⟶ M3 is of 1.5 order.

ψ (the reaction diffusion modulus) = 0.931358E+00

θ (the time) = 0.110400E+01

λ	FILM MODEL	PENETRATION MODEL	RATIO
	σ_{BAf}	σ_{BAp}	$\sigma_{BAf}/\sigma_{BAp}$
0.100000E-05	-0.213154E+00	-0.251173E+00	0.848632E+00
0.100000E-03	-0.213154E+00	-0.251172E+00	0.848635E+00
0.100000E-01	-0.213166E+00	-0.251098E+00	0.848933E+00
0.100000E+01	-0.210797E+00	-0.244185E+00	0.863265E+00
0.100000E+03	-0.133653E+00	-0.127098E+00	0.105157E+01
0.100000E+05	-0.338163E-01	-0.491727E-01	0.687704E+00

TABLE XI

Reaction M1 → M2 is of 1.0 order and M2 → M3 is of 1.5 order.

ψ (the reaction diffusion modulus) = 0.206439E+01

θ (the time) = 0.542400E+01

λ	FILM MODEL	PENETRATION MODEL	RATIO
	σ_{BAf}	σ_{BAp}	$\sigma_{BAf}/\sigma_{BAp}$
0.100000E-05	-0.525899E+00	-0.565250E+00	0.930382E+00
0.100000E-03	-0.525901E+00	-0.565237E+00	0.930407E+00
0.100000E-01	-0.525446E+00	-0.564018E+00	0.931612E+00
0.100000E+01	-0.482847E+00	-0.484880E+00	0.995807E+00
0.100000E+03	-0.190452E+00	-0.178973E+00	0.106413E+01
0.100000E+05	-0.427100E-01	-0.677118E-01	0.630762E+00

TABLE XII

Reaction M1 ⟶ M2 is of 1.0 order and M2 ⟶ M3 is of 1.5 order.

ψ (the reaction diffusion modulus) = 0.291625E+01

θ (the time) = 0.108240E+02

λ	FILM MODEL	PENETRATION MODEL	RATIO
	σ_{BAf}	σ_{BAp}	$\sigma_{BAf}/\sigma_{BAp}$
0.100000E-05	-0.651801E+00	-0.684553E+00	0.952154E+00
0.100000E-03	-0.651808E+00	-0.684523E+00	0.952207E+00
0.100000E-01	-0.650364E+00	-0.681564E+00	0.954222E+00
0.100000E+01	-0.554022E+00	-0.541663E+00	0.102281E+01
0.100000E+03	-0.194646E+00	-0.188601E+00	0.103205E+01
0.100000E+05	-0.419237E-01	-0.711512E-01	0.589219E+00

TABLE XIII

Reaction M1 ⟶ M2 is of 1.0 order M2 ⟶ M3 is of 1.5 order.

ψ (the reaction diffusion modulus) = 0.412192E+01

θ (the time) = 0.216240E+02

λ	FILM MODEL	PENETRATION MODEL	RATIO
	σ_{BAf}	σ_{BAp}	$\sigma_{BAf}/\ \sigma_{BAp}$
0.100000E-05	-0.747193E+00	-0.778436E+00	0.959865E+00
0.100000E-03	-0.747211E+00	-0.778373E+00	0.959965E+00
0.100000E-01	-0.743755E+00	-0.772270E+00	0.963076E+00
0.100000E+01	-0.579572E+00	-0.572484E+00	0.101237E+01
0.100000E+03	-0.192977E+00	-0.193758E+00	0.995970E+00
0.100000E+05	-0.394591E-01	-0.729936E-01	0.540583E+00

TABLE XIV

Reaction M1 $\longrightarrow$ M2 is of 1.0 order and M2 $\longrightarrow$ M3 is of 1.5 order.

ψ (the reaction diffusion modulus) = 0.504737E+01

θ (the time) = 0.324239E+02

λ	FILM MODEL σ_{BAf}	PENETRATION MODEL σ_{BAp}	RATIO $\sigma_{BAf}/\sigma_{BAp}$
0.100000E-05	-0.789270E+00	-0.822378E+00	0.959740E+00
0.100000E-03	-0.789297E+00	-0.822286E+00	0.959881E+00
0.100000E-01	-0.783962E+00	-0.813481E+00	0.963712E+00
0.100000E+01	-0.582405E+00	-0.583095E+00	0.998815E+00
0.100000E+03	-0.190835E+00	-0.195532E+00	0.975980E+00
0.100000E+05	-0.375011E-01	-0.736272E-01	0.509337E+00

TABLE XV

Reaction M1 → M2 is of 1.0 order and M2 → M3 is of 1.5 order.

ψ (the reaction diffusion modulus) = 0.582766E+01

θ (the time) = 0.432240E+02

λ	FILM MODEL	PENETRATION MODEL	RATIO
	σ_{BAf}	σ_{BAp}	$\sigma_{BAf}/\sigma_{BAp}$
0.100000E-05	-0.813855E+00	-0.849342E+00	0.958218E+00
0.100000E-03	-0.813891E+00	-0.849223E+00	0.958395E+00
0.100000E-01	-0.806852E+00	-0.838019E+00	0.962808E+00
0.100000E+01	-0.581930E+00	-0.588464E+00	0.988895E+00
0.100000E+03	-0.188967E+00	-0.196429E+00	0.962010E+00
0.100000E+05	-0.359067E-01	-0.739479E-01	0.485567E+00

TABLE XVI

Reaction M1→M2 is of 1.0 order and M2→M3 is of 1.5 order.

ψ (the reaction diffusion modulus) = 0.683302E+01

θ (the time) = 0.594240E+02

λ	FILM MODEL	PENETRATION MODEL	RATIO
	σ_{BAf}	σ_{BAp}	$\sigma_{BAf}/\sigma_{BAp}$
0.100000E-05	-0.836619E+00	-0.875456E+00	0.955638E+00
0.100000E-03	-0.836562E+00	-0.875301E+00	0.955742E+00
0.100000E-01	-0.827362E+00	-0.860934E+00	0.961005E+00
0.100000E+01	-0.580129E+00	-0.592888E+00	0.978479E+00
0.100000E+03	-0.186560E+00	-0.197169E+00	0.946191E+00
0.100000E+05	-0.339475E-01	-0.742121E-01	0.457439E+00

TABLE XVII

Reaction M1 ⟶ M2 is of 1.0 order and M2 ⟶ M3 is of 2.0 order.

ψ (the reaction diffusion modulus) = 0.118923E+00

θ (the time) = 0.180000E-01

λ	FILM MODEL	PENETRATION MODEL	RATIO
	σ_{BAf}	σ_{BAp}	$\sigma_{BAf}/\sigma_{BAp}$
0.100000E-05	-0.468774E-02	-0.502903E-02	0.932135E+00
0.100000E-03	-0.468774E-02	-0.502903E-02	0.932135E+00
0.100000E-01	-0.468774E-02	-0.502903E-02	0.932135E+00
0.100000E+01	-0.465200E-02	-0.502901E-02	0.925032E+00
0.100000E+03	-0.465232E-02	-0.502724E-02	0.925421E+00
0.100000E+05	-0.462080E-02	-0.486582E-02	0.949645E+00

TABLE XVIII

Reaction M1→M2 is of 1.0 order and M2→M3 is of 2.0 order.

ψ (the reaction diffusion modulus) = 0.931358E+00

θ (the time) = 0.110400E+01

λ	FILM MODEL	PENETRATION MODEL	RATIO
	σ_{BAf}	σ_{BAp}	σ_{BAf}/ σ_{BAp}
0.100000E-05	-0.214881E+00	-0.251173E+00	0.855511E+00
0.100000E-03	-0.214881E+00	-0.251173E+00	0.855511E+00
0.100000E-01	-0.214876E+00	-0.251151E+00	0.855566E+00
0.100000E+01	-0.212677E+00	-0.249020E+00	0.854056E+00
0.100000E+03	-0.182366E+00	-0.181657E+00	0.100390E+01
0.100000E+05	-0.758907E-01	-0.701529E-01	0.108178E+01

TABLE XIX

Reaction M1 ⟶ M2 is of 1.0 order and M2 ⟶ M3 is of 2.0 order.

ψ (the reaction diffusion modulus) = 0.206439E+01

θ (the time) = 0.542399E+01

λ	FILM MODEL	PENETRATION MODEL	RATIO
	σ_{BAf}	σ_{BAp}	$\sigma_{BAf}/\sigma_{BAp}$
0.100000E-05	-0.530950E+00	-0.565250E+00	0.939318E+00
0.100000E-03	-0.530948E+00	-0.565243E+00	0.939325E+00
0.100000E-01	-0.530738E+00	-0.564618E+00	0.939994E+00
0.100000E+01	-0.507111E+00	-0.519583E+00	0.975995E+00
0.100000E+03	-0.285607E+00	-0.268579E+00	0.106340E+01
0.100000E+05	-0.100282E+00	-0.945728E-01	0.106036E+01

TABLE XX

Reaction M1 $\longrightarrow$ M2 is of 1.0 order and M2 $\longrightarrow$ M3 is of 2.0 order.

ψ (the reaction diffusion modulus) = 0.291625E+01

θ (the time) = 0.108240E+02

λ	FILM MODEL	PENETRATION MODEL	RATIO
	σ_{BAf}	σ_{BAp}	$\sigma_{BAf}/\sigma_{BAp}$
0.100000E-05	-0.659104E+00	-0.684553E+00	0.962822E+00
0.100000E-03	-0.659096E+00	-0.684536E+00	0.962837E+00
0.100000E-01	-0.658356E+00	-0.682766E+00	0.964247E+00
0.100000E+01	-0.596959E+00	-0.590022E+00	0.101175E+01
0.100000E+03	-0.294189E+00	-0.284705E+00	0.103331E+01
0.100000E+05	-0.101089E+00	-0.990919E-01	0.102016E+01

TABLE XXI

Reaction M1 $\longrightarrow$ M2 is of 1.0 order and M2 $\longrightarrow$ M3 is of 2.0 order.

ψ (the reaction diffusion modulus) = 0.412192E+01

θ (the time) = 0.216240E+02

λ	FILM MODEL	PENETRATION MODEL	RATIO
	$\overset{\sigma}{\text{BAf}}$	$\overset{\sigma}{\text{BAp}}$	$\overset{\sigma}{\text{BAf}}/\overset{\sigma}{\text{BAp}}$
0.100000E-05	-0.757539E+00	-0.778436E+00	0.973155E+00
0.100000E-03	-0.757519E+00	-0.778394E+00	0.973181E+00
0.100000E-01	-0.755457E+00	-0.774309E+00	0.975652E+00
0.100000E+01	-0.635961E+00	-0.629165E+00	0.101080E+01
0.100000E+03	-0.293372E+00	-0.293343E+00	0.100009E+01
0.100000E+05	-0.987549E-01	-0.101512E+00	0.972834E+00

TABLE XXII

Reaction M1 ⟶ M2 is of 1.0 order and M2 ⟶ M3 is of 2.0 order.

ψ (the reaction diffusion modulus) = 0.504737E+01

θ (the time) = 0.324239E+02

λ	FILM MODEL	PENETRATION MODEL	RATIO
	$\overset{\sigma}{\mathrm{BAf}}$	$\overset{\sigma}{\mathrm{BAp}}$	$\overset{\sigma}{\mathrm{BAf}}/\overset{\sigma}{\mathrm{BAp}}$
0.100000E-05	-0.801928E+00	-0.822378E+00	0.975132E+00
0.100000E-03	-0.801892E+00	-0.822314E+00	0.975165E+00
0.100000E-01	-0.798495E+00	-0.816106E+00	0.978421E+00
0.100000E+01	-0.642955E+00	-0.642725E+00	0.100035E+01
0.100000E+03	-0.291279E+00	-0.296314E+00	0.983007E+00
0.100000E+05	-0.965877E-01	-0.102345E+00	0.943744E+00

TABLE XXIII

Reaction M1 ⟶ M2 is of 1.0 order and M2 ⟶ M3 is of 2.0 order.

ψ (the reaction diffusion modulus) = 0.582766E+01

θ (the time) = 0.432240E+02

λ	FILM MODEL	PENETRATION MODEL	RATIO
	σ_{BAf}	σ_{BAp}	σ_{BAf}/ σ_{BAp}
0.100000E-05	-0.828467E+00	-0.849342E+00	0.975422E+00
0.100000E-03	-0.828417E+00	-0.849256E+00	0.975462E+00
0.100000E-01	-0.823753E+00	-0.841099E+00	0.979376E+00
0.100000E+01	-0.644195E+00	-0.649590E+00	0.991694E+00
0.100000E+03	-0.289397E+00	-0.297817E+00	0.971727E+00
0.100000E+05	-0.947444E-01	-0.102766E+00	0.921939E+00

TABLE XXIV

Reaction M1$\longrightarrow$M2 is of 1.0 order and M2$\longrightarrow$M3 is of 2.0 order.

ψ (the reaction diffusion modulus) = 0.683302E+01

θ (the time) = 0.594240E+02

λ	FILM MODEL	PENETRATION MODEL	RATIO
	$\overset{\sigma}{\text{BAf}}$	$\overset{\sigma}{\text{BAp}}$	$\overset{\sigma}{\text{BAf}}/\ \overset{\sigma}{\text{BAp}}$
0.100000E-05	-0.853756E+00	-0.875456E+00	0.975212E+00
0.100000E-03	-0.853694E+00	-0.875340E+00	0.975271E+00
0.100000E-01	-0.847277E+00	-0.864549E+00	0.980021E+00
0.100000E+01	-0.643497E+00	-0.655247E+00	0.982068E+00
0.100000E+03	-0.286955E+00	-0.299056E+00	0.959534E+00
0.100000E+05	-0.923865E-01	-0.103113E+00	0.895967E+00

CHAPTER VI

DISCUSSION OF RESULTS

The penetration theory and film model selectivities, as well as the ratio $\sigma_{BAf}/\sigma_{BAp}$ for various values of m (1, 1.5, and 2), are presented in tables (1-8) for m = 1, tables (9-16) for m = 1.5 and in tables (17-24) for m = 2. All calculations were done for $n = \nu = 1$. The penetration theory equations were integrated over a wide range of θ. The variations of θ were

$$0 \leq \theta \leq 127 \text{ for } m = 1 \text{ and}$$

$$0.0001 \leq \theta \lesssim 60 \text{ for } m = 1.5 \text{ and } 2.$$

The corresponding range of ψ was

$$0 \leq \psi \lesssim 10 \text{ and}$$

$$0.07 \lesssim \psi \lesssim 6.8.$$

Both penetration and film theory equations were integrated with λ as a parameter. The parameter was varied between 10^{-6} to 10^{4}. All computations were done in double precision arithmetic and consumed about four hours on an IBM 7094 II computer. Figures 1.1, 1.2 and 1.3 show plots of the ratio ($\sigma_{BAf}/\sigma_{BAp}$) against λ for different values of ψ. Figure 1.1 is for m = 1, 1.2 for m = 1.5 and 1.3 for m = 2. These figures represent the tabulated values and any maxima they display cannot be considered positionally accurate.

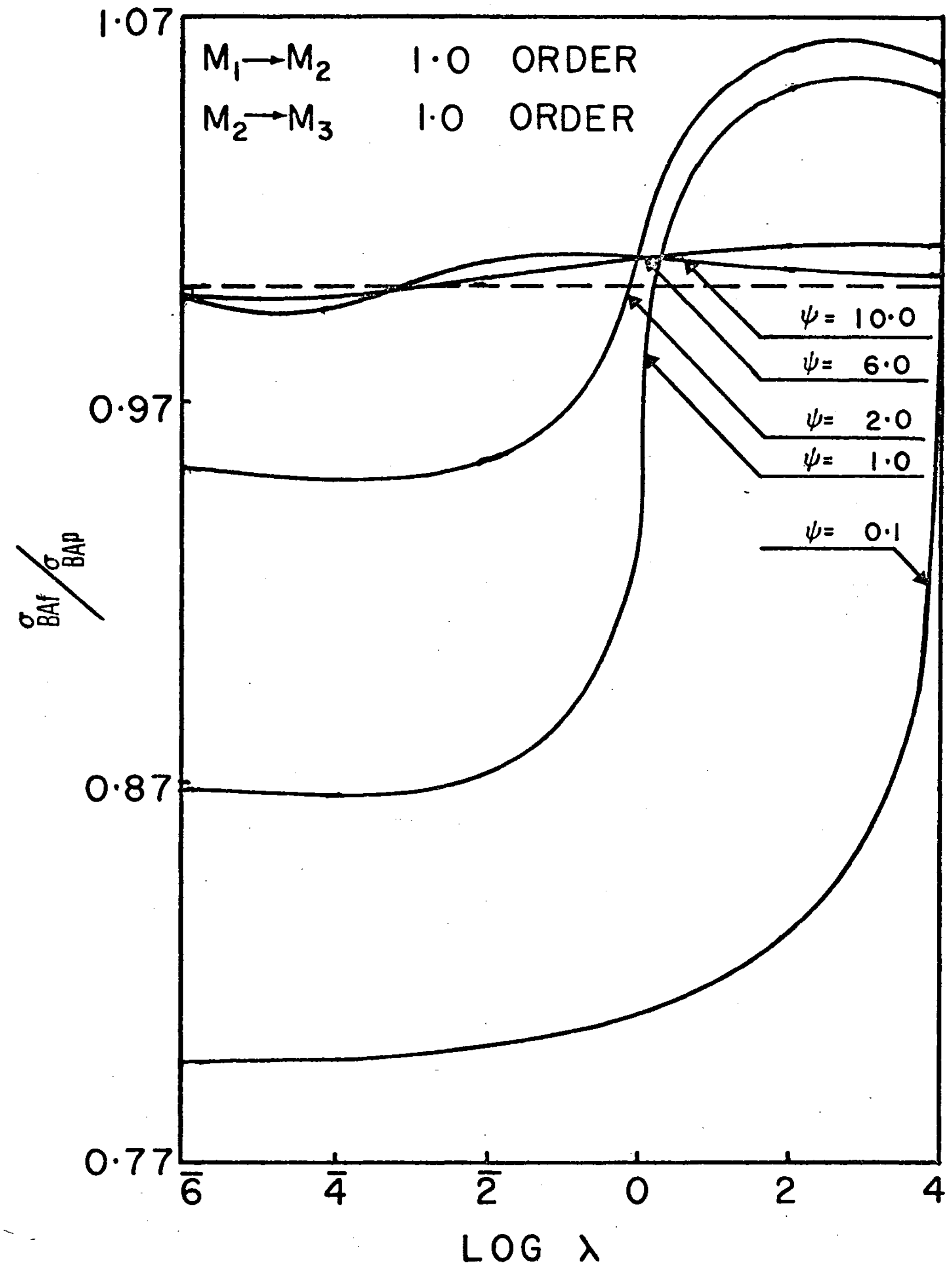

FIG 1·1 COMPARISON OF FILM AND PENETRATION MODELS FOR THE TWO STEP REACTION $M_1 \rightarrow M_2 \rightarrow M_3$

It is clear from figures 1.1, 1.2 and 1.3 that the ratio ($\sigma_{BAf}/\sigma_{BAp}$) deviates from unity over a wide range of ψ and λ. It is also apparent that these deviations are considerable. In fact the deviation of ($\sigma_{BAf}/\sigma_{BAp}$) from unity in some cases is as much as 55%.

These observations cast doubt on the validity of the argument that the insensitivity of the transfer coefficient ratio to the hydrodynamic model makes it impossible to gain an insight into the fluid dynamics of the process. With deviations as large as 55% no such insensitivity can be claimed. The large deviations also point out the need for a careful selection of the mass transfer model for a given physical situation. It is obvious that an indiscriminate selection of a mass transfer model, (a practice based on the concept that the predicted transfer coefficient ratio is insensitive to the model used) can lead to erroneous results.

Results presented in tables (1-24) and figures (1.1, 1.2, and 1.3) clearly lead one to the conclusion that the film and penetration theory models do not predict the same transfer coefficient ratio for a two step chemical reaction involving a volatile intermediate. However, if the system is not a counter diffusing one, the two models predict almost the same results. This difference in the behavior of the two systems is essentially caused by the entirely different behavior of the intermediate M2 at the

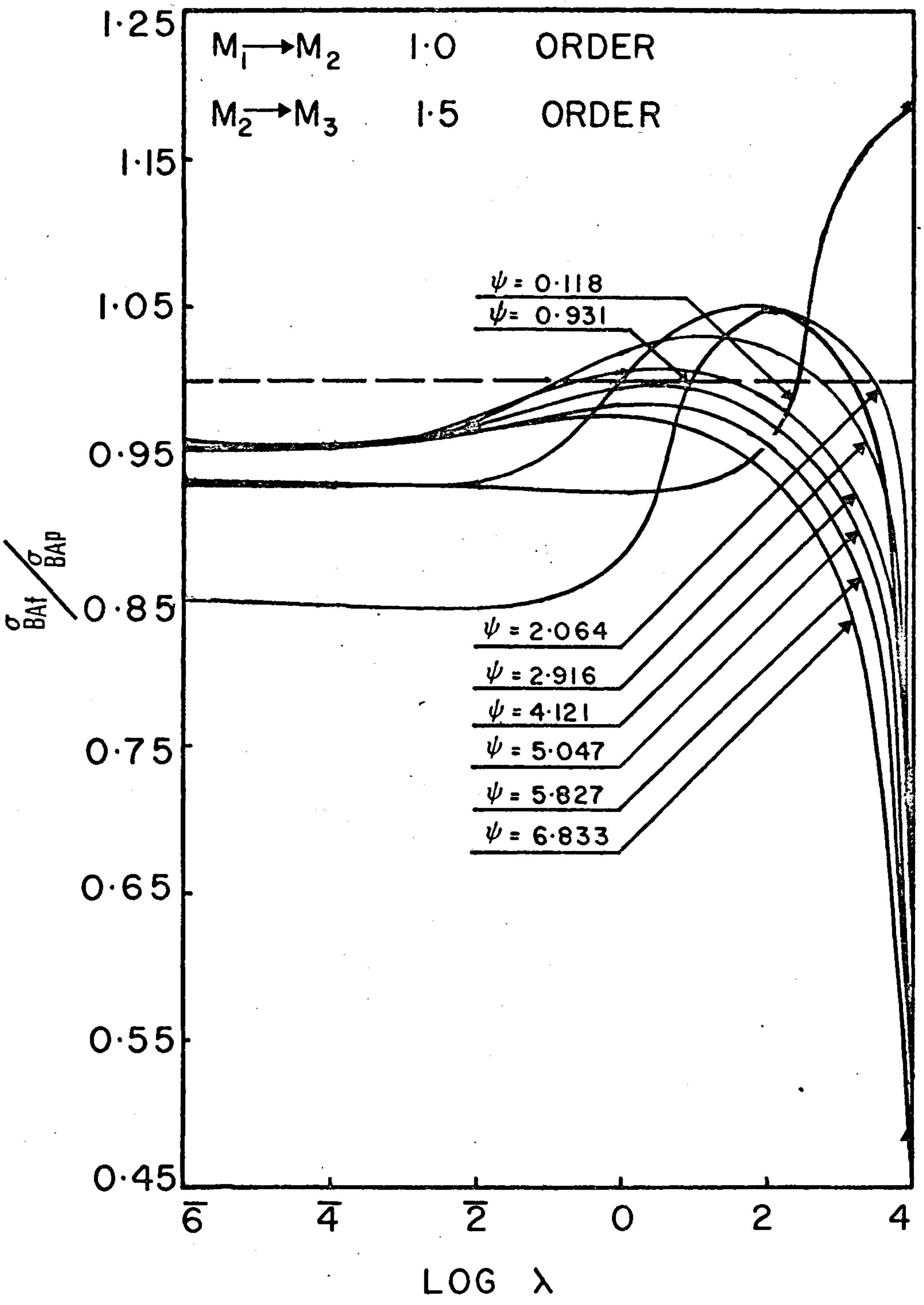

FIG 1·2 COMPARISON OF FILM AND PENETRATION MODELS FOR THE TWO STEP REACTION $M_1 \rightarrow M_2 \rightarrow M_3$

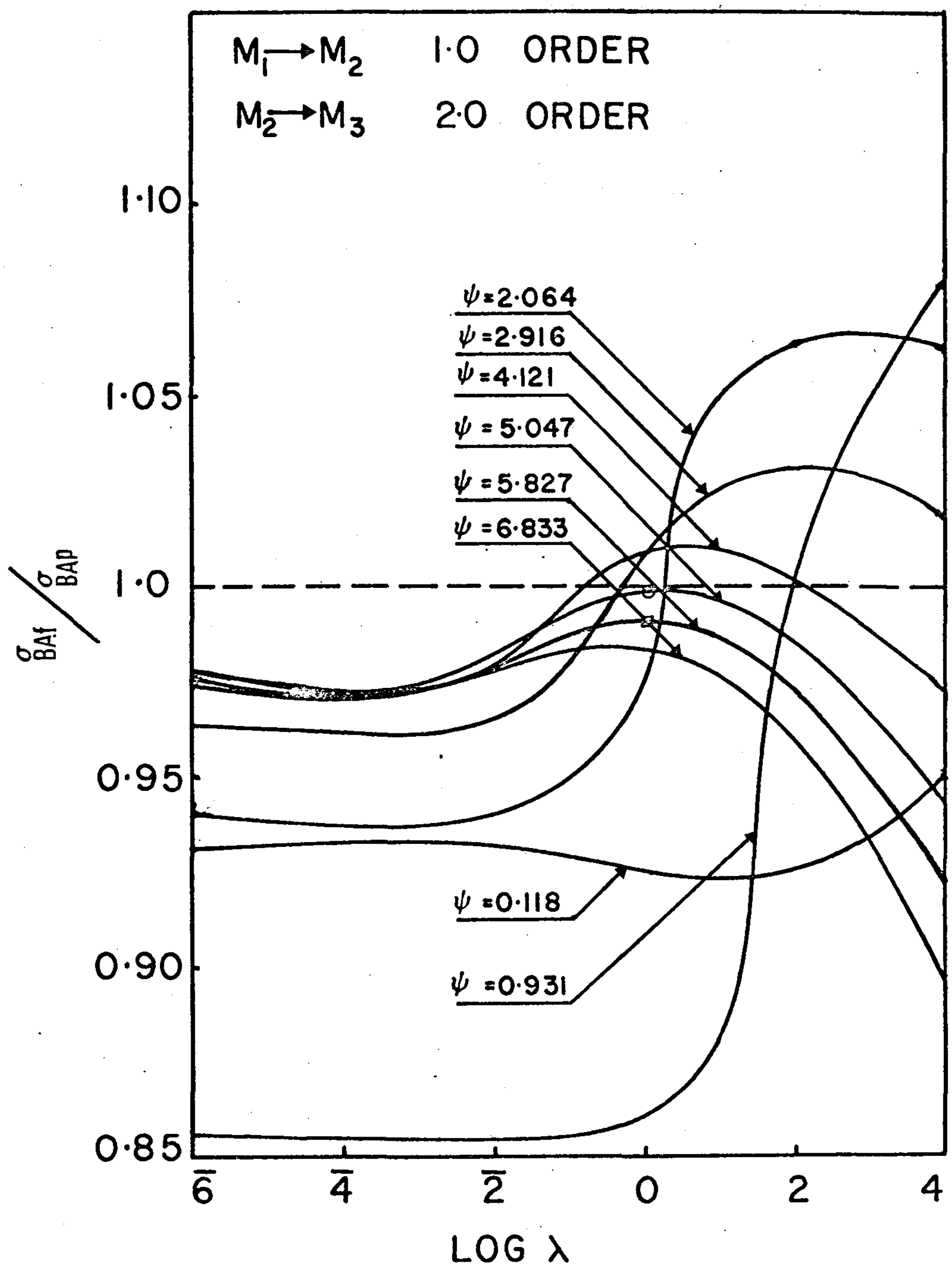

FIG 1·3 COMPARISON OF FILM AND PENETRATION MODELS FOR THE TWO STEP REACTION $M_1 \longrightarrow M_2 \longrightarrow M_3$

gas liguid interface. Thus, whereas for a non-volatile intermediate the film and penetration theory boundary conditions are given as

$$\left.\frac{dC_{M2}}{dx}\right|_{x=0} = 0 \text{ and } \left.\frac{\delta C_{M2}}{\delta x}\right|_{x=0} = 0,$$

the corresponding boundary conditions for a volatile intermediate are given as

$$C_{M2} = \overset{*}{C}_{M2} \quad ; \quad x = 0.$$

Figures 1.1, 1.2, and 1.3 are also helpful in examining the effects of the complexity of kinetics on the deviations of $(\sigma_{BAf}/\sigma_{BAp})$. It is clear that more complex kinetics does not necessarily result in a greater deviation. Thus, the maximum deviations of $(\sigma_{BAf}/\sigma_{BAp})$ are $\leq 22\%$ for $m = 1$, $\leq 55\%$ for $m = 1.5$ and $\leq 16\%$ for $m = 2$. As a matter of fact, for $m = 2$, the deviations do not exceed 10% except for very small values of ψ. These facts contradict Szekely et al's (31) speculations. These authors had anticipated greater deviations with more complex kinetics.

Plots of $(\sigma_{BAf}/\sigma_{BAp})$ against λ, with ψ as a parameter, display another interesting fact about the hydrodynamic models used. It is clear that for $\lambda < 1$, the film theory model predicts results which are lower than the ones computed by the use of the penetration model. There is then a transition regime, $1 < \lambda < 10^2$, in which the results from the two models tend to be the same, followed by another regime with $\lambda > 10^2$, for which the film model

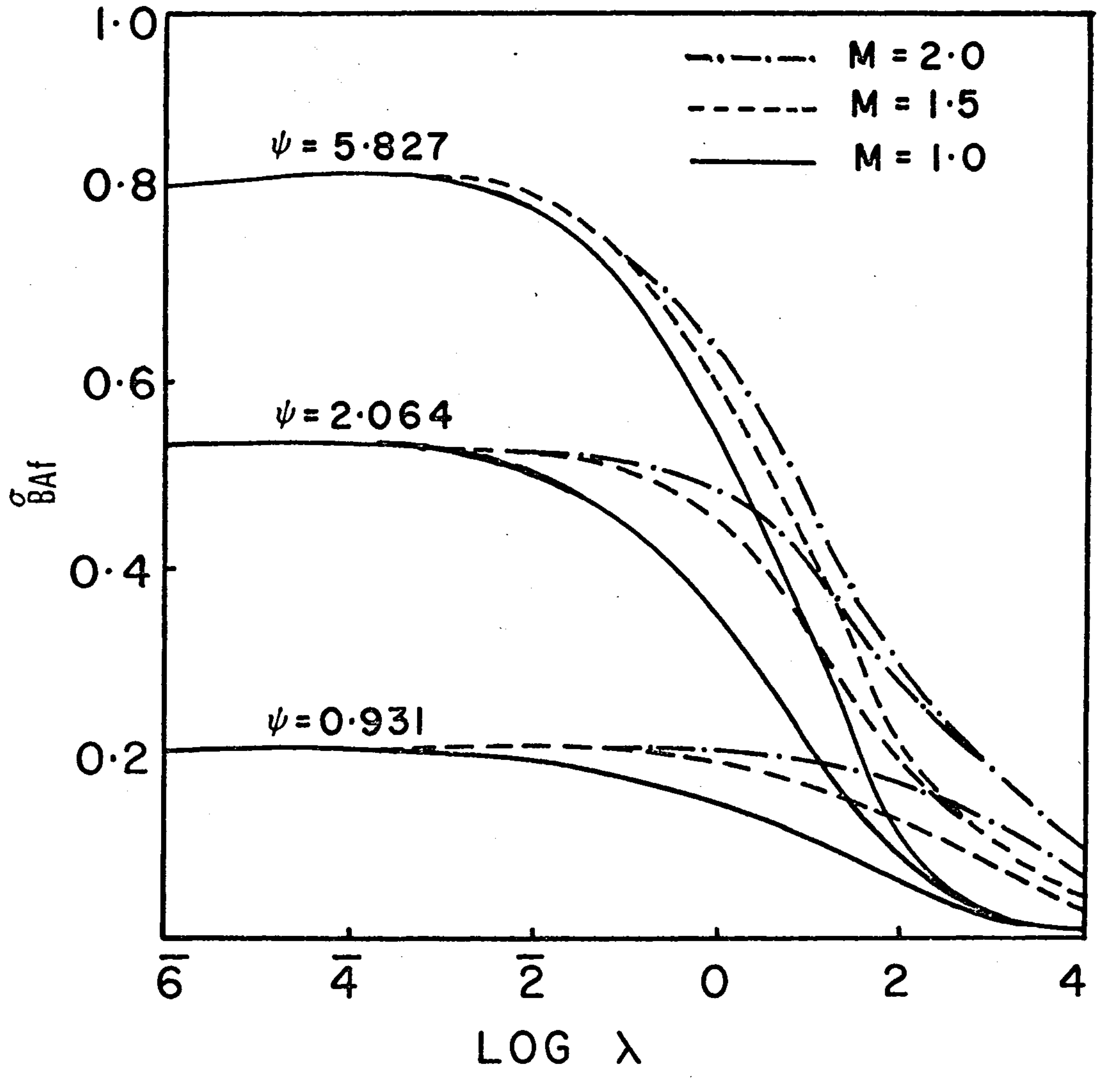

FIG 1·4 EFFECT OF SYSTEM PARAMETERS ON SELECTIVITY results again tend to fall below the results predicted by the penetration theory.

Figure 1.4 displays the effect of various system parameters (ψ, λ and m) on the film model selectivity of the intermediate M2. A similar plot for the penetration theory reveals identical trends and hence is not included here. It is apparent from figure 1.4 that at a fixed value of ψ , whereas selectivity decreases with the increasing value of m in the regime $\lambda > 10^{-3}$, for the regime $\lambda < 10^{-3}$ the order of the second reaction has no effect on σ_{BAf}. This is not a surprising result. It simply means that when the selectivity of the intermediate depends only on it's rate of formation ($\lambda < 10^{-3}$), the order of the second reaction is unimportant. That, in this regime, selectivity increases with increasing values of ψ further justifies this conclusion. On the other hand when the concentration of the intermediate is low ($\lambda > 10^{3}$), the lower order second reaction consumes more of the intermediate than a higher order second reaction. This explains why for $\lambda > 10^{3}$, selectivity increases with increasing values of m.

CHAPTER VII

CONCLUSIONS

i. For the counter diffusing systems, the film and penetration theory models do not predict identical results. The gap between the predictions of the two models can be more than 50%. For systems with no counter diffusion, this gap has not been found to exceed 6%. A need for a careful selection of a mass transfer model for counter diffusing systems has therefore been established.

ii. Deviations between the results predicted by the two models do not appear to be directly related to increasing complexity in the reaction kinetics. Szekely et al's (31) conjecture that more complex kinetics should accentuate the difference in the results predicted by the two models, is not substantiated.

iii. The ratio $(\sigma_{BAf}/\sigma_{BAp})$ deviates considerably from unity over a wide range of ψ and λ. This is in contrast to Astarita's (1) argument that the various mass transfer models would display their differences, if any, at $\psi = 1$. However, it should be mentioned that Astarita (1) had linear non diffusing systems in mind.

iv. The selectivity parameter is sensitive to the order of the second reaction in the $\lambda > 10^{-3}$ regime. However, the order of the second step reaction does not affect the parameter σ_{BA} for values of $\lambda < 10^{-3}$.

v. The disparity between the results obtained from the film and penetration models, brings out the need for a criterion that may aid the selection of a more appropriate model for a given physical situation. Such a criterion will undoubtedly require the juxtaposition of fresh experimental work with existent theory. To date no concerted effort in this direction can be detected. A search for such a criterion is therefore recommended.

APPENDIX A

MISCELLANEOUS

A. Instantaneous Surface Flux for Higbie's (14) Model:

The transformations

$$C_1 = C_i - \overset{o}{C}_i \quad , \qquad D_1 = D_i \ ,$$

change equation (10) and it's initial and boundary conditions to

$$\frac{D_1 \delta^2 C_1}{\delta x^2} = \frac{\delta C_1}{\delta t} \tag{1A}$$

$$\overset{*}{C}_1 = \overset{*}{C}_i - \overset{o}{C}_i \ ; \quad t \geq o, \quad x = o \qquad (2A),$$

$$C_1 = o \quad ; \quad t = 0, \quad o < x \leq \infty \qquad (3A),$$

$$C_1 \rightarrow o \text{ or finite}; \quad t \geq o \ ; \quad x \rightarrow \infty \qquad (4A).$$

A Laplace transformation of equation (1A) yields:

$$D_1 \int_o^\infty \frac{\delta C_1}{\delta x^2} e^{-pt} dt = \int_o^\infty \frac{\delta C_1}{\delta t} e^{-pt} dt \ ,$$

$$D_1 \frac{d^2 \bar{C}_1}{dx^2} = p\bar{C}_1 \ .$$

Boundary conditions (2A) and (4A) lead to

$$\bar{C}_1 = \frac{\overset{*}{C}_1}{p} e^{-x\sqrt{p/D_1}} \qquad (5A).$$

Inversion by the use of standard tables (28) gives

$$C_1 = \left(\overset{*}{C}_i - \overset{o}{C}_i\right)\left[1-\frac{2}{\pi}\int_0^{x/\left(2\sqrt{D_i t}\right)} e^{-\xi^2}\, d\xi\right] \qquad (6A),$$

or,

$$C_i = \left(\overset{*}{C}_i - \overset{o}{C}_i\right)\left[1-\mathrm{erf}\left(x/\left(2\sqrt{D_i t}\right)\right)\right] + \overset{o}{C}_i \qquad (7A).$$

The flux at x = 0 and t = 't' is given as

$$X(t) \equiv -D_i\left(\frac{\delta C_i}{\delta x}\right)_{x=0} = \left(\overset{*}{C}_i - \overset{o}{C}_i\right)\sqrt{\frac{D_i}{\pi t}} \qquad (8A).$$

B. Derivation of the Expression for σ_{BAp} for ν=m=n=1

$$\frac{\delta^2 a}{\delta y^2} = \frac{\delta a}{\delta \theta} + a \qquad (28), (p17).$$

The transformation

$a = e^{-\theta} A(y,\theta)$ suggested by Carslaw et al (8) changes (28) to:

$$\frac{\delta^2 A}{\delta y^2} = \frac{\delta A}{\delta \theta} \qquad (9A)$$

A Laplace transformation on equation (9A) yields

$$\frac{d^2 \bar{A}}{dy^2} = p\bar{A} .$$

Using the boundary conditions (30a and 30b)

$$\bar{A} = \frac{1}{p-1} e^{-y\sqrt{p}} \qquad (10A)$$

can be obtained.

Inversion according to the Standard tables (28) yields,

$$A = \frac{1}{2} e^{\theta} \left[e^{-y} \mathrm{erfc}\left(\frac{y}{2\sqrt{\theta}} - \sqrt{\theta}\right) + {}^{y}\mathrm{erfc}\left(\frac{y}{2\sqrt{\theta}} + \sqrt{\theta}\right)\right] \qquad (11A)$$

$$a = \frac{1}{2}\left[e^{-y} \mathrm{erfc}\left(\frac{y}{2\sqrt{\theta}} - \sqrt{\theta}\right) + e^{y} \mathrm{erfc}\left(\frac{y}{2\sqrt{\theta}} + \sqrt{\theta}\right)\right] \qquad (12A)$$

The instantaneous value of ($\delta a/\delta y)y=0$ is

$$\left(- \frac{\delta a}{\delta y}\right)_{y=0} = \mathrm{erf}\sqrt{\theta} + \frac{e^{-\theta}}{\sqrt{\pi\theta}} \qquad (13A)$$

and,

$$\int_0^{\theta} \left(- \frac{\delta a}{\delta y}\right)_{y=0} d\theta = \int_0^{\theta} \left(\mathrm{erf}\sqrt{\theta} + \frac{e^{-\theta}}{\sqrt{\pi\theta}}\right) d\theta$$

$$\int_0^{\theta} \left(- \frac{\delta a}{\delta y}\right)_{y=0} d\theta = \left(\theta + \frac{1}{2}\right)\mathrm{erf}\sqrt{\theta} + \sqrt{\frac{\theta}{\pi}}\, e^{-\theta} \qquad (14A)$$

Equation (29), p.(17),

$$\frac{\delta^2 b}{\delta y^2} = \frac{\delta b}{\delta \theta} + \lambda b - a \qquad (29)$$

is transformed into

$$\frac{d^2 \bar{b}}{dy^2} = p\bar{b} + \lambda \bar{b} - \frac{2e^{-y(p+1)^{\frac{1}{2}}}}{p} \qquad (15A)$$

The complimentary function is,

$$\bar{b} = \hat{c}_2 e^{y\sqrt{p+\lambda}} + \hat{c}_1 e^{-y\sqrt{p+\lambda}} \qquad (16A),$$

and the particular integral is,

$$\bar{b} = -\frac{2}{p(1-\lambda)} e^{-y\sqrt{p+1}}$$

therefore,

$$\bar{b} = \hat{c}_2 e^{y\sqrt{p+\lambda}} + \hat{c}_1 e^{-y\sqrt{p+\lambda}} - \frac{2}{p(1-\lambda)} e^{-y\sqrt{p+1}} \qquad (17A)$$

The use of boundary conditions (31cc, p.18) and (31b, p.18) leads to,

$$\hat{c}_2 = 0 \qquad \text{and} \qquad \hat{c}_1 = \frac{2}{p(1-\lambda)}$$

$$\bar{b} = \frac{2}{p(1-\lambda)} e^{-y\sqrt{p+\lambda}} - \frac{2}{p(1-\lambda)} e^{-y\sqrt{p+1}} \qquad (18A)$$

Inversion yields,

$$b = \left(\frac{1}{1-\lambda}\right)\left[e^{-y\sqrt{\lambda}}\operatorname{erfc}\left(\frac{y}{2\sqrt{\theta}} - \sqrt{\lambda\theta}\right) + e^{y\sqrt{\lambda}}\operatorname{erfc}\left(\frac{y}{2\sqrt{\theta}} + \sqrt{\lambda\theta}\right)\right]$$

$$- \frac{1}{1-\lambda}\left[e^{-y}\operatorname{erfc}\left(\frac{y}{2\sqrt{\theta}} - \sqrt{\theta}\right) + e^{y}\operatorname{erfc}\left(\frac{y}{2\sqrt{\theta}} + \sqrt{\theta}\right)\right] \qquad (19A)$$

$$\left(-\frac{\delta b}{\delta y}\right)_{y=0} = -\left(\frac{1}{1-\lambda}\right)\left[\frac{e^{-\theta} - e^{-\lambda\theta}}{\sqrt{\pi\theta}} + \operatorname{erf}\sqrt{\theta} - \sqrt{\lambda}\operatorname{erf}\sqrt{\lambda\theta}\right] \qquad (20A)$$

$$\int_0^{\theta}\left(-\frac{\delta b}{\delta y}\right)_{y=0} d\theta = -\left(\frac{1}{1-\lambda}\right)\left[\left(\theta+\frac{1}{2}\right)\operatorname{erf}\sqrt{\theta}+\sqrt{\frac{\theta}{\pi}}\,e^{-\theta} - \left(\left(\theta\sqrt{\lambda}+\frac{1}{2\sqrt{\lambda}}\right)\operatorname{erf}\sqrt{\lambda\theta}+\sqrt{\frac{\theta}{\pi}}\,e^{-\lambda\theta}\right)\right] \quad (21A)$$

If $\theta = \frac{4\psi_p^2}{\pi}$, is substituted in equations (14A and 21A)

$$\sigma_{BAp} = \frac{\int_0^{\theta} -\left.\frac{\delta b}{\delta y}\right|_{y=o}}{\int_0^{\theta} -\left.\frac{\delta a}{\delta y}\right|_{y=o}}$$

can be simplified to

$$\sigma_{BAp} = -\left(\frac{1}{1-\lambda}\right)\left\{1-\left[\frac{\left(4\pi\psi_p^2\sqrt{\lambda}+\frac{1}{2\sqrt{\lambda}}\right)\operatorname{erf}\left(2\psi_p\sqrt{\lambda/\pi}\right)+\frac{2\psi}{\pi}e^{-(4/\pi)\lambda\psi_p^2}}{\left(\frac{4}{\pi}\psi_p^2+\frac{1}{2}\right)\operatorname{erf}\left(\frac{2\psi}{\sqrt{\pi}}\right)+\frac{2\psi}{\pi}e^{-(4/\pi)\psi_p^2}}\right]\right\} \quad (22A)$$

C. Error Function

The error function erf ( ) needed for equation (40) can be computed on a digital computer with the help of the following expression given by Hastings(13):

$$\operatorname{erf}(x) = \frac{2}{\sqrt{\pi}}\int_0^{x} e^{-t^2}\,dt \quad (23A)$$

$$|x| \leq 0.32 \quad = \frac{2x}{\sqrt{\pi}}\left(1-\frac{x^2}{3}+\frac{x^4}{10}-\frac{x^6}{42}+\frac{x^8}{216}\right) \quad (24A)$$

$$|x| > 0.32 \quad = 1-\left(a_1\ell+a_2\ell^2+a_3\ell^3+a_4\ell^4+a_5\ell^5\right)\frac{2e^{-x^2}}{\sqrt{\pi}} \quad (25A)$$

where,

$$\ell = \frac{1}{1+0.3275911|x|} \quad (26A)$$

and

$$a_1 = 0.225836846 \qquad a_3 = 1.259695130$$

$$a_2 = -0.252128668 \qquad a_4 = -1.287822453 \tag{27A}$$

and

$$a_5 = 0.94064607 \tag{28A}$$

D. Simpson's Rule

Integration of equally spaced data is best performed by the use of Simpson's rule given here as equation (20A).

$$F(x) = \int_{x_o}^{\hat{X}_N} f(x) = \frac{h}{3}\Big[(f_o + f_N) + 2(f_2 + f_4 + \dots \quad f_{N-2}) + 4(f_1 + f_3 + f_5 + \dots \quad f_{N-1})\Big] \tag{29A}$$

where

$$h = \mathbf{x}_{i+1} - \mathbf{x}_i \quad \text{and } N \text{ is even.}$$

APPENDIX B

DIFFERENCE APPROXIMATIONS FOR DERIVATIVES

Derivative approximations used for the solution of various equations, are listed below:

a) Second Derivatives

$$\frac{\delta^2 f(x,t)}{\delta x^2}, \quad \frac{d^2 f}{dx^2} .$$

$$f(x+\Delta x,t) = f(x,t) + \Delta x f'(x,t) + \frac{\Delta x^2}{2!} f''(x,t) \text{----} (1B)$$

$$f(x-\Delta x,t) = f(x,t) - \Delta x f'(x,t) + \frac{\Delta x^2}{2!} f''(x,t) \text{----} (2B)$$

$$\frac{\delta^2 f}{\delta x^2} \equiv f_{xx}(x,t) = \frac{f(x+\Delta x,t) - 2f(x,t) + f(x-\Delta x,t)}{\Delta x^2} \quad (3B)$$

Equation (3B) is modified for $\frac{d^2 f}{dx^2}$ to

$$\frac{d^2 f}{dx^2} = f''(x) = \frac{f(x+\Delta x) - 2f(x) + f(x-\Delta x)}{\Delta x^2} \quad (4B)$$

b) First Derivative

$$\frac{\delta f}{\delta t}(x,t), \quad \frac{df(x)}{\delta x}$$

$$f(x,\Delta t+t) = f(x,t) + \Delta t f\,(x,t) + \qquad (5B)$$

$$\frac{\delta f}{\delta t} = f_t(x,t) = \frac{f(x,\Delta t+t) - f(x,t)}{\Delta t} \qquad (6B)$$

Similarly,

$$\frac{df}{dx} = \frac{f(x+\Delta x) - f(x)}{\Delta x} \qquad (7B)$$

APPENDIX C

STABILITY ANALYSIS FOR FINITE DIFFERENCE SCHEMES

Implicit finite difference schemes were chosen in preference to the explicit schemes for the solution of equations (28 and 29 p.17). Although the explanations given below are generally true only for linear equations with constant coefficients and for a certain class of boundary conditions, in practice such arguments are taken to be true for non linear cases also.

Definitions refer to the parabolic equation,

$$\frac{\delta^2 u}{\delta x^2} = \frac{\delta u}{\delta t} \qquad (1C)$$

Implicit Approximation:

Equation (1C) can be written in the finite difference form as

$$\frac{U_{p+1,\, q+1} - 2U_{p,q+1} + U_{p-1,\, q+1}}{h^2} = \frac{U_{p,q+1} - U_{p,q}}{k} \qquad (2C)$$

where,

$h = \Delta x$

$k = \Delta t$

$r = k/h^2$

$$rU_{p-1,q+1} - (2r+1)\,U_{p,q+1} + rU_{p+1,q+1} = -U_{p,q}\ ,$$

$$p = (1,2,\ldots\quad) \qquad (3C)$$

Equation (3C) represents a set of simultaneous equations similar to the one described in Appendix D(equations 1D). It is obvious that the calculation of the values of $U_{p-1,q+1}$, $U_{p,q+1}$ and $U_{p+1.q+1}$ etc., necessitates the solution of a set of simultaneous equations. A scheme that involves the solution of a set of simultaneous equations to evaluate the unknown pivotal values, is called an implicit scheme.

Explicit Approximation:

Another approximation for equation (1C) can be written as

$$\frac{U_{p+1,q} - 2U_{p,q}+U_{p-1,q}}{h^2} = \frac{U_{p,q+1}-U_{p,q}}{k} \qquad (4C)$$

$U_{p,q+1} = U_{p,q} + r(U_{p+1,q} - 2U_{p,q} + U_{p-1,q})$. In this case the unknown pivotal value $U_{p,q+1}$ can be found through a step by step method. The computation of this value does not involve a solution of a set of simultaneous equations. Such a scheme is called an explicit finite difference scheme.

Discretisation Error:

If 'U' represents the exact solution to the partial differential equation (1C), and $\widetilde{U}$, the exact solution of the difference equations used to approximate the P.D.E., then $(U-\tilde{U})$, is called the **discretisation** error.

$$\text{Discretisation error} \quad e_d = U - \tilde{U} \qquad (5C)$$

Round-Off Error:

The equations that are actually solved on a digital computer are the finite difference equations, and if it were possible to carry out all the calculations to an infinite number of decimal places, the exact solution U can be obtained. In practice however, each calculation is carried out to a finite number of decimal places—a procedure that introduces a "round-off" error every time it is used. The solution that is obtained is $\overset{*}{U}$, the numerical solution and is not '$\tilde{U}$'.

$$\text{Round-Off Error} \quad e_r = \tilde{U} - \overset{*}{U} \qquad (6C)$$

$$\text{Total Error} = e_r + e_d \qquad (7C)$$

Stability:

A difference system is said to be stable, if small errors occuring in its earlier computational steps do not give rise to errors of increasing magnitude or possible oscillations during the remainder of the computations. The treatment due to VonNeuman, as extended by O'Brien et al (26), is used to develop a criterion for stability. This criterion is used later on to show the stability of the implicit scheme used for the solution of equation (29). It is assumed that errors at the pivotal points along $t = 0$ between $x = 0$, and $x = \ell \equiv Nh$, can be represented by a finite Fourier expansion:

$$E_p = \sum_{n=0}^{N} A_n e^{in\pi x/\ell} \equiv \sum_{n=0}^{N} A_n e^{i\beta nph} \qquad p = (0,1,\ldots N) \tag{8C}$$

where,

$i = \sqrt{-1}$

and

$\beta_n = {n\pi}/{Nh}$

$ph = x$

Then, the (N+1) equations are sufficient to determine the (N+1) unknowns $A_o, A_1, \ldots \quad A_n$ uniquely, showing that an arbitrary distribution of initial errors can be expressed in this complex exponential form.. As finite difference equations are assumed to be linear (separate solutions of linear equations are additive) considerations of the propagation of an error due to a single term such as $e^{i\beta ph}$ should suffice. The coefficient A_n is a constant and can be neglected. It is further assumed that the "error function" is the product of a 't' term and an 'x' term, similar to the ones used for deriving analytical solutions of partial differential equations. **Therefore** , at $t = t$, the term '$e^{i\beta ph}$', becomes $e^{i\beta ph}e^{\alpha t}$. Thus, at $t = 0$, this term is still $e^{i\beta ph}$. If $t = qk$,

$$E_{p,q} = e^{i\beta x} e^{\alpha t} = e^{i\beta ph} e^{\alpha qk} = e^{i\beta ph} (\xi)^{q} \tag{9C}$$

where, $\xi = e^{\alpha k}$ and α is a constant. It is obvious that as q increases $E_{p,q}$ will not increase provided

$$\left| \xi \right| \leq 1 \tag{10C}$$

Stabilty Analysis of An Explicit Scheme:

Equation (4C) which approximates equation (1C) should also approximate the "error function $E_{p,q}$". Substitution of $U_{p,q} = E_{p,q} = e^{i\beta ph}(\xi)^{q}$ in (4C) leads to,

$$e^{i\beta ph}(\xi)^{q+1} = e^{i\beta ph}(\xi)^{q} + r \left[e^{i\beta (p+1)h}(\xi)^{q} - 2e^{i\beta ph} (\xi)^{q} + e^{i\beta (p-1)h}(\xi)^{q} \right]$$

or,

$$\xi = 1-4r\,\mathrm{Sin}^2 \left(\beta \frac{\Delta x}{2}\right) \tag{11C}$$

Since, for stability $| \xi | \leq 1$

$$\left| 1-4\, r\, \mathrm{Sin}^2 \left(\beta \frac{\Delta x}{2}\right) \right| \leq 1 \tag{12C}$$

In general, components of all frequencies 'β' may be present, if they are not present in the initial conditions or brought in by boundary conditions, then they are likely to be introduced by round-off error. Since the unbounded growth of $E_{p,q}$ (or in effect $e^{\alpha t}$) is to be guarded against and for some β, $\mathrm{Sin}^2 \left(\beta \Delta x/2\right)$ is going to be unity, it becomes clear that for (12C) to be true,

$$r \leq 1/2 \tag{13C}$$

Stability Analysis of An Implicit Scheme:

Substitution of $U_{p,q} = E_{p,q} = e^{i\beta ph}(\xi)^q$ in equation (3C) leads to

$$r e^{i\beta(p-1)h}(\xi)^{q+1} - (2r+1)e^{i\beta ph}(\xi)^{q+1} + r e^{i\beta(p+1)h}(\xi)^{q+1} = -e^{i\beta ph}(\xi)^q ,$$

or,

$$r e^{-i\beta h}\xi - (2r+1)\xi + r e^{i\beta h}\xi = -1 \qquad (14C)$$

$$\frac{1}{4r \sin^2(\beta\Delta x/2)} = \xi \qquad (15C).$$

Since for stability $|\xi| \leq 1$,

$$\frac{1}{4r \sin^2(\beta\Delta x/2)} \leq 1 \qquad (16C)$$

Therefore, the implicit scheme is stable provided

$$r > 0 \qquad (17C).$$

APPENDIX D

GAUSSIAN ELIMINATION FOR TRIANGULAR EQUATIONS

The following triangular system of equations was frequently encountered in the course of finite difference solutions for various partial differential equations:

$$\begin{array}{rcl}
b_1v_1 + c_1v_2 & = & d_1 \\
a_2v_1 + b_2v_2 + c_2v_3 & = & d_2 \\
a_3v_2 + b_3v_3 + c_3v_4 & = & d_3 \\
\text{---} \quad\quad \text{---} \quad\quad \text{---} & & \\
a_{M-2}v_{M-3} + b_{M-2}v_{M-2} + c_{M-2}v_{M-1} & = & d_{M-2} \\
a_{M-2}v_{M-2} + b_{M-1}v_{M-1} & = & d_{M-1}
\end{array} \tag{1D}$$

where, a_i, b_i, c_i, d_i are known quantities, and v_i are the unknown variables.

The solution of these linear algebraic equations can be readily obtained by Gaussian elimination and back substitution. The first equation can be used to eliminate v_1 from the second, the new second equation used to eliminate v_2 from the third and so on, until finally, the new last but one equation can be used to eliminate v_{M-2} from the last equation, giving one equation with only one

v_{M-1}. The unknowns v_{M-2}, v_{M-3},... v_2,v_1 can then be found in turn, by back substitution. Noting that coefficient 'c' in each new equation is the same as in the corresponding old equation, assume that the following stage of the elimination has been reached:

$$\beta_{i-1} v_{i-1} + c_{i-1} v_i = S_{i-1} \tag{2D}$$

$$a_i v_{i-1} + b_i v_i + c_i v_{i+1} = d_i \tag{3D}$$

where,

$$\beta_1 = b_1 \qquad S_1 = d_1 \tag{4D}$$

Eliminating v_{i-1} between (2D and 3D) leads to,

$$\left(b_i - \frac{a_i c_{i-1}}{\beta_{i-1}}\right) v_i + c_i v_{i+1} = d_i - \frac{a_i S_{i-1}}{\beta_{i-1}} \tag{5D}$$

$$\beta_i v_i + c_i v_{i+1} = S_i \tag{6D}$$

$$\beta_i = b_i - \frac{a_i c_{i-1}}{\beta_{i-1}} \tag{7D}$$

$$S_i = d_i - \frac{a_i S_{i-1}}{\beta_{i-1}} \tag{8D}$$

$$(i = 2,3,\ldots M-1)$$

The last pair of simultaneous equations are:

$$\beta_{M-2} v_{M-2} + c_{M-2} v_{M-1} = S_{M-2} \tag{9D}$$

$$a_{M-2}v_{M-2} + b_{M-1}v_{M-1} = d_{M-1} \qquad (10D).$$

Eliminating v_{M-2} between equations (9D, and 10D) gives,

$$\left(b_{M-1} - \frac{a_{M-2}c_{M-2}}{\beta_{M-2}}\right)v_{M-1} = d_{M1} - \frac{S_{M-2}}{\beta_{M-2}} \qquad (11D)$$

$$\beta_{M-1}v_{M-1} = S_{M-1} \qquad (12D),$$

$$v_{M-1} = \frac{S_{M-1}}{\beta_{M-1}} \equiv \nu_{M-1} \qquad (13D).$$

From (6D) it follows that,

$$\beta_i v_i + c_i v_{i+1} = S_i ,$$

$$v_i = \frac{S_i - c_i v_{i+1}}{\beta_i} \equiv \nu_i - \frac{c_i v_{i+1}}{\beta_i} \qquad (14D)$$

$$i = (M-2, M-3, \ldots, 1).$$

Form equation (8D), ν_i can be shown to be,

$$\frac{S_i}{\beta_i} = \nu_i = \frac{d_i}{\beta_i} - \frac{a_i \nu_{i-1}}{\beta_i} = \frac{d_i - a_i \nu_{i-1}}{\beta_i}$$

$$(i = 2, 3, \ldots \quad M-1) \qquad (15D).$$

Similarily (4D) leads to,

$$\nu_1 = \frac{d_1}{\beta_1} \qquad (16D).$$

For the purpose of digital computation , these equations can be summed up as:

$$v_{M-1} = \nu_{M-1} \quad ,$$

$$v_i = \nu_i - \frac{c_i v_{i+1}}{\beta_i} \quad , \quad (i = M-2,\ M-3, \ldots \quad 1) \quad ,$$

$$\beta_1 = b_1 ; \quad \nu_1 = {}^{d}1/\ \beta_1 \quad ,$$

$$\beta_i = b_i - \frac{a_i c_{i-1}}{\beta_{i-1}} \quad , \quad (i = 2,3, \ldots \quad M-1),$$

and

$$\nu_i = \frac{d_{i-} a_i \nu_{i-1}}{\beta_i}, \quad i = 2,3, \ldots \quad M-1.$$

APPENDIX E

QUASILINEARISATION

The non linear equations considered are of the form $L[u] - f(u,\vec{y}) = 0$ (1E)

where, L is a linear operator (differential or partial differential) possessing certain additional properties such as positivity, $\vec{y}$ is a vector, and u is the unknown function, whose value as a function of $\vec{y}$ is to be determined. The function f(u,y) is a strictly convex (or concave) function of 'u' for all $\vec{y} \in D$, is continuous in U and $\vec{y}$ and has a bounded second partial derivative with respect to 'u' for all u and $\vec{y} \in D$. In addition, it is further assumed that on the boundary B of domain,

$$u = 0 \qquad \vec{y} \in B. \tag{2E}$$

The domain D is supposed to be sufficiently small to ensure the existence and uniqueness of the solution of equation (1E).

'f' is strictly convex as a function of 'u' if,

$$f''(u) > 0 \tag{3E}$$

If 'f' is a strictly convex function of 'u' and is twice differentiable, by the mean value theorem, equation (1E) can be written as

$$L[U] \doteq f(u,\vec{y}) = f(v,\vec{y}) + (u-v)f_v(v,\vec{y},) + \frac{1}{2}(u-v)^2 f_{vv}(v,\vec{y}) \tag{5E}$$

or,

$$f(u,y)- \left[f(v,\vec{y}) + (u-v)f_v\ (v,\vec{y})\right] \geq 0 \qquad (6E)$$

The equality holding for u=v.

It is obvious that,

$$L\ [u] = f(u,y) = \left[f(v,\vec{y}) + (u-v)f_v(v,\vec{y})\right]_{\max v} \qquad (7E)$$

If the function $w(v,\vec{y})$ is the solution of the equation,

$$L\ [u] = \left[f(v,\vec{y}) + (u-v)f_v(v,\vec{y})\right] \qquad (8E),$$

then

$$L\ [w] = \left[f(v,y) + (w-v)f_v(v,\vec{y})\right] \qquad (9E),$$

with $w=0$ on B

Equation (8E) which is equation (7E) without the 'max v' is called the associated linear equation.

Equation (7E) can also be written as

$$L[u] = f(u,\vec{y}) = f(v,y)+(u-v)f_v(v,\vec{y})+ |\delta| \qquad (10E),$$

Equations (9E) and (10E) when combined with the linearity property of the operator L, yield:

$$L\ [u-w] = (u-w)f_v(v,\vec{y})+ |\delta| \qquad (11E),$$

or

$$L\ [Z]- Zf_v(v,\vec{y}) \geq 0 \qquad (12E),$$

where, Z=u-w. Z obviously is zero on B. If Z, which is zero on B, satisfies the inequality,

$$L\ [Z] - Zf_v(v) \geq 0 \qquad (13E),$$

throughout the domain D, for all admissable functions 'v' then,

$$Z \geq 0 \qquad (14E),$$

provided the operator L possesses the positivity property. It follows therefore that,

$$u \geq w(v,\vec{y}) \qquad (15E).$$

Also, if v is chosen equal to 'u', equation (9E) becomes

$$L\left[w\right] - wf_u(u,\vec{y}) = f(u,\vec{y}) - uf_u(u,\vec{y}) \qquad (16E),$$

which has a unique solution if

$$w(v,y) = u(y) \qquad (17E)$$

If $u \geq w(v,y)$ and $w(v,y) = u(y)$ for $v = u$, then it is obvious that

$$u = \max_v w(v,y) \qquad (18E).$$

This establishes a least upper bound on the sequence w. Kalaba et al (16) have shown that this sequence is uniformly bounded and converges uniformly and monotonously to 'u'. This convergence has been shown to be quadratic in the sense that each new element of this sequence approximately doubles the digits of accuracy.

Construction of the Monotone Sequence

An arbitrary function $v_o(y)$ is chosen, and used to solve equation (9E) for w. This w is called $u_o(y)$. Thus,

$$L\left[w\right] = L\left[u_o(y)\right] = f(v_o(y),y) + \left(u_o(y) - v_o(y)\right)f_v(v_o(y),y) \qquad (19E)$$

Equation (19E), is a linear equation with variable coefficients and hence can be solved for $u_o(y)$. The functions, $u_o(y)$ and $v_o(y)$ have the same boundary conditions as the function u. on B. The new function

$u_o(y)$ is subsequently used to determine an improved function $v_1(y)$, as the function which maximises the expression (7E).

$$\max_v \left[f(v) + (u-v)f_v(v,y)\right]$$ throughout the domain D. Since 'f' is strictly convex, the expression is maximised when

$$u_o(y) = v_1(y).$$

With a new $v_1(y)$ the whole cycle is repeated. Thus the following recurrence relationship can be written:

$$L\left[u_o(y)\right] = f\left(v_o(y),y\right) + \left(u_o(y) - v_o(y)\right) f_v\left(v_o(y),y\right) \qquad (20E)$$

$$L\left[u_1(y)\right] = f\left(v_1(y),y\right) + \left(u_1(y) - v_1(y)\right) f_v\left(v_1(y),y\right)$$

$$\text{but } v_1(y) = u_o(y)$$

therefore,

$$L\left[u_1(y)\right] = f\left(u_o(y),y\right) + \left(u_1(y)-u_o(y)\right) f_v\left(u_o(y),y\right) \qquad (21E)$$

By induction, therefore

$$L\left[u_o(y)\right] = f\left(v_o(y),y\right) + \left(u_o(y)-v_o(y)\right) f_v\left(v_o(y),y\right) \qquad (20E)$$

$$L\left[u_{n+1}(y)\right] = f(u_n(y),y) + \left[u_{n+1}(y)-u_n(y)\right] f_v(u_n(y),y) \qquad (22E)$$

$$n = 0,\ldots,n.$$

The actual calculations involve only the setting up of equation (20E and 22E) and the solution of these linear equations.

NOMENCLATURE

Latin Letters

C_i = concentration of species i, $\overset{*}{C}_i, \overset{o}{C}_i$ interface and bulk concentrations respectively

D_i = liquid phase diffusivity of species i

$\overset{o}{K}_L$ = mass transfer coefficient without chemical reaction. Equations (15a), and (61)

L = linear operator

M = number of increments along 'θ' coordinate

M_i = system component

N = number of increments along 'distance coordinates'

$S_{Ai}, S_{Bi}, S_{Ci}, S_{Di}$ = coefficients in a triangular system of equations

U = velocity

Z = dimensionless transformed distance, equation (44)

a = dimensionless concentration $C_{M1} / \overset{*}{C}_{M1}$

b = dimensionless concentration $C_{M2} \Big/ \overset{*}{C}_{M1}$

c = a transformation constant, equation (44)

erf, erfc = error function and complimentary error function

k_1 = specific reaction rate constant

m = order of the second step reaction

n = order of the first step reaction

r_i = reaction rate for the ith reaction

t = time, $\overset{*}{t}$ a specified time. Equation (15a)

v_o = a first approximation for b. Equation (80)

x = distance coordinate

y = dimensionless space coordinate for penetration theory model equations = $x\sqrt{2k_1 \overset{*}{C}{}_{M1}^{n-1} \Big/ D_{M1}}$

for film theory model equations = (x/δ_f)

Greek Letters

α = a fluid phase

β = a fluid phase in which reactions take place

Δ = Laplacian Operator

∇ = Gradiant Operator

θ = dimensionless time = $2tk_1C_{M1}^{*n-1}$

λ = specific reaction ratio $\dfrac{k_2\ C_{M1}^{m*}}{k_1\ C_{M1}^{n*}}$

ν = diffusivity ratio D_{M1}/D_{M2}.

ξ = distance coordinate

σ_{BA} = selectivity of M2 with respect to M1

X = instantaneous flux, equations (12) (60)

ψ = reaction diffusion modulus,

in general $\sqrt{2D_{M1}k_1C_{M1}^{*n-1}}/\overset{o}{K}_L$

penetration theory equation (33)

$\Delta x, \Delta y, \Delta z, \Delta\theta$ = increments along respective axis

δ_f = film thickness

Subscripts

p = penetration theory

f = film theory

Superscripts

$\sim$ = average

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PART II

EFFECT OF CATALYST POISONING ON SELECTIVITY——A MODELLESS APPROACH

ABSTRACT

The effect of independent poisoning on the selectivity for an intermediate B in a complex reaction $A \longrightarrow B \longrightarrow F$, catalysed by porous spherical pellets has been investigated by solving the relevent partial differential equations, instead of by the use of a restrictive model, like the Shell Poisoning Model. The results indicate that when the catalyst is poisoned for the reaction $A \longrightarrow B$ only, the selectivity either does not change significantly or decreases as the catalyst pellets age. On the other hand when the catalyst is poisoned for both the reaction $A \longrightarrow B$ and the reaction $B \longrightarrow F$, the selectivity either remains constant or increases with increasing poisoning. Although, the effect of the Poison Thiele Modulus h_p on the selectivity could not be explained qualitatively for the case when the catalyst is poisoned for both the reactions, selectivity for B was found to decrease with increasing values of h_p, when the catalyst is poisoned for the reaction $A \longrightarrow B$ only. It has also been shown that selectivity for B increases with increasing values of the intrinsic selectivity parameter (k_A/ k_B).

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CHAPTER I

INTRODUCTION

In spite of the great care taken in purifying the feed streams to a catalytic reactor, these streams are usually contaminated with small amounts of impurities which can act as poisons for the catalyst particles. Such poisoning can drastically affect the activity and selectivity characteristics of the catalyst, thus altering considerably the distribution and quality of the products.

In studying the behavior of a catalyst poison, it has become customary to approach the problem from two opposite and extreme positions. According to one, the poison is uniformly distributed at all times throughout the catalyst particle. The other extreme position is based on the assumption that the poison molecules are adsorbed in such a way that the outside pore structure of a catalyst pellet becomes completely poisoned before the interior loses any activity. Wheeler (48) has called the first type of poisoning the 'homogeneous' poisoning, the second type of poisoning the 'pore mouth' poisoning. It is obvious that real catalyst particles will seldom behave according to either of these two idealised models. It is very unlikely that the catalyst particle will be homogeneously deactivated, nor is it very likely that the catalyst pellet will be sharply divided by a definite poison front into a fully poisoned zone and a completely non-poisoned region. On the other hand, as Masmune and Smith (26) have pointed out, the extent of deactivation in general will depend upon time and the radial position within the pellet. A model of catalyst poisoning based on such realistic ideas can be called a 'Modified Homogeneous Poisoning Model'. The 'Homogeneous Poisoning Model'--based on the uniform distribution of poison throughout the pellet, and the 'Shell' or the 'Pore Mouth Poisoning Model'--based on the existence of sharply defined poisoned and non poisoned zones in the pellet, are then the two limiting cases of the* 'Modified Homogeneous Poisoning Model'. When the intraparticle resistence to diffusion of the poison molecules is negligible, the poison will be uniformly distributed and the 'Modified Homogeneous Poisoning Model' ('M.H.P. Model') would behave like the 'Homogeneous Poisoning Model'. But in contrast, when the diffusion resistance is very large in comparison to the resistence of the poisoning process, the poison would be concentrated in a shell of the catalyst, and the 'M.H.P. Model' will approach the 'Shell Poisoning Model' (or the 'Pore Mouth Poisoning Model'). In the case of the 'Shell Poisoning Model', the thickness of the poisoned shell will grow with process time, until the entire pellet is

---

*Abbreviated as 'M.H.P. Model'

deactivated.

Although during the past few years, a number of studies (5,26,34, and40) based on the 'M.H.P. Model' have been published, these studies have invariably dealt with the effect of 'fouling' on the activity and effectiveness factor of the catalyst. But 'fouling' and poisoning affect the catalyst in different ways. 'Fouling' is caused by the deposition of carbonacious material (the so-called 'coke') on the pellet and thus results in deactivation of the catalyst for all reactions. Thus, it is but logical that 'fouling' studies ought to deal mainly with activity and effectiveness factor of the catalyst. Poisoning on the other hand sometimes involves irreversible adsorption of impurities on the catalyst surface. Thus, a catalyst may be progressively poisoned by small molecules of a certain species to such an extent that the reversible adsorption of certain other reactant (or intermediate) species, particularly ones with larger molecules, can no longer take place. However the same surface may still accomodate other reactants (or intermediates) with smaller molecules by reversible adsorption in the space between the poison molecules. Thus in a process involving two or more than two simultaneous reactions (exclusive of the poisoning reaction), it is better to study the effect of poisoning on the selectivity characteristics of the catalyst rather than on its activity or effectiveness factor.

With the solitary exception of a study by Sada and Wen (37) who investigated the effect of 'Pore Mouth Poisoning' of a catalyst on the overall selectivity in a complex kinetic scheme, the effect of catalyst poisoning on the overall selectivity for a complex reaction scheme has not been investigated. It was therefore decided to study the effect of catalyst poisoning on the selectivity 'S_{BF}' of an intermediate B by using a realistic model like the 'M.H.P. Model' and not the limiting 'Shell' or the 'Homogeneous Poisoning Model'. For the sake of model comparison however, it was decided to investigate the 'Shell Model' as well. The consecutive reaction $A \longrightarrow B \longrightarrow F$ was chosen for investigation, as it is a fairly common reaction in industrial practice. It was planned to study the poisoning when:

i. The catalyst is poisoned for the reaction $A \longrightarrow B$ and not for the reaction $B \longrightarrow F$.

ii. The catalyst is poisoned for the reaction $A \longrightarrow B$ as well as the reaction $B \longrightarrow F$.

It was assumed that the poisoning of the catalyst would be caused by an independent reaction between the impurities in the feed streams and the active sites of the catalyst particles.

CHAPTER II

REVIEW OF LITERATURE

The important problem of the effect of diffusional transport on the activity and selectivity of a porous catalyst has been a subject of study for quite a number of years. Frank-Kamenetskii (17) has treated in detail the activity and selectivity alterations caused by intraparticle mass transport under isothermal conditions. Wheeler (48) classified the various types of selectivities and derived an expression for the type III isothermal selectivity of an intermediate B in a complex reaction system, $A \xrightarrow{k_1} B \xrightarrow{k_2} C$, catalysed by a porous cylindrical catalyst particle. The relationship derived by Wheeler (48) expressed selectivity (number of moles of B formed per mole of A reacted) in terms of the ratio (k_1/k_2) and the Thiele Modulus $L\sqrt{\frac{2k_i}{rD_i}}$ ϕStergaard (32) analysed a more complex first order reaction system —— $M1 \xrightarrow{k_2} M2 \xrightarrow{k_3} M3 \longrightarrow \ldots$. Mn—— and derived expressions for conversion to the first intermediate as a function of the Thiele Modulus and various specific rate constants. ϕStergaard based his analysis on spherical catalyst particles. Carberry (12) and Beek (6) have reported the effect of nonisothermal conditions on the selectivity of the intermediate B in the catalysed reaction

$A \longrightarrow B \longrightarrow C$. A treatment of selectivity is at least implicit in the work of Schilson and Amundson (38) who investigated the mass and heat transport effects on a complex reaction system. Carberry (13) has also extended Wheeler's (48) selectivity analysis for catalysts with simple cylindrical pores to catalysts having a bimodal pore size distribution in which diffusion is assumed to occur in the macro and micro pores in series. ϕstergaard (33) has recently published a study dealing with the mass and heat transport effects on the selectivity of the desired product formed in a catalysed first order parallel reaction. In a study dealing with the effects of heat and mass transport on the activity, selectivity and yield in the consecutive reaction system $A \longrightarrow B \longrightarrow C$, Butt (11) has extended and generalised the treatment given in Carberry's (12) and Beek's (6) papers.

In addition to these theoretical studies, a few experimental studies on catalyst selectivity have also been made. Weisz and Swegler (47) cracked cyclohexane to cyclohexene and thence to benzene on a chrome alumina catalyst, and found that the selectivity of cyclohexene increased with decreasing particle size. This was in agreement with the theoretical results predicted by Wheeler (48). Johnson et al (21) in their study of gas oil cracking on silica alumina catalyst of various sizes have also reported that selectivity to form gasoline increased with decreasing particle size. Investigation of palladium catalyst for selectivity studies of the hydrogenation of acetylene also yielded results which confirmed the theoretical predictions made by Wheeler (48). Palladium catalyst studies were done by Mars and Gorgels (25).

The poisoning of the catalyst particles was discussed systematically for the first time by Wheeler (48) who described the two different ways—the 'homogeneous' poisoning and the 'Pore Mouth' poisoning—by which the catalyst pellet can get poisoned. In 'homogeneous' poisoning it is assumed that the poison molecule makes many collisions with the catalyst surface before adsorption occurs. Thus the poison molecules have an opportunity to diffuse deep into the catalyst pellet prior to being "cleaned up" by the pore walls. Wheeler (48) assumed that such a poison will be evenly distributed at all times throughout the catalyst pellet. Assuming that the intrinsic activity k of the pore wall decreases to $k(1-\alpha)$, that is linearly with the fraction of the surface poisoned, Wheeler (48) derived an expression for the fall in the activity of the whole pore. According to Wheeler (48), in 'pore mouth' poisoning the poison is so strongly adsorbed that the outer region of the pore becomes completely poisoned before any alteration occurs in the activity of the interior of the pore. In developing their unreacted-core shrinking model, Yagi and Kunii (50) also had assumed the existence of a completely reacted region and a completely unreacted region in a solid reacting particle. They had assumed that a sharp interface separated these two regions. Yagi and Kunii (51), Levenspiel (24) and Narsimhan (30) have also suggested that the rate of movement of this interface is very much slower than the rate of any gaseous diffusion process. The interface therefore, can be taken to be stationary at any time and the steady state diffusion problem solved to find the concentration profile. The mass flux, as found from this expression, can then be equated to the rate of disappearance of the unreacted solid in order to locate the interface as a function of time. Bischoff (7,8) and Bowen (10) have established the validity of the 'pseudo-steady state' assumption made in describing this so called unreacted-core shrinking model. Weisz and Goodwin (46) used Yagi and Kunii's (51) model in a study dealing with the burn-off time of carbonaceous deposits within porous catalyst particles. Ausman and Watson (5) used the same model for treating the regeneration of the fouled catalyst particles during a part of the regeneration period. Carberry et al (14) used Weisz and Goodwin's (46) treatment to analyse the time dependent 'pore mouth' poisoning problem. As Carberry et al (14) have pointed out, this is an extension of the concept of 'pore mouth' poisoning as outlined by Wheeler (48). According to Carberry et al (14) "Wheeler's treatment embraces only those circumstances in which a quantity of poison is imposed upon the system for a period of time sufficient to cause a fixed and thereafter time independent deactivation. More commonly, a poison or coke bearing agent is fed to the catalyst system in continuous though often small supply.". The continuous poisoning obviously leads to a time dependent regime. In this treatment, Carberry et al (14) have relaxed the restriction in the original Yagi and Kunii's (50) and Wheeler's (48) models that the fouling process is controlled by the diffusion through the poisoned layer. Carberry et al (14) were primarily concerned with predicting the position of the poison front in a spherical catalyst particle. Petersen (35) has also dealt with the effect of 'pore mouth' poisoning on the activity and effectiveness factor of a catalyst particle. Experimental conclusions of Schwab et al (39) and Anderson et al (3) have also been explained on the basis of the 'Pore Mouth Poisoning' or the 'Shell Poisoning Model'. Recently Olson (31) has extended Carberry's (14) analysis of a 'pore mouth' poisoned catalyst particle to poisoning of fixed bed reactors. Olson (31) has treated the case of a fixed bed reactor which develops "Pore Mouth Poisoning" of a variable extent throughout the system. He has also dealt with the problem of poisoning of a guard bed reactor. The time dependent activity of these reactors was evaluated.

Without invoking the 'Shell Poisoning Model', Ausman and Watson (5) studied mass transfer in a catalyst pellet during regeneration. It was the first time that a poisoning (or fouling) study had been done without using the very restrictive 'Shell Poisoning Model'. As Carberry et al (14) have pointed out the 'Shell Poisoning Model' is valid only if the Thiele Modulus (based on the specific reaction rate for burning) exceeds a certain critical value. Ausman and Watson (5) assumed that the local rate of regeneration reaction was independent of the carbon content and depended only on the partial pressure of oxygen. They calculated the intraparticle distribution of the deposit (coke) as a function of time and the radial position. As has been suggested before (page 2), for the sake of convenience Ausman and Watson (5) type analysis can be called the "Modified Homogeneous Poisoning Model" analysis.* The 'Shell Poisoning Model' is one extreme case (Thiele Modulus $>$ Critical Thiele Modulus) of the 'M.H.P. Model'. The other extreme case is the 'Homogeneous Poisoning Model'. Froment and Bischoff (18) analysed the effects of catalyst fouling (coke deposition) on the

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*To be more exact, in the case of regeneration problems, the term "Modified Homogeneous Regeneration Model" should be used.

activity of a fixed bed reactor. The coke was formed as a result of either the reactions $A \longrightarrow B \longrightarrow \text{Coke}$ or the reactions $$\begin{tikzcd} A \arrow[r] \arrow[d] & B. \\ \text{Coke} \end{tikzcd}$$ The rate of coke forming reaction was assumed to be negligible compared to the rate of formation of the main product B. They also suggested that change in the rate of the main reaction, caused by the fouling reaction, should be directly related to the amount of fouling material present (or coke deposited), rather than to process time as assumed by Voorhies (44), Blanding (9), Wilson et al (49), Watson et al (45) and Katsobashili (22). This suggestion by Froment and Bischoff (18) has lead to the use of several forms of the deactivation function Ω . Froment and Bischoff (18) assumed an exponential form $\Omega = \exp(-\alpha q)$ and a hyperbolic form $\Omega = 1/(1 + \beta q)$ where α and β are constants. Anderson and Whitehouse (4) used four forms of Ω function for poisoning of the catalyst: $\Omega = 1\text{-}aS_x$, $\Omega = \exp(-aS_x)$, $\Omega = (1+aS_x)^{-1}$ and $\Omega = \sqrt{(1-aS_x)}$, where a is a constant and S_x is the relative poison conentration. It should be mentioned that netiher Froment and Bischoff (18) nor Anderson and Whitehouse (4) included the effects of mass or heat transport in their analyses. VanZoonen (43) used the form $\Omega = \alpha/q$, for studying the effect of coke deposition on hydroisomerisation of olefins over silica alumina-nickel sulphide catalyst. The reactions in VanZoonen's (43) study can be described as

$$\begin{tikzcd} A \arrow[r] \arrow[d] & B \text{ (desired product)} \\ \text{Coke} & \end{tikzcd}$$

Like Froment and Bischoff (18) and Anderson and Whitehouse (4), VanZoonen (43) did not consider the effect of mass transport inside the catalyst particles. **Levenspiel** et al (24) have recently generalised the deactivation rate equation and have shown how the various forms of Ω can be derived form the general equation. Masmune and Smith (26) using the 'M.H.P. Model' in a treatment similar to the one used by Ausman and Watson (5), derived equations to describe the bulk rate of gaseous reaction on a spherical porous catalyst whose activity changes because of a fouling reaction. The reactions investigated by these authors were:

$$\begin{tikzcd} A \arrow[r] & B\text{(desired)} \arrow[r] & \text{Coke,} & A \arrow[r] \arrow[d] & B\text{(desired),} & A \arrow[r] & B\text{(desired)} \\ & & & \text{Coke} & & S \arrow[r] & \text{Coke} \end{tikzcd}$$

All reactions were of first order, and in all cases, the fouling reaction was assumed to be much slower than the main reaction. A deactivation function of the form $\Omega = (1-\psi)$ was used. ψ $\langle \psi = q/q_0 \rangle$ was supposed to be a function of time and radial position. **Masmune and Smith** (26,27) took into account the effects of intraparticle heat and mass transport by using effectiveness factors. A similar study by Takeuchi et al (41) has also been reported.

A few experimental studies based on the 'M.H.P. Model' (Ausman-Watson (5) treatment) have also appeared recently. Suga et al (40) have reported the effect of coke deposition on the activity of solid catalysts and of diffusion in particles. Their study is modeled on Masmune and Smith's (26) treatment, except that the deposition of coke inside the particle was taken to be independent of radial position. Thus, Suga et al (40) solved ordinary differential equations instead of the partial differential equations proposed by Masmune and Smith (26). Suga et al's (40) experimental work dealt with the reactions:

$$\begin{tikzcd}
\text{A(n-}C_4H_{10}\text{)} \arrow[r] \arrow[d] & \text{B(the desired product n-}C_4H_8\text{)} \arrow[r] & \text{Coke} \\
\text{D(Gas)} & &
\end{tikzcd}$$

The coke forming raction was assumed to be very slow. Ozawa and Bischoff (34) using an 'M.H.P. Model' studied the effect of coke formation on the reactions:

$$\begin{tikzcd}
C_2H_4 \arrow[r] \arrow[d] & \text{Products} \\
\text{Coke} &
\end{tikzcd}$$

They also analysed Eberly et al's (16) data. Ozawa and Bischoff's (34) treatment is essentially the same as that of Masmune et al (26). Murakami et al (29) have reported an experimental study dealing with the effectiveness factors for porous spherical catalyst particles on which the following reactions are taking place:

$$\begin{tikzcd}
 & \text{Alcohol} \arrow[r] & \text{Aldehyde} \arrow[r] & \text{Coke} \\
\text{or} & \text{Toulene} \arrow[r] \arrow[d] & \text{Xylene(desired)} + \text{Benzene} & \\
 & \text{Coke} + \text{Benzene.} & &
\end{tikzcd}$$

Unlike other investigators Murakami et al (29) have assumed that the coke forming reactions proceeded at an appreciable rate.

From a review of the work done thus far, it is apparent that very little attention has been paid to the study of the effects of catalyst poisoning on the selectivity of a desirable product formed during the course of a complex reaction. The exceptions are a study by Froment and Bischoff (19) and a study by Sada and Wen (37). Although Froment and Bischoff (19) dealt with the effect of fouling on the product distribution from fixed bed catalytic reactors, they ignored the effects of intraparticle mass and heat transport. Sada and Wen's (37) investigation does take into account the intraparticle mass transport and is comprehensive in its treatment of the effects of catalyst poisoning on the selectivities of a desirable product, but the analysis is based on the very restrictive 'Shell Poisoning Model'.

It is the purpose of this study to examine how an independent poisoning reaction due to impurities in the feed streams affects the overall selectivity of spherical porous catalyst systems. The main reactions considered are:

$$A \xrightarrow{k_A} B(\text{desired product}) \xrightarrow{k_B} F.$$

The poisoning is assumed to be caused by a reaction between the active sites of the catalyst particles and the impurities in the feed stream. The most important feature is the consideration of the effects of intraparticle mass transport, not by assuming the 'Shell Poisoning Model' (though the 'Shell Poisoning Model' is used for comparison purposes) but by using the 'Modified Homogeneous Poisoning Model' ('M.H.P. Model'). The poisoning is studied when:

i. the poison deactivates the catalyst for the reaction $A \longrightarrow B$ only,

ii. the poison deactivates the catalyst for the reaction $A \longrightarrow B$ as well as the reaction $B \longrightarrow F$.

CHAPTER III

THEORETICAL CONSIDERATIONS

A. General

There are a number of ways a catalyst can get poisoned and fouled. Of the various causes and types of poisoning and fouling, only the independent poisoning due to impurities in the feed streams, is treated in this study. Independent poisoning implies that the deactivation of the active sites in the catalyst is caused only by the impurities in the feed stream, and that the presence of other compounds does not affect at all the activity of the catalyst. For the purpose of this study it is assumed that poisoning is caused by an irreversible adsorption of poison molecules on the active sites. The main reactions proceed by the reversible adsorption on the fresh sites. It is conceivable that because of the different sizes of the reactant (or intermediate) molecules, the catalyst can be poisoned either for the reaction $A \longrightarrow B$, or for both the reactions $A \longrightarrow B$ and $B \longrightarrow F$ of a complex scheme $A \longrightarrow B$(desired product)$\longrightarrow F$.

It is usually assumed that the adsorption leading to poisoning of the active sites is a very fast process, and this in turn has led to the use of the so called 'Shell Poisoning Model', but the adsorption of poison molecules on the active sites may not be that strong or fast, in which case the 'Shell Poisoning Model' is no longer valid. On the other hand the 'Modified Homogeneous Poisoning Model' can be used for all situations.

The 'M.H.P. Model' is characterised by two assumptions regarding the process of poisoning:

i. that the extent of poisoning depends on time and radial positions within the pellet and

ii. that the poisoning process does not divide the catalyst pellet into two sharply defined regions, a poisoned zone and a fresh zone.

The first assumption distinguishes the 'M.H.P. Model' from the 'Homogeneous Poisoning Model' in which the extent of poisoning is assumed to be independent of radial position (the actual assumption is zero diffusion **resistence**). The second assumption differentiates the 'M.H.P. Model' from the 'Shell Poisoning Model'. The 'Shell Poisoning Model' is based on the stipulation that a poisoned catalyst consists of a completely poisoned region and an entirely non-poisoned region separated by a sharp interface. The so called 'Psuedo Steady State' assumption helps to locate the position of this interface. According to this assumption the rate of movement of this interface is very much slower than the rate at which the poison diffuses inside the pellet (this amounts to the statement that the diffusional resistance is controlling i.e., $h_p \longrightarrow \infty$). Thus the interface can be taken to be stationary at any time, and the steady state diffusion problem solved to find the concentration profile for the poison. The mass flux of poison as found from this expression is then equated to the rate of disappearance of the non poisoned part of the pellet in order to determine the location of the poison front in time. Though this study is primarily concerned with the 'M.H.P. Model', the 'Shell Poisoning Model' is also included for the purposes of comparison. In order to avoid undue mathematical difficulties, uniform temperature across the pellet was assumed (this is a limiting assumption; because temperature is very seldom constant across a pellet). The catalyst pellet was assumed to be spherical in shape. The description of chemical reactions and isothermal mass balances for the two models are given in section (B) and (C) of this chapter.

B. The 'Modified Homogeneous Poisoning Model' ('M.H.P.Model')

1. Description of chemical reactions:

The main reactions considered in this study are of the form

$$A \xrightarrow{k_A} B\text{(desired products)} \qquad (1)$$

$$B \xrightarrow{k_B} F\text{ (undesired products)} \qquad (2)$$

It was assumed that the following two types of poisoning could occur:

i. the poison could affect the active sites in such a way that the catalyst is deactivated with respect to the reaction A ⟶ B only.

ii. the deactivation of the catalyst particle could occur with respect to the reaction A ⟶ B as well as the reaction B ⟶ F.

Equation (3) describes the poisoning reaction

$$P + \overset{*}{S} \xrightarrow{k_P} \overset{*}{S}P \qquad (3)$$

The reactions (1), (2) and (3) were assumed to be of the first order with respect to A, B, and P, respectively. The effect of poisoning on the rates of reactions (1) and (3) or reactions (1), (2) and (3) is assumed to be linear in form.** The deactivation function Ω is given as,

$$\Omega = 1 - (q/q_o) = 1 - \psi \qquad (3a)$$

where, (q/q_o) is the fraction of sites that have been deactivated.

Corresponding to cases (i) and (ii), the reaction rate and mass balance equations for spherical porous catalysts can be written as follows:

**Levenspiel et al (24) have summed up other forms of Ω.

2. Intraparticle concentration equations (the 'M.H.P. Model'):

a. Case I: Poisoning of catalyst for reaction (1) only.

i. for the poison P:-

the reaction rate is given by equation (4)

$$R_P = k_P(1 - \psi)C_P \tag{4}$$

and the isothermal mass balance by equation (5)

$$\nabla(D_P\nabla C_P) = \epsilon_P \frac{\delta C_P}{\delta t} + k_P\rho(1 - \psi)C_P \tag{5}$$

molecular transport = accumulation + reaction

The deactivation of active sites of the catalyst particle is described as:

$$-\frac{\delta}{\delta t}(q_0 - q) = k_P(1 - \psi)C_P \tag{6}$$

The partial derivative of q in equation (6), has been used to describe the relationship

$$q = f(r,t) \tag{7}$$

ii. For the reactant A:-

the reaction rate and the isothermal mass balance are respectively given by,

$$R_A = k_A C_A(1 - \psi) \tag{8}$$

$$\nabla(D_A\nabla C_A) = \epsilon_P \frac{\delta C_A}{\delta t} + \rho k_A(1 - \psi)\, C_A \tag{9}$$

iii. For the intermediate B: similiar equations for the intermediate 'B' can be written:

$$R_B = k_B C_B - k_A(1-\psi)C_A \qquad (10)$$

$$\nabla(D_B \nabla C_B) = \epsilon_P \frac{\delta C_B}{\delta t} + \rho k_B C_B - \rho k_A(1-\psi)C_A \qquad (11)$$

b. Case 2: Poisoning of catalyst for reactions (1) and (2)

Equations (4-9) adequately describe the reaction rates and mass balances of the species A and P for this case as well. Equations (10) and (11) have to be modified to,

$$R_B = k_B(1-\psi)C_B - k_A(1-\psi)C_A \qquad (12)$$

$$\nabla(D_B \nabla C_B) = \epsilon_P \frac{\delta C_B}{\delta t} + \rho(1-\psi)\left[k_B C_B - k_A C_A\right] \qquad (13).$$

3. Boundary and initial conditions ('Modified Homogeneous Poisoning Model')

It can be safely assumed that the deactivation function does not vary sharply with time. Thus it follows that the time necessary to reach steady state with respect to the accumulation of mass in the void spaces of the pellet is negligible in comparison to the time required for the catalyst deactivation function Ω to change significantly. This permits the dropping of the accumulation term from equations (5),(9),(11) and (13). It is also clear that at

$t = \delta$ (where $\delta \approx 0$), the deactivation function Ω will be unity. The spherical symmetry of the particle implies a zero concentration gradient at the centre of the particle. The mass balance equations can be simplified by assuming that the effective diffusivities, D_i, are constant. This assumption, though apparently unrealistic, holds true for a number of situations. When the poisoning process is due to the adsorption of poisoning molecules on the active sites of the catalyst surface, poisoning will not alter the physical structure of the pores in the catalyst. Therefore, under such conditions it is valid to treat the effective diffusivities as constant.

For the sake of mathematical simplicity, the resistence to diffusion in the gas phase around the spherical pellet was assumed to be negligible. With these assumptions the isothermal intraparticle concentration equation for case (1) and case (2) can be written as follows:

a. Simplified concentration equation for Case 1:

$$D_P \Delta C_P = \rho k_P (1-\psi) C_P \tag{14}$$

$$\frac{\delta \psi}{\delta t} = \frac{k_P}{q_0}(1-\psi) C_P \tag{15}$$

$$D_A \Delta C_A = \rho k_A (1-\psi) C_A \tag{16}$$

$$D_B \Delta C_B = \rho k_B C_B - \rho k_A (1 - \psi) C_A \qquad (17)$$

The initial and boundary conditions for

i. equations (14 and 15) are:

$$\psi = 0;\ r_0 \geq r \geq 0;\ t \approx 0 \qquad (18)$$

$$C_P = \overset{*}{C}_P \quad r = r_0;\ t \geq 0 \qquad (19)$$

$$\frac{\delta C_P}{\delta r} = 0 \quad r = 0;\ t \geq 0 \qquad (20)$$

and

$$D_P \Delta C_P = \rho k_P C_P, \quad t \approx 0 \qquad (21)$$

ii. equation (16) are,

$$C_A = \overset{*}{C}_A; \quad r = r_0; \quad t \geq 0 \qquad (22)$$

$$\frac{\delta C_A}{\delta r} = 0; \quad r = 0; \quad t \geq 0 \qquad (23)$$

$$D_A \Delta C_A = \rho k_A C_A; \quad t \approx 0 \qquad (24)$$

iii. equation (17) are,

$$C_B = \overset{*}{C}_B = 0 \quad r = r_0; \quad t \geq 0 \qquad (25)$$

$$\frac{\delta C_B}{\delta r} = 0 \quad r = 0; \quad t \geq 0 \qquad (26)$$

$$D_B \Delta C_B = \rho k_B C_B - \rho k_A C_A; \quad t \approx 0 \qquad (27)$$

The condition

$C_B = \overset{*}{C}_B = 0$ was chosed for simplicity. Any other value would have been equally good.

b. Simplified concentration equations for case 2.

Except for equation (17), equations (14-27) are valid for case 2 as well, equation (17) is modified to

$$D_B \Delta C_B = \rho k_B(1 - \psi)C_B - \rho k_A(1 - \psi)C_A \quad (28).$$

4. Non-dimensional intraparticle concentration equations (the 'M.H.P. Model')

The intraparticle concentration equations (14-28) can be described in the non-dimensional form as follows:

a. non-dimensional equations for case 1.

i. Poison P:

$$\frac{\delta^2\phi_P}{\delta\xi^2} + \frac{2}{\xi}\frac{\delta\phi_P}{\delta\xi} = h_P^2 \ (1 - \psi)\ \phi_P \quad (29)$$

$$\frac{\delta\psi}{\delta\theta} = h_P^2 \ (1 - \psi)\phi_P \quad (30)$$

$$\psi = 0 \ ; \qquad 1 \geq \xi \geq 0 \qquad \theta \approx 0 \quad (31)$$

$$\phi_P = 1 \ ; \qquad \xi = 1 \qquad \theta \geq 0 \quad (32)$$

$$\frac{\delta \phi_P}{\delta \xi} = 0 \qquad \xi = 0 \qquad \theta \geq 0 \tag{33}$$

$$\text{or } \phi_P = \text{finite} \qquad \theta \geq 0$$

and

$$\frac{\delta^2 \phi_P}{\delta \xi^2} + \frac{2}{\xi}\frac{\delta \phi_P}{\delta \xi} = h_P^2 \phi_P \qquad \theta \approx 0 \tag{34}$$

The solution to equation (34) describes the distribution of poison in the catalyst particles at $\theta = \delta \approx 0$. δ represents the extremely small interval of time required for bringing the voids of the catalyst pellet to a "psuedo steady" state for the first time. Equation (35) is a solution for equation (34)

$$\phi_P = \frac{\operatorname{Sinh} h_P \xi}{\xi \operatorname{Sinh} h_P} \qquad \text{at } \theta \approx 0 \tag{35}$$

ii. reactant A:

$$\frac{\delta^2 \phi_A}{\delta \xi^2} + \frac{2}{\xi}\frac{\delta \phi_A}{\delta \xi} = h_A^2 (1 - \psi)\phi_A \tag{36}$$

$$\psi = 0 ; \qquad 1 \geq \xi \geq 0 \qquad \theta \approx 0 \tag{37}$$

$$\phi_A = 1 ; \qquad \xi = 1 \qquad \theta \geq 0 \tag{38}$$

$$\frac{\delta \phi_A}{\delta \xi} = 0 \qquad \xi = 0 \qquad \theta \geq 0 \tag{39}$$

and

$$\frac{\delta^2\phi_A}{\delta\xi^2} + \frac{2}{\xi}\,\frac{\delta\phi_A}{\delta\xi} = h_A^2\,\phi_A \qquad \theta \approx 0 \qquad (40)$$

Equation (41) is the solution of equation (40) and describes the initial concentration of A at $\theta = \delta \approx 0$.

$$\phi_A = \frac{\mathrm{Sinh}\ h_A\,\xi}{\xi\,\mathrm{Sinh}\ h_A} \quad ; \quad \theta \approx 0 \qquad (41)$$

iii. Intermediate 'B'

$$\frac{\delta^2\phi_B}{\delta\xi^2} + \frac{2}{\xi}\,\frac{\delta\phi_B}{\delta\xi} = h_B^2\,\phi_B - \nu\,h_A^2\,(1-\psi)\phi_A \qquad (42)$$

$$\psi = 0 \qquad 0 \le \xi \le 1 \qquad \theta \ge 0 \qquad (43)$$

$$\phi_B = 0 \qquad \xi = 1 \qquad \theta \ge 0 \qquad (44)$$

$$\frac{\delta\phi_B}{\delta\xi} = 0 \qquad \xi = 0 \qquad \theta \ge 0 \qquad (45)$$

and

$$\frac{\delta^2\phi_B}{\delta\xi^2} + \frac{2}{\xi}\,\frac{\delta\phi_B}{\delta\xi} = h_B^2\,\phi_B - \nu\,h_A^2\,\phi_A \ : \ \theta \approx 0 \qquad (46)$$

Equation (46) can be solved by substituting equation (41) for ϕ_A. The solution is

$$\phi_B = \frac{\nu h_A^2}{h_A^2 - h_B^2}\left(\frac{\mathrm{Sinh}\ h_B\,\xi}{\xi\ \mathrm{Sinh}\ h_B}\right) - \frac{\nu\,h_A^2}{(h_A^2 - h_B^2)}\left(\frac{\mathrm{Sinh}\ h_A\,\xi}{\xi\ \mathrm{Sinh}\ h_A}\right) \qquad (47).$$

$$\theta \approx 0$$

b. non-dimensional equations for case 2:

With the exception of equation (42), equations (29-47) describe equally well the non-dimensional intraparticle concentration of the various species in a catalyst pellet deactivated for the reaction

$$A \longrightarrow B \quad (1),$$

as well as the reaction

$$B \longrightarrow F \quad (2) \quad .$$

Equation (42) is replaced by **equation (48):**

$$\frac{\delta^2 \phi_B}{\delta \xi^2} + \frac{2}{\xi} \frac{\delta \phi_B}{\delta \xi} = h_B^2 \ (1 - \psi)\phi_B - \nu h_A^2 \ (1 - \psi)\phi_A \qquad (48)$$

5. Selectivity S_{BFh}: 'Modified Homogeneous Poisoning Model'

Petersen (35) has defined selectivity, S_{BF}, as the ratio of the flux of the desired product to that of the undesirable product at the surface of the catalyst particle. Since in the present study the catalyst particle is assumed to be getting progressively poisoned, Petersen's (35) selectivity is equivalent to an instantaneous selectivity for the purposes of the present investigation. Equation (49) gives this instantaneous selectivity;

$$S_{BFh} = \left(\frac{-D_B \nabla C_B}{-D_F \nabla C_F} \right)_{\text{surface}}, \quad t = t \qquad (49)$$

Equation (49) can also be written as,

$$S_{BFh} = -\left[\frac{1}{1 + \nu \dfrac{\nabla \phi_A}{\nabla \phi_B}}\right] \qquad (50).$$

C. 'Shell Poisoning Model'

1. Description of chemical reactions:- The description of chemical reactions for the 'Modified Homogeneous Poisoning Model' given in section (B1), is generally valid for the 'Shell Poisoning Model' also. The difference, as pointed out before (page 2), lies in the approach to poisoning of the catalyst particles. Whereas, in the 'Shell Poisoning Model' it is supposed that there is a sharp boundary between the completely fouled and fresh catalyst (at a position which changes with time), no such sharp distinction of boundaries is assumed for the 'Modified Homogeneous Poisoning Model'. The intraparticle concentration equations for case 1, (catalyst particle poisoned only for the reaction $A \longrightarrow B$) and case 2 (catalyst particle poisoned for both reaction $A \longrightarrow B$ and reaction $B \longrightarrow F$), are derived in the following pages. In dealing with the 'Shell Poisoning Model', a "pseudo steady" state treatment for the movement of the poison front is assumed.

2. Intraparticle concentration equations ('Shell Poisoning Model')

a. Case 1*: Poisoning of catalyst for the reaction

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*Treatment for case 1 follows that of Sada and Wen (37).

$A \longrightarrow B$ only:

i. The following set of mass balance equations can be written for the poisoned region of the catalyst pellet:

$$\nabla(D_P \nabla C_P) = 0 \qquad (51)$$

$$\nabla(D_A \nabla C_A) = 0 \qquad (52)$$

$$\nabla(D_B \nabla C_B) = \rho k_B C_B \qquad (53)$$

ii. The set of equations that describe the intraparticle conentration of the various species in the unpoisoned (or fresh) region of the catalyst pellet are,

$$C_P = 0 \qquad (54)$$

$$\nabla(\acute{D}_A \nabla \acute{C}_A) = \rho k_A \acute{C}_A \qquad (55)$$

$$\nabla(\acute{D}_B \nabla \acute{C}_B) = \rho k_B \acute{C}_B - \rho k_A \acute{C}_A \qquad (56)$$

b. Case 2: Poisoning of catalyst for both reaction $A \longrightarrow B$ and reaction $B \longrightarrow F$

Equations (57,58,59) describe the mass balance of P, A and B respectively, in the poisoned shell of the catalyst pellet.

$$\nabla(D_P \nabla C_P) = 0 \qquad (57)$$

$$\nabla(D_A \nabla C_A) = 0 \qquad (58)$$

$$\nabla(D_B \nabla C_B) = 0 \qquad (59)$$

Similar equations for the non-poisoned core are,

$$C_P = 0 \tag{60}$$

$$\nabla(\acute{D}_A \nabla \acute{C}_A) = \rho k_A \acute{C}_A \tag{61}$$

$$\nabla(\acute{D}_B \nabla \acute{C}_B) = \rho k_B \acute{C}_B - \rho k_A \acute{C}_A \tag{62}$$

3. Initial and boundary conditions for the 'Shell Poisoning Model':

Equations (51-62) show the concentration of the various reacting species in the pellet. Since the poisoning process is assumed to proceed from the outer surface towards the inner region with a clear boundary between the poisoned and the unpoisoned regions of the catalyst, it is reasonable to equate the concentration of 'P' to zero at the boundary separating the fouled and the fresh parts of the catalyst pellet. The 'Shell Poisoning Model' also postulates that the poison front will move towards the centre of the pellet with the passage of time. Thus, if at a given instance of time 't', the position of the poison front is r_P, the concentration of 'P' at the poison front is given by equation (63)

$$C_P = 0 \qquad r = r_P(t) \qquad (63).$$

It is also apparent that since no poison is present in the unspoiled core, the rate at which the poison diffuses into the fresh core equals the rate at which the active sites are lost. Thus,

$$D_P \nabla C_P = -\rho q_0 \frac{dr_P}{dt}, \quad r = r_P, \qquad (64)$$

also, $$r_P = r_0 ; \qquad t = 0 \qquad (65).$$

If the resistance to diffusion in the gas phase is assumed to be negligible, then,

$$C_P = \overset{*}{C}_P \; ; \qquad r = r_0 \qquad (66)$$

Boundary conditions for the concentration profiles of 'A' and 'B' inside the pellet are obvious. Equations (67-73) are the mathematical statements for these conditions. Thus,

$$C_A = \acute{C}_A \; ; \qquad r = r_P \qquad (67)$$

$$\nabla C_A = \nabla \acute{C}_A \; ; \qquad r = r_P \qquad (68)$$

$$\nabla \acute{C}_A = 0 \; ; \qquad r = 0$$

$$\text{or } \acute{C}_A = \text{finite}; \; r = 0$$

and for negligible diffusion resistence in the gas phase,

$$C_A = \overset{*}{C}_A \qquad r = r_0 \qquad (69).$$

Similarly,

$$C_B = \acute{C}_B \qquad r = r_P \qquad (70),$$

$$\nabla C_B = \nabla \acute{C}_B \qquad r = r_P \qquad (71),$$

and

$$\nabla \acute{C}_B = 0 \qquad r = 0 \qquad (72).$$

$$\text{or } \acute{C}_B = \text{finite}; \; r = 0$$

The concentration of 'B' in the gas phase outside the catalyst pellet was assumed to be zero for the 'M.H.P. Model'. The same assumption is made here. Thus,

$$C_B = 0 \qquad r = r_0 \qquad (73).$$

As pointed out earlier (p.22), under certain conditions the poisoning of the catalyst does not alter its physical characteristics. Thus,

$$\acute{D}_1 = D_1 = \text{constant} \qquad (74).$$

4. Non-dimensionalised intraparticle concentration equations. ('Shell Poisoning Model')

Assuming "pseudo steady" state treatment, the intraparticle concentration equations (51-73) can be non-dimensionalised to yield the following equations:

a. Case 1: (catalyst is poisoned for the reaction A ⟶ B)

i. Equations for the poisoned region:

Poison P

$$\frac{d^2\phi_P}{d\xi^2} + \frac{2}{\xi}\frac{d\phi_P}{d\xi} = 0 \qquad 1 \geq \xi_P \geq \xi \qquad (75)$$

$$\phi_P = 1 \;; \qquad \xi = 1 \qquad (76)$$

$$\phi_D = 0 \qquad \xi = \xi_P \qquad (77)$$

$$\frac{d\phi_P}{d\xi_P} = \frac{d\xi_P}{d\theta} \qquad \xi = \xi_P \qquad (78)$$

Reactant A

$$\frac{d^2\phi_A}{d\xi^2} + \frac{2}{\xi}\frac{d\phi_A}{d\xi} = 0 \qquad (79)$$

$$\phi_A = 1 \qquad \xi = 1 \qquad (80)$$

$$\phi_A = \phi_A' \qquad \xi = \xi_P \qquad (81)$$

$$\frac{d\phi_A}{d\xi} = \frac{d\phi_A'}{d\xi} \qquad \xi = \xi_P \tag{82}$$

Intermendiate B

$$\frac{d^2\phi_B}{d\xi^2} + \frac{2}{\xi}\frac{d\phi_B}{d\xi} = h_B^2\phi_B \tag{83}$$

$$\phi_B = 0 \qquad \xi = 1 \tag{84}$$

$$\phi_B = \phi_B' \qquad \xi = \xi_P \tag{85}$$

$$d\phi_B/d\xi = d\phi_B'/d\xi \qquad \xi = \xi_P \tag{86}$$

ii. Equations for the non-poisoned core:

Poison P

$$\phi_P = 0 \qquad \xi_P \geq \xi \geq 0 \tag{87}$$

$$\frac{d\phi_P}{d\xi_P} = \frac{d\xi_P}{d\theta} \qquad \xi = \xi_P \tag{78}$$

Reactant A

$$\frac{d^2\phi_A'}{d\xi^2} + \frac{2}{\xi}\frac{d\phi_A'}{d\xi} = h_A^2\phi_A' \tag{88}$$

$$\phi_A' = \phi_A \quad ; \qquad \xi = \xi_P \tag{81}$$

$$\frac{d\phi_A'}{d\xi} = \frac{d\phi_A}{d\xi} \quad ; \qquad \xi = \xi_P \tag{92}$$

$$\phi'_A = \text{finite} \quad ; \quad \xi = 0$$

and

$$\frac{d\phi'_A}{d\xi} = 0 \quad ; \quad \xi = 0 \qquad (89)$$

Intermediate B

$$\frac{d^2\phi'_B}{d\xi^2} + \frac{2}{\xi}\frac{d\phi'_B}{d\xi} = h_B^2\,\phi'_B - h_A^2\,\phi'_A \qquad (90)$$

$$\phi'_B = \phi_B \quad ; \quad \xi = \xi_P \qquad (85)$$

$$\frac{d\phi'_B}{d\xi} = \frac{d\phi_B}{d\xi} \quad ; \quad \xi = \xi_P \qquad (86)$$

$$\phi'_B = \text{finite} \quad ; \quad \xi = 0 \qquad (95)$$

and

$$\frac{d\phi'_B}{d\xi} = 0 \quad ; \quad \xi = 0 \qquad (91)$$

b. Case 2: (catalyst is poisoned for reaction A ⟶ B, as well as for reaction B ⟶ F).

With the exception of equation (83), equations (75-91) of subsection (4a) describe the non-dimensional intraparticle concentration of the species P,A, and B, for this case also. Equation (83) is replaced by

$$\frac{d^2\phi_B}{d\xi^2} + \frac{2}{\xi}\frac{d\phi_B}{d\xi} = 0 \qquad (83a).$$

5. Selectivity S_{BFs}

In the context of the 'Shell Model' for the poisoning of the catalyst pellet, instantaneous selevtivity, S_{BFs}, at a given instance of time 't', is defined as the ratio of the surface flux of the desired product 'B', to the surface flux of the undesired product 'F'. The given instance of time 't', fixes the position of the poison front in the spherical pellet. Thus, 'Shell Model' selectivity can be calculated at various positions (ξ_P) of the poison front, instead of various instances of time 't'. Simultaneous solution of equations (75-78) and equation (87), can yield an expression relating θ to ξ_P, and thus fix the position of the poison front in time. As in the case of the 'M.H.P. Model, the 'Shell Poisoning Model' instantaneous selectivity, S_{BFs}, is given as

$$S_{BFs} = -\left[\frac{1}{1 + \nu \dfrac{\Delta\phi_A}{\Delta\phi_B}}\right] \qquad \text{for} \quad \xi = \xi_P \qquad (50).$$

CHAPTER IV

SOLUTIONS OF 'MODIFIED HOMOGENEOUS POISONING MODEL' AND 'SHELL POISONING MODEL' EQUATIONS

For the sake of mathematical convenience ν was assumed to be unity in the treatment of both the models.

A. Numerical calculations for the 'M.H.P. Model' selectivity S_{BFh}

1. Selectivity calculations for Case 1: (catalyst poisoned for reaction $A \longrightarrow B$ only).

In order to evaluate the r.h.s of equation (50), non-dimensional equations (29-47) have to be solved simultaneously. It is not possible to obtain analytical solutions describing the intraparticle concentration of P, A and B as functions of time and position. Numerical finite difference techniques however, are available, and were used for computing the terms of the r.h.s of equation (50) in order to calculate S_{BFh}. The procedure used is outlined below.

Procedure:

i. Solution of poison equations:

The poison equation (30) is simulated first. In the finite difference form it can be written as,

$$\frac{\psi_{m,n+1} - \psi_{m,n}}{\Delta\theta} = h_P^2 (1 - \psi_{m,n}) \phi_{p(m,n)}$$

or,

$$\psi_{m,n+1} = \left[1 - \Delta\theta h_P^2 \phi_{P(m,n)}\right] \psi_{m,n} + \Delta\theta h_P^2 \phi_{P(m,n)},$$

$$m = 1,2,\ldots M$$

$$n = 1,2,\ldots N \qquad (93),$$

where, $\Delta\theta$ is an increment along the non-dimensional time axis. The θ axis can be divided into a number of subdivisions, $\big((N-1)$ in this instance$\big)$, with $\theta \approx 0$ position being labeled as 1. Similarly the ξ axis can be divided into (M-1) subdivisions. In this instance the position $\xi = 0$ was labeled as 1 and $\xi = 1$ as M. In order to initiate the equation on the computer, values of $\phi_{P(m,1)}$, $\psi_{m,1}$ and $\phi_{P(M,n)}$ are needed. These values can be found from equations (35), (31) and (32), respectively. For example, except for m = 1, equation (35) leads to

$$\phi_{P(m,1)} = \frac{\text{Sinh } h_P (m-1) \Delta\xi}{(m-1)\Delta\xi \text{ Sinh} h_P} \qquad m = 2,3,\ldots M \qquad (94).$$

Equation (35) as stated on page (25) fails at m = 1, since at $\xi = 0$ it gives a value of ϕ_P of the form $\frac{0}{0}$.

However, with the help of L'Hopital's rule, equation (35) yields

$$\phi_{P(1,1)} = \frac{h_P}{\text{Sinh} h_P} \qquad (95).$$

Equation (31) leads to

$$\psi_{m,1} = 0 \tag{96}$$

and equation (32) becomes

$$\phi_{P(M,n)} = 1 \tag{97}.$$

The next equation to be simulated is the poison equation (29). In the finite difference form equation (29) becomes

$$\frac{\phi_{P(m-1,n)} - 2\phi_{P(m,n)} + \phi_{P(m+1,n)}}{\Delta\xi^{2}} + 2\left[\frac{\left[\phi_{P(m+1,n)} - \phi_{P(m,n)}\right]}{(m-1)\,\Delta\xi^{2}}\right] = h_P^{2}\left[1-\psi_{m,n}\right]\phi_{P(m,n)} \tag{98a}$$

or

$$+\,(-1)\left[\frac{m-1}{m+1}\right]\phi_{P(m-1,n)} +$$

$$\left(\Delta\xi^{2}\,h_P^{2}\left[\frac{m-1}{m+1}\right]\left[1-\psi_{m,n}\right]+\frac{2m}{m+1}\right)\phi_{P(m,n)}+(-1)\,\phi_{P(m+1,n)} = 0,$$

$$m = 2,\ldots M-2$$

$$n = 2,\ldots N \tag{98b}.$$

Where $\Delta\xi$ is the increment along the ξ axis. As $\xi \longrightarrow 0$, the second term on the ℓ.h.s of the equation assumes the form 2 (0/0). This is also reflected in the second term of the ℓ. h.s of equation (98a) for m = 1, if

$$2\,\frac{\left[\phi_{P(m+1,n)} - \phi_{P(m,n)}\right]}{(m-1)\,\Delta\xi^{2}}$$ is expressed as,

$$\frac{2}{\Delta\xi}\left[\frac{\phi_{P(m+1,n)}-\phi_{P(m,n)}}{\Delta\xi}\right]\Big/(m-1) .$$

The L'Hopital rule can again be used to overcome this difficulty. By this rule

$$\frac{2}{\xi}\left.\frac{\delta\phi_P}{\delta\xi}\right|_{\xi=0} = 2\left.\frac{\delta^2\phi_P}{\delta\xi^2}\right|_{\xi=0}. \qquad (99).$$

With this modification, equation (29) can be written as,

$$3\,\frac{\delta^2\phi_P}{\delta\xi^2} = h_P^2\,(1-\psi)\phi_P \quad ; \quad \xi = 0 \qquad (100)$$

and can be simulated as,

$$3\left[\frac{\phi_{P(2,n)}-2\phi_{P(1,n)}+\phi_{P(-2,n)}}{\Delta\xi^2}\right] = h_P^2\left(1-\psi_{1,n}\right)\ \phi_{P(1,n)} \qquad (101).$$

Equation (101) can be further simplified by taking into account the spherical symmetry of the concentration profiles. Thus,

$$\phi_{P(2,n)} = \phi_{P(-2,n)} \qquad (102).$$

Equation (102) when substituted into equation (101) yields

$$\left(\frac{6+\Delta\xi^2\,h_P^2\left(1-\psi_{1,n}\right)}{6}\right)\phi_{P(1,n)} - \phi_{P(2,n)} = 0 \qquad n = 2,3,\ldots N \qquad (103).$$

Other equations needed for starting the solution of equation (98b) are

$$\phi_{P(1,1)} = \frac{h_P}{\mathrm{Sinh}\, h_P} \qquad (95)$$

$$\phi_{P(m,1)} = \frac{\mathrm{Sinh}(m-1)\Delta\xi h_P}{\Delta\xi(m-1)\mathrm{Sinh}\, h_P} \qquad m = 2,3\ldots M \qquad (94)$$

and $\phi_{P(M,n)} = 1$ $\qquad n = 1,2,\ldots N \qquad (97).$

Equations (97), (98b) and (103) constitute a triangular set of simultaneous equations of the form,

$$S_{B1P}\,\phi_{P(1,n)} + S_{C1P}\,\phi_{P(2,n)} = S_{D1P}$$

$$S_{A2P}\,\phi_{P(1,n)} + S_{B2P}\,\phi_{P(2,n)} + S_{C2P}\,\phi_{P(3,n)} = S_{D2P}$$

$$S_{A3P}\,\phi_{P(2,n)} + S_{B3P(3,n)} + S_{C3P}\,\phi_{P(4,n)} = S_{D3P}$$

$$\text{———} \qquad \text{———} \qquad \text{———}$$

$$S_{A(M-2)P}\,\phi_{P(M-3,n)} + S_{B(M-2)P}\,\phi_{P(M-2,n)}$$

$$+S_{C(M-2)P}\,\phi_{P(M-1,n)} = S_{D(M-2)P}$$

$$S_{A(M-1)P}\,\phi_{P(M-2,n)} \quad S_{B(M-1)P}\,\phi_{P(M-1,n)} = S_{D(M-1)P}$$

$$n = 2,3,\ldots N \qquad (104)$$

where,

$$S_{AiP} = -\frac{(i-1)}{(i+1)} \qquad i = 2,3,\ldots M-1 \qquad (105)$$

$$S_{B1P} = \left[\frac{6 + \Delta\xi^2\, h_P^2\left[1 - \psi_{1,n}\right]}{6}\right] \qquad n = 2,3,\ldots N \qquad (106)$$

$$S_{BiP} = \left[\Delta^2\xi \; h_P^2 \frac{(i-1)}{(i+1)} \left[1- \psi_{i,n} \right] + \frac{2i}{i+1} \right] \qquad \begin{array}{l} i = 2,3,\ldots M-1 \\ n = 2,3,\ldots N \end{array} \qquad (107)$$

$$S_{CiP} = -1 \qquad i = 1,2,3,\ldots M-2 \qquad (108)$$

and

$$S_{DiP} = 0 \qquad i = 1,2,3,\ldots M-2 \qquad (109)$$

$$S_{D(M-1)P} = 1 \qquad (110).$$

The intraparticle concentration profile of the species 'P' for n = 1 is given by equations (94,95 and 97). Solution of equations (104) yields values of $\phi_{P(i,n)}$,

$$i = 1,2,\ldots M-1$$
$$n = 2,3,\ldots N .$$

Such a solution can be obtained by the use of the Gaussian elimination process (for details see Part 1, Appendix D). Douglas (15) has shown that the round-off error for this type of Gaussian elimination is less than the discretisation error involved in writing the difference equations for differential equations. Thus, equations (93-97) and (104) can be solved simultaneously to get ψ as a function of ξ and θ.

ii. Solution of equations for the reactant A:

By using a treatment similar to the one discussed in the preceding subsection, p.d.e's (36-41) can also be written in the finite difference form. The difference equations for the reactant A are summarised below:

$$\phi_{A(1,1)} = h_A / \mathrm{Sinh}\, h_A \qquad (111)$$

$$\phi_{A(m,1)} = \frac{\mathrm{Sinh}(m-1)\Delta\xi\, h_A}{(m-1)\Delta\xi\, \mathrm{Sinh}\, h_A} \; ; \qquad m = 2,3,\ldots M \qquad (112)$$

$$\phi_{A(2,n)} = \left(\frac{6 + \Delta\xi^2\, h_A^2 \left[1 - \psi_{1,n}\right]}{6}\right) \phi_{A(1,n)} \; ; \quad n = 2,3,\ldots N \quad (113)$$

$$\phi_{A(m+1,n)} = \left[\Delta\xi^2 \left(h_A^2 \left(\frac{m-1}{m+1}\right)\left(1 - \psi_{m,n}\right)\right) + \frac{2m}{m+1}\right] \phi_{A(m,n)} + (-1)\frac{(m-1)}{(m+1)} \phi_{A(m-1,n)}$$

$$m = 2,3,\ldots M-2$$

$$n = 2,3,\ldots N \quad (114)$$

and

$$\phi_{A(M,n)} = 1 \qquad n = 1,2,3,\ldots N \quad (115).$$

Equations (113-115) constitute another set of triangular simultaneous algebraic equations. These can be written as

$$S_{B1A}\,\phi_{A(1,n)} + S_{C1A}\,\phi_{A(2,n)} = S_{D1A}$$

$$S_{A2A}\,\phi_{A(1,n)} + S_{B2A}\,\phi_{A(2,n)} + S_{C2A}\,\phi_{A(3,n)} = S_{D2A}$$

$$S_{A3A}\,\phi_{A(2,n)} + S_{B3A}\,\phi_{A(3,n)} + S_{C3A}\,\phi_{A(4,n)} = S_{D3A}$$

— — —

$$S_{A(M-2)A}\,\phi_{A(M-3,n)} + S_{B(M-2)A}\,\phi_{A(M-2,n)} + S_{C(M-2)A}\,\phi_{A(M-1,n)} = S_{D(M-2)A}$$

$$S_{A(M-1)A}\,\phi_{A(M-2,n)} + S_{B(M-1)A}\,\phi_{A(M-1,n)} = S_{D(M-1)A},$$

$$n = 2,3,\ldots N \quad (116).$$

where,

$$S_{AiA} = -\frac{(i-1)}{(i+1)} \qquad i = 2,3,\ldots M-1 \quad (117)$$

$$S_{B1A} = \frac{6+\Delta\xi^2\, h_A^2 \left(1-\psi_{1,n}\right)}{6} \qquad n = 2,3,\ldots N \quad (118)$$

$$S_{B1A} = \left(\Delta\xi^2\, h_A^2 \,\frac{(i-1)}{(i+1)}\left(1-\psi_{i,n}\right)+\frac{2i}{i+1}\right), \qquad i = 2,3,\ldots M-1$$

$$n = 2,3,\ldots N \quad (119)$$

$$S_{CiA} = -1\ ; \qquad i = 1,2,\ldots M-2 \quad (120)$$

$$S_{DiA} = 0\ ; \qquad i = 1,2,\ldots M-2 \quad (121)$$

$$S_{D(M-1)A} = 1 \quad (122)$$

Equations (111), (112) and (115) describe the concentration profile of ϕ_A in the particle, for n = 1. If $\psi_{m,n}$ is known, $\phi_{A(i,n)}$; $i = 1,2,\ldots M-1$, $n = 2,3,\ldots N$ can be easily found. From a knowledge of $\phi_{A(i,n)}$; $\nabla\phi_A\Big|_{\xi=1}$ at any value of θ can be easily computed. Equation (123) gives the required expression

$$\nabla\phi_A\Bigg|_{\substack{\theta=\theta\\ \xi=1}} \equiv \frac{\delta\phi_A}{\delta\xi}\Bigg|_{\substack{\theta=\theta\\ \xi=1}} = \frac{1-\phi_{A(M-1,n)}}{\Delta\xi}$$

$$n = 1,2,\ldots N \quad (123)$$

iii. Solution of equations for the intermediate B:

Finite difference equations corresponding to equations (111-123) for A, can also be written for B.

Solutions for these finite difference equations are also found similarly. The difference equations for B are listed below:

$$\phi_{B(1,1)} = \left(\frac{h_A^2}{h_A^2 - h_B^2}\right)\left[\frac{h_B}{\text{Sinh}\ h_B} - \frac{h_A}{\text{Sinh}\ h_A}\right] \qquad (124)$$

$$\phi_{B(m,1)} = \left(\frac{h_A^2}{h_A^2 - h_B^2}\right)\left[\frac{\text{Sinh}\ h_B(m-1)\Delta\xi}{(m-1)\Delta\xi\ \text{Sinh}\ h_B} - \frac{\text{Sinh}\ h_A(m-1)\Delta\xi}{(m-1)\Delta\xi\ \text{Sinh}\ h_A}\right]$$

$$m = 2,3,\ldots M \qquad (125)$$

$$\phi_{B(2,n)} = \left(\frac{6 + \Delta\xi^2 h_B^2}{6}\right)\phi_{B(1,n)} + (-1)\left(\frac{\Delta\xi^2 h_A^2\left[1-\psi_{1,n}\right]}{6}\right)$$

$$n = 2,3,\ldots N \qquad (126a)$$

$$\phi_{B(m+1,n)} = \left[\Delta\xi^2 h_B^2\ \frac{(m-1)}{(m+1)} + \frac{2m}{m+1}\right]\phi_{B(m,n)} + (-1)\frac{(m-1)}{(m+1)}\phi_{B(m-1,n)}$$
$$+ (-1)\left[\Delta\xi^2 h_A^2\ \frac{(m-1)}{(m+1)}\left(1-\psi_{m,n}\right)\right]\phi_{A(m,n)}\ ,$$

$$m = 2,3,\ldots M-2$$

$$n = 2,3,\ldots N \qquad (127a)$$

$$\phi_{B(M,n)} = 0$$

$$n = 1,2,\ldots N \qquad (128).$$

The corresponding set of triangular algebraic equations resulting from equations (126a-128) are as follows:

$$S_{B1B}\,\phi_{B(1,n)}+S_{C1B}\,\phi_{B(2,n)} = S_{D1B}$$

$$S_{A2B}\,\phi_{B(1,n)}+S_{B2B}\,\phi_{B(2,n)}+S_{C2B}\,\phi_{B(3,n)} = S_{D2B}$$

$$S_{A3B}\,\phi_{B(2,n)}+S_{B3B}\,\phi_{B(3,n)}+S_{C3B}\,\phi_{B(4,n)} = S_{D3B}$$

$$S_{A(M-2)B}\,\phi_{B(\overline{M-3},n)}+S_{B(M-2)B}\,\phi_{B(\overline{M-2})}+S_{C(M-2)B}\,\phi_{B(\overline{M-1},n)}= S_{D(M-2)B}$$

$$S_{A(M-1)B}\,\phi_{B(M-2,n)}+S_{B(M-1)B}\,\phi_{B(M-1,n)} = S_{D(M-1)B}$$

$n = 2,3,\ldots N$ (129)

where,

$$S_{AiB} = \frac{i-1}{i+1} \qquad i = 2,3,\ldots M-1 \qquad (130)$$

$$S_{B1B} = \left(\frac{6 + \Delta\xi^2\, h_B^2}{6}\right) \qquad (131a)$$

$$S_{BiB} = \left(\Delta\xi^2\, h_B^2\, \frac{(i-1)}{i+1} + \frac{2i}{i+1}\right) \qquad i = 2,3,\ldots\ M-1 \qquad (132a)$$

$$S_{CiB} = -1 \qquad i = 1,2,\ldots\ M-2 \qquad (133)$$

$$S_{D1B} = \left(\frac{\Delta\xi^2\, h_A^2 \left[1-\psi_{i,n}\right]}{6}\right)\phi_{A(1,n)} \qquad (134)$$

$$n = 2,3,\ldots\ N \qquad (135)$$

$$S_{DiB} = \Delta\xi^2\, h_A^2 \left(1-\psi_{i,n}\right)\frac{(i-1)}{(i+1)}\,\phi_{A(i.n)} \qquad i = 2,3,\ldots\ M-1 \qquad (136)$$

$n = 2,3,\ldots\ N$

The intraparticle concentration of intermediate B at n=1 is given by equations (124), (125) and (128). Once $\psi_{i,n}$ and $\phi_{A(i,n)}$ are known, equations (129) can be solved to obtain

$$\phi_{B(i,n)}, \qquad i = 1,2,\ldots \quad M-1. \qquad n = 2,3,\ldots \quad N$$

Having found $\phi_{B(i,n)}$, it is easy to compute

$\nabla\phi_B\Big|_{\substack{\theta=\theta\\ \xi=1}}$. Equation (137) can be used for this purpose.

$$\nabla\phi_B\Big|_{\substack{\theta=\theta\\ \xi=1}} \equiv \frac{\delta\phi_B}{\delta\xi}\Big|_{\substack{\theta=\theta\\ \xi=1}} = -\frac{\phi_{B(M-1,n)}}{\Delta\xi} \quad n = 2,3,\ldots \quad N \tag{137}$$

It is obvious that the knowledge of the ℓ.h. sides of equations (123) and (137), is all that is required for computing S_{BFh} from equation (50).

2. Selectivity Calculations for Case 2. (Catalyst is poisoned for both reaction A $\longrightarrow$ B and reaction B $\longrightarrow$ F):-

Equations (93-137) of the previous section, with the exception of equations (126a),(127a),(131a), and (132a) describe equally well, the intraparticle concentration of various species when the catalyst pellet has been poisoned for both the reaction A $\longrightarrow$ B and the reaction B $\longrightarrow$ F. Equations (126a),(127a),(131a) and (132a) are replaced respectively, by equations (126b), (127b), (131b) and (132b). The new equations are given below:

$$\phi_{B(2,n)} = \left(\frac{6+\Delta^2\xi\, h_B^2\left(1-\psi_{1,n}\right)}{6}\right)\phi_{B(1,n)} - \left(\frac{\Delta^2\xi\, h_A^2\left(1-\psi_{1,n}\right)}{6}\right)\phi_{A(1,n)}$$

$$n = 2,3,\ldots \qquad N \quad (126b)$$

$$\phi_{B(m+1,n)} = \left(\Delta^2\xi\, h_B^2\left(1-\psi_{m,n}\right)\left(\frac{m-1}{m+1}\right)+\frac{2m}{m+1}\right)\cdot\phi_{B(m,n)} - \frac{(m-1)}{(m+1)}\phi_{B(m-1,n)}$$

$$-\left(\Delta^2\xi\, h_A^2\left(\frac{m-1}{m+1}\right)\left(1-\psi_{m,n}\right)\right)\phi_{A(m,n)}$$

$$m = 2,3,\ldots \qquad M-2$$

$$n = 2,3,\ldots \qquad N \quad (127b)$$

$$S_{B1B} = \left(\frac{6+\Delta^2\xi\, h_B^2\left(1-\psi_{1,n}\right)}{6}\right), \qquad n = 2,3,\ldots \qquad N \quad (131b)$$

$$S_{BiB} = \left(\Delta^2\xi\, h_B^2\left(1-\psi_{i,n}\right)\left(\frac{i-1}{i+1}\right)+\frac{2i}{i+1}\right) ;$$

$$i = 2,3,\ldots \qquad M-1$$

$$n = 2,3,\ldots \qquad N \quad (132b).$$

B. Analytical Expressions for the Shell Poisoning Model Selectivity S_{BFs}

1. Intraparticle Concentration Profiles of P, A and B for Case 1* (Catalyst is poisoned for the reaction A ⟶ B only) :-

a. Concentration Profile for Species P

i. Poisoned Region:

Equations (75-77) can be solved simultaneously to get the 'pseudo-steady state' concentration profile of 'P' in the poisoned shell of the pellet. Equation (138) gives such a profile

$$\phi_P = \frac{\xi - \xi_P}{\xi(1-\xi_P)} \qquad \xi \leq \xi_P \leq 1 \qquad (138)$$

ii. Non-Poisoned Region:

$$\phi'_P = 0 \qquad 0 \leq \xi \leq \xi_P \qquad (87)$$

iii. Location of the Poison Front.

The simultaneous solution of equations (78) and (138) yields an expression relating, θ — the dimensionless time, and ξ_P — the position of the poison front, inside the catalyst pellet.

Equation (139) shows this relationship

$$\theta = \frac{1}{6}\left(\left(1-\xi_P\right)^2\left(1+2\xi_P\right)\right) \qquad (139).$$

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*This treatment follows that of Sada and Wen (37).

Concentration Profile for Reactant A:-

A simultaneous solution of equations (79-82) and (88, 89 and 92) gives the concentration profiles for the reactant A.

i . The poisoned region profile is given as,

$$\phi_A = \left[\frac{h_A\left(\xi - \xi_P\right) + \tanh h_A \xi_P}{\xi\left(h_A\left(1-\xi_P\right) + \tanh h_A \xi_P\right)}\right] \qquad \xi_P \leq \xi \leq 1 \qquad (140)$$

ii . The non-poisoned region concentration is given by equation (141)

$$\phi'_A = \frac{\text{Sinh } h_A \xi}{\xi \text{Cosh } h_A \xi_P \left(h_A\left(1-\xi_P\right) + \tanh h_A \xi_P\right)} ; \qquad 0 \leq \xi \leq \xi_P \qquad (141)$$

Concentration Profile for the Intermediate B:-

The intraparticle concentration profile of B for both the poisoned and the non-poisoned regions of the catalyst can be obtained by solving the equations (83-86) and (90, 91, and 95).

. The profile for the poisoned region is given by equation (142).

$$\phi_B = \frac{g_1}{\xi} \frac{\text{Sinh}(1-\xi)h_B}{\text{Sinh } h_B}, \qquad \xi_P \leq \xi \leq 1 \qquad (142)$$

where,

$$g_1 = -\left(\frac{h_A^{\,2}}{\left(h_A^{\,2} - h_B^{\,2}\right)\left(\tanh h_A \xi_P + h_A\left(1-\xi_P\right)\right)\mathrm{Cosh}\, h_A \xi_P}\right) *$$

$$\left(\frac{\left(\mathrm{Sinh}\, h_B - \mathrm{Cosh}\left(h_B - h_B \xi_P\right)\ \mathrm{Sinh}\, h_B \xi_P\right)\ h_B\ \mathrm{Sinh}\, h_A \xi_P}{h_B\ \mathrm{Sinh}(1-\xi_P)h_B}\right) -$$

$$\left(\frac{h_A\ \mathrm{Sinh}(h_B \xi_P)\ \mathrm{Cosh}(h_A \xi_P)\ \mathrm{Sinh}(1-\xi_P)h_B}{h_B\ \mathrm{Sinh}(1-\xi_P)h_B}\right) \qquad (143)$$

ii. Similarly the profile for the non-poisoned region can be written as,

$$\phi_B' = -\left(\frac{h_A^{\,2}}{\left(h_A^{\,2} - h_B^{\,2}\right)\left(\tanh h_A \xi_P + h_A\left(1-\xi_P\right)\right)\mathrm{Cosh}\, h_A \xi_P}\right) *$$

$$\left[\left(\frac{\mathrm{Sinh}\, h_A \xi}{\xi}\right) - g_2\left(\frac{\mathrm{Sinh}\, h_B \xi}{\xi}\right)\right] \qquad (144)$$

where,

$$g_2 = \left(\frac{h_A\ \mathrm{Cosh}\left(h_A \xi_P\right)\mathrm{Sinh}(1-\xi_P)h_B + h_B\ \mathrm{Cosh}(h_B - h_B \xi_P)\mathrm{Sinh}(h_A \xi_P)}{h_B\ \mathrm{Sinh}\, h_B}\right)$$

$$0 \le \xi \le \xi_P \qquad (145).$$

2. Concentration profiles for Case 2: (catalyst poisoned for both the reactions A⟶B and B⟶F).

As far as the concentration profiles of 'P' and 'A' are concerned, equations (138-141) and (87) describe them for case 2, as well. Only the profile of 'B' is different. The concentration profile of 'B', pertinent to this case, is given by the equations listed below:

i. Poisoned region profile:

$$\phi_B = g_3\frac{(1-\xi)}{\xi} \tag{146}$$

where,

$$g_3 = \left[\frac{h_A^2}{\left(h_A^2-h_B^2\right)\left(\mathrm{Sinh}\,h_A\xi_P + h_A(1-\xi_P)\,\mathrm{Cosh}\,h_A\xi_P\right)}\right] * \left[\frac{h_A\mathrm{Cosh}(h_A\xi_P)\;\mathrm{Sinh}\,h_B\xi_P - h_B\mathrm{Cosh}(h_B\xi_P)\,\mathrm{Sinh}\left(h_A\xi_P\right)}{\mathrm{Sinh}\,h_B\xi_P + (1-\xi_P)h_B\mathrm{Cosh}\,h_B\xi_P}\right]$$

$$0\le\xi\le\xi_P \tag{147}$$

ii. Non-poisoned region profile:

$$\phi_B' = -\left[\frac{h_A^2}{\left(h_A^2-h_B^2\right)\left(\mathrm{Sinh}\,h_A\xi_P + (1-\xi_P)h_A\mathrm{Cosh}\left(h_A\xi_P\right)\right)}\right] * \left[\frac{\mathrm{Sinh}\,h_A\xi_P - g_4\,\mathrm{Sinh}\,h_B\xi}{\xi}\right],$$

$$0\le\xi\le\xi_P \tag{148}$$

where,

$$g_4 = \frac{\text{Sinh } h_A \xi_P + (1-\xi_P) h_A \text{Cosh } h_A \xi_P}{(1-\xi_P) h_B \text{Cosh } h_B \xi_P + \text{Sinh } h_B \xi_P} \qquad (149).$$

3. Selectivity S_{BFs}

a. Selectivity for Case 1:

An expression for the term,

$$\left(\left[d\phi_A / d\xi\right]_{\xi=1} \Big/ \left[d\phi_B / d\xi\right]_{\xi=1}\right)_{\xi=\xi_P},$$

can be easily derived from equations (140) and (142). This expression, when substituted in equation (50),

$$S_{BFs1} = -\frac{1}{1 + \left[\dfrac{\nabla\phi_A}{\nabla\phi_B}\right]_{\xi=\xi_P}^{\xi=1}}$$

$$\equiv -\frac{1}{1 + \left(\left[(d\phi_A / d\xi)_{\xi=1}\right] \Big/ \left[(d\phi_B / d\xi)_{\xi=1}\right]\right)_{\xi=\xi_P}} \qquad (50)$$

yields,

$$S_{BFs1} = \frac{1}{\left[(h_B/h_A) - (h_A/h_B)\right] \beta_1 - 1} \qquad (150)$$

where,

$$\beta_1 \equiv -\frac{\left(\dfrac{\tanh h_A \xi_P}{h_A} - \xi_P\right) \text{Sinh } h_B}{\left(\tanh h_A \xi_P - \dfrac{h_A \tanh h_B \xi_P}{h_B}\right) \text{Cosh } h_B \xi_P} \qquad (151).$$

b. Selectivity for Case 2 .

The corresponding expression for S_{BFs} for the case where the catalyst has been poisoned for both the reaction $A \longrightarrow B$ and the reaction $B \longrightarrow F$ is given as,

$$S_{BFs2} = -\left[\frac{1}{1+\beta_2}\right] \qquad (152),$$

where,

$$\beta_2 = -\left[\frac{h_A \xi_P - \tanh h_A \xi_P}{g_3\left[h_A\left(1-\xi_P\right) + \tanh h_A \xi_P\right]}\right] \qquad (153)$$

and g_3 is the same as defined by the equation (143).

CHAPTER V

RESULTS

TABLE 1.1

Catalyst is poisoned for the reaction A ⟶ B only.

h_A (Thiele Modulus) for A = 2.5

h_B (Thiele Modulus) for B = 1.0

SHELL POISONING MODEL

NO	θ	S_{BF}
1	0.0172	10.132
2	0.0344	8.649
3	0.0516	7.804
4	0.0688	7.230
5	0.0860	6.822
6	0.1032	6.487
7	0.1204	6.217
8	0.1376	5.996
9	0.1548	5.813

TABLE 1.2

Catalyst is poisoned for the reaction $A \longrightarrow B$ only

h_A (Thiele Modulus) for A = 2.5

h_B (Thiele Modulus) for B = 1.0

h_P (Thiele Modulus) for P = 1.0

'M.H.P. MODEL'

NO	θ	S_{BF}
1	0.0172	16.707
2	0.0334	16.671
3	0.0516	16.636
4	0.0688	16.601
5	0.0860	16.567
6	0.1032	16.533
7	0.1204	16.500
8	0.1376	16.467
9	0.1548	16.435

TABLE 1.3

Catalyst is poisoned for the reaction A $\longrightarrow$ B only

h_A (Thiele Modulus) for A = 2.5

h_B (Thiele Modulus) for B = 1.0

h_P (Thiele Modulus) for P = 4.0

'M.H.P. MODEL'

NO	θ	S_{BF}
1	0.0172	15.942
2	0.0344	15.213
3	0.0516	14.553
4	0.0688	13.957
5	0.0860	13.423
6	0.1032	12.946
7	0.1204	12.524
8	0.1376	12.153
9	0.1548	11.829

TABLE 1.4

Catalyst is poisoned for the reaction A $\longrightarrow$ B only

h_A (Thiele Modulus) for A = 2.5

h_B (Thiele Modulus) for B = 1.0

h_P (Thiele Modulus) for P = 10.0

'M.H.P. MODEL'

NO	θ	S_{BF}
1	0.0172	13.173
2	0.0344	10.960
3	0.0516	9.580
4	0.0688	8.668
5	0.0860	8.028
6	0.1032	7.555
7	0.1204	7.196
8	0.1376	6.924
9	0.1548	6.727

TABLE 1.5

Catalyst is poisoned for reaction A$\longrightarrow$B only

h_A(Thiele Modulus) for A = 2.5

h_B(Thiele Modulus) for B = 1.0

h_P(Thiele Modulus) for P = 50.0

'M.H.P. MODEL'

NO	θ	S_{BF}
1	0.0172	10.404
2	0.0344	8.861
3	0.0516	7.991
4	0.0688	7.405
5	0.0860	6.974
6	0.1032	6.643
7	0.1204	6.380
8	0.1376	6.169
9	9.1548	5.968

TABLE 1.6

Catalyst is poisoned for the reaction A $\longrightarrow$ B only

h_A (Thiele Modulus) for A = 5.0

h_B (Thiele Modulus) for B = 1.0

SHELL POISONING MODEL

NO	θ	S_{BF}
1	0.0172	11.012
2	0.0344	9.085
3	0.0516	8.049
4	0.0688	7.371
5	0.0860	6.905
6	0.1032	6.531
7	0.1204	6.237
8	0.1376	6.003
9	0.1548	5.814

TABLE 1.7

Catalyst is poisoned for reaction A ⟶ B only

h_A (Thiele Modulus) for A = 5.0

h_B (Thiele Modulus) for B = 1.0

h_P (Thiele Modulus) for P = 1.00

'M.H.P. MODEL'

NO	θ	S_{BF}
1	0.0172	21.256
2	0.0344	21.170
3	0.0516	21.084
4	0.0688	21.000
5	0.0860	20.915
6	0.1032	20.831
7	0.1204	20.749
8	0.1376	20.667
9	0.1548	20.586

TABLE 1.8

Catalyst is poisoned for the reaction A$\longrightarrow$B only

h_A (Thiele Modulus) for A = 5.0

h_B (Thiele Modulus) for B = 1.0

h_P (Thiele Modulus) for P = 4.0

'M.H.P. MODEL'

NO	θ	S_{BF}
1	0.0172	20.007
2	0.0344	18.786
3	0.0516	17.675
4	0.0688	16.669
5	0.0860	15.763
6	0.1032	14.952
7	0.1204	14.230
8	0.1376	13.592
9	0.1548	13.033

TABLE 1.9

Catalyst is poisoned for the reaction A ⟶ B only

h_A (Thiele Modulus) for A = 5.0

h_B (Thiele Modulus) for B = 1.0

h_P (Thiele Modulus) for P = 10.0

'M.H.P. MODEL'

NO	θ	S_{BF}
1	0.0172	15.852
2	0.0344	12.511
3	0.0516	10.509
4	0.0688	9.2440
5	0.0860	8.3894
6	0.1032	7.7798
7	0.1204	7.3301
8	0.1376	6.9963
9	0.1548	6.7594

TABLE 1.10

Catalyst is poisoned for the reaction $A \longrightarrow B$ only

h_A (Thiele Modulus) for A = 5.0

h_B (Thiele Modulus) for B = 1.0

h_P (Thiele Modulus) for P = 50.0

'M.H.P. MODEL'

NO	θ	S_{BF}
1	0.0172	11.353
2	0.0344	9.326
3	0.0516	8.250
4	0.0688	7.552
5	0.0860	7.056
6	0.1032	6.685
7	0.1204	6.398
8	0.1376	6.175
9	0.1548	5.965

TABLE 1.11

Catalsyt is poisoned for the reaction A$\longrightarrow$B only

h_A (Thiele Modulus) for A = 10.0

h_B (Thiele Modulus) for B = 1.0

SHELL POISONING MODEL

NO	θ	S_{BF}
1	0.0172	12.532
2	0.0344	9.864
3	0.0516	8.515
4	0.0688	7.662
5	0.0860	7.089
6	0.1032	6.638
7	0.1204	6.293
8	0.1376	6.025
9	0.1548	5.818

TABLE 1.12

Catalyst is poisoned for reaction A ⟶ B only

h_A (Thiele Modulus) for A = 10.0

h_B (Thiele Modulus) for B = 1.0

h_P (Thiele Modulus) for P = 1.0

'M.H.P. MODEL'

NO	θ	S_{BF}
1	0.0172	31.208
2	0.0344	31.048
3	0.0516	30.889
4	0.0688	30.731
5	0.0860	30.574
6	0.1032	30.418
7	0.1204	30.262
8	0.1376	30.108
9	0.1548	29.954

TABLE 1.13

Catalyst is poisoned for the reaction A ⟶ B only

h_A (Thiele Modulus) for A = 10.0

h_B (Thiele Modulus) for B = 1.0

h_P (Thiele Modulus) for P = 4.0

'M.H.P. MODEL'

NO	θ	S_{BF}
1	0.0172	29.117
2	0.0334	27.016
3	0.0516	25.069
4	0.0688	23.277
5	0.0860	21.637
6	0.1032	20.143
7	0.1204	18.789
8	0.1376	17.570
9	0.1548	16.477

TABLE 1.14

Catalyst is poisoned for the reaction A ⟶ B only

h_A (Thiele Modulus) for A = 10.0

h_B (Thiele Modulus) for B = 1.0

h_P (Thiele Modulus) for P = 10.0

'M.H.P. MODEL'

NO	θ	S_{BF}
1	0.0172	21.936
2	0.0334	16.078
3	0.0516	12.672
4	0.0688	10.619
5	0.0860	9.293
6	0.1032	8.376
7	0.1204	7.713
8	0.1376	7.223
9	0.1548	6.872

TABLE 1.15

Catalyst is poisoned for the reaction A $\longrightarrow$ B only

h_A (Thiele Modulus) for A = 10.0

h_B (Thiele Modulus) for B = 1.0

h_P (Thiele Modulus) for P = 50.0

'M.H.P. MODEL'

NO	θ	S_{BF}
1	0.0172	13.071
2	0.0334	10.196
3	0.0516	8.764
4	0.0688	7.869
5	0.0860	7.249
6	0.1032	6.796
7	0.1204	6.454
8	0.1376	6.193
9	0.1548	5.954

TABLE 2.1

Catalyst is poisoned for both the reaction A ⟶ B and the reaction B ⟶ F

h_A (Thiele Modulus) for A = 2.5

h_B (Thiele Modulus) for B = 1.0

SHELL POISONING MODEL

NO	θ	S_{BF}
1	0.0172	12.463
2	0.0344	12.679
3	0.0516	13.668
4	0.0688	15.344
5	0.0860	17.796
6	0.1032	21.893
7	0.1204	29.164
8	0.1376	45.118
9	0.1548	106.848

TABLE 2.2

Catalyst is poisoned for both the reaction $A \longrightarrow B$ and the reaction $B \longrightarrow F$

h_A (Thiele Modulus) for A = 2.5

h_B (Thiele Modulus) for B = 1.0

h_P (Thiele Modulus) for P = 1.0

'M.H.P. MODEL'

NO	θ	S_{BF}
1	0.0172	16.965
2	0.0344	17.192
3	0.0516	17.422
4	0.0688	17.657
5	0.0860	17.895
6	0.1032	18.137
7	0.1204	18.384
8	0.1376	18.635
9	0.1548	18.890

TABLE 2.3

Catalyst is poisoned for both the reaction $A \longrightarrow B$ and the $B \longrightarrow F$

h_A (Thiele Modulus) for A = 2.5

h_B (Thiele Modulus) for B = 1.0

h_P (Thiele Modulus) for P = 4.0

'M.H.P. MODEL'

NO	θ	S_{BF}
1	0.0172	17.935
2	0.0344	19.345
3	0.0516	21.024
4	0.0688	23.044
5	0.0860	25.500
6	0.1032	28.513
7	0.1204	32.244
8	0.1376	36.905
9	0.1548	42.781

TABLE 2.4

Catalyst is poisoned for both the reaction A⟶B and the reaction B⟶F

h_A (Thiele Modulus) for A = 2.5

h_B (Thiele Modulus) for B = 1.0

h_P (Thiele Modulus) for P = 10.0

'M.H.P. MODEL'

NO	θ	S_{BF}
1	0.0172	16.062
2	0.0344	16.134
3	0.0516	17.086
4	0.0688	19.008
5	0.0860	22.221
6	0.1032	27.544
7	0.1204	37.005
8	0.1376	56.374
9	0.1548	106.694

TABLE 2.5

Catalyst is poisoned for both the reaction A ⟶ B and the reaction B ⟶ F

h_A (Thiele Modulus) for A = 2.5

h_B (Thiele Modulus) for B = 1.0

h_P (Thiele Modulus) for P = 50.0

'M.H.P. MODEL'

NO	θ	S_{BF}
1	0.0172	12.771
2	0.0344	13.005
3	0.0516	14.074
4	0.0688	15.906
5	0.0860	18.814
6	0.1032	23.644
7	0.1204	32.744
8	0.1376	55.493
9	0.1548	208.206

TABLE 2.6

Catalyst is poisoned for both the reaction A → B and the reaction B → F.

h_A (Thiele Modulus) for A = 5.0

h_B (Thiele Modulus) for B = 1.0

SHELL POISONING MODEL

NO	θ	S_{BF}
1	0.0172	13.796
2	0.0344	13.604
3	0.0516	14.398
4	0.0688	15.952
5	0.0860	18.321
6	0.1032	22.349
7	0.1204	29.563
8	0.1376	45.465
9	0.1548	107.141

TABLE 2.7

Catalyst is poisoned for both the reaction A ⟶ B and the reaction B ⟶ F

h_A (Thiele Modulus) for A = 5.0

h_B (Thiele Modulus) for B = 1.0

h_P (Thiele Modulus) for P = 1.0

'M.H.P. MODEL'

NO	θ	S_{BF}
1	0.0172	21.584
2	0.0344	21.829
3	0.0516	22.077
4	0.0688	22.329
5	0.0860	22.585
6	0.1032	22.845
7	0.1204	23.110
8	0.1376	23.378
9	0.1548	23.651

TABLE 2.8

Catalyst is poisoned for both the reaction A ⟶ B and the reaction B ⟶ F

h_A (Thiele Modulus) for A = 5.0

h_B (Thiele Modulus) for B = 1.0

h_P (Thiele Modulus) for P = 4.0

'M.H.P. MODEL'

NO	θ	S_{BF}
1	0.0172	22.615
2	0.0344	24.091
3	0.0516	25.827
4	0.0688	27.898
5	0.0860	30.398
6	0.1032	33.450
7	0.1204	37.217
8	0.1376	41.912
9	0.1548	47.819

TABLE 2.9

Catalyst is poisoned for both the reaction A ⟶ B and the reaction B ⟶ F

h_A (Thiele Modulus) for A = 5.0

h_B (Thiele Modulus) for B = 1.0

h_P (Thiele Modulus) for P = 10.0

'M.H.P. MODEL'

NO	θ	S_{BF}
1	0.0172	19.723
2	0.0344	18.975
3	0.0516	19.384
4	0.0688	20.970
5	0.0860	23.978
6	0.1032	29.179
7	0.1204	38.573
8	0.1376	57.918
9	0.1548	108.245

TABLE 2.10

Catalyst is poisoned for both the reaction A ⟶ B and the reaction B ⟶ F

h_A (Thiele Modulus) for A = 5.0

h_B (Thiele Modulus) for B = 1.0

h_P (Thiele Modulus) for P = 50.0

'M.H.P. MODEL'

NO	θ	S_{BF}
1	0.0172	14.201
2	0.0344	13.992
3	0.0516	14.849
4	0.0688	16.550
5	0.0860	19.367
6	0.1032	24.130
7	0.1204	33.178
8	0.1376	55.885
9	0.1548	208.497

TABLE 2.11

Catalyst is poisoned for both the reaction A ⟶ B and the reaction B ⟶ F

h_A (Thiele Modulus) for A = 10.0

h_B (Thiele Modulus) for B = 1.0

SHELL POISONING MODEL

NO	θ	S_{BF}
1	0.0172	16.219
2	0.0344	15.361
3	0.0516	15.874
4	0.0688	17.278
5	0.0860	19.561
6	0.1032	23.533
7	0.1204	30.710
8	0.1376	46.581
9	0.1548	108.208

TABLE 2.12

Catalyst is poisoned for both the reaction $A \longrightarrow B$ and the reaction $B \longrightarrow F$

h_A (Thiele Modulus) for A = 10.0

h_B (Thiele Modulus) for B = 1.0

h_P (Thiele Modulus) for P = 1.0

'M.H.P. MODEL'

NO	θ	S_{BF}
1	0.0172	31.689
2	0.0344	32.013
3	0.0516	32.342
4	0.0688	32.675
5	0.0860	33.013
6	0.1032	33.355
7	0.1204	33.701
8	0.1376	34.052
9	0.1548	34.407

TABLE 2.13

Catalyst is poisoned for both the reaction A ⟶ B and the reaction B ⟶ F

h_A (Thiele Modulus) for A = 10.0

h_B (Thiele Modulus) for B = 1.0

h_P (Thiele Modulus) for P = 4.0

'M.H.P. MODEL'

NO	θ	S_{BF}
1	0.0172	33.178
2	0.0344	35.182
3	0.0516	37.442
4	0.0688	40.038
5	0.0860	43.071
6	0.1032	46.671
7	0.1204	51.002
8	0.1376	56.281
9	0.1548	62.791

TABLE 2.14

Catalyst is poisoned for both the reaction A ⟶ B and the reaction B ⟶ F

h_A (Thiele Modulus) for A = 10.0

h_B (Thiele Modulus) for B = 1.0

h_P (Thiele Modulus) for P = 10.0

'M.H.P. MODEL'

NO	θ	S_{BF}
1	0.0172	28.355
2	0.0344	25.872
3	0.0516	25.080
4	0.0688	25.987
5	0.0860	28.678
6	0.1032	33.815
7	0.1204	43.348
8	0.1376	63.014
9	0.1548	113.809

TABLE 2.15

Catalyst is poisoned for both the reaction A ⟶ B and the reaction B ⟶ F

h_A (Thiele Modulus) for A = 10.0

h_B (Thiele Modulus) for B = 1.0

h_P (Thiele Modulus) for P = 50.0

'M.H.P. MODEL'

NO	θ	S_{BF}
1	0.0172	16.929
2	0.0344	15.959
3	0.0516	16.500
4	0.0688	18.030
5	0.0860	20.752
6	0.1032	25.470
7	0.1204	34.505
8	0.1376	57.224
9	0.1548	209.593

TABLE 3.1[*]

Catalyst is poisoned for the reaction $A \longrightarrow B$ only.

$\theta = 0.0516$ $h_B = 1.0$ $h_A = 2.5$ $h_P = 1.0$

NO.	RADIAL POSITION	ϕ_A	ϕ_B	ϕ_P	ψ
1	1.000	1.0000	0.0000	1.0000	0.0503
2	0.800	0.7619	0.2209	0.9481	0.0470
3	0.600	0.6059	0.3594	0.9091	0.0457
4	0.400	0.5090	0.4421	0.8822	0.0443
5	0.200	0.4571	0.4851	0.8666	0.0436
6	0.000	0.4417	0.4977	0.8618	0.0433

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[*] Tables (3.1-3.36) display results based on the 'M.H.P. Model'

TABLE 3.2

Catalyst is poisoned for the reaction A$\longrightarrow$B only.

$\theta = 0.0860$ $h_B = 1.0$ $h_A = 2.5$ $h_P = 1.0$

NO.	RADIAL POSITION	ϕ_A	ϕ_B	ϕ_P	ψ
1	1.000	1.0000	0.0000	1.0000	0.0824
2	0.800	0.7672	0.2160	0.9496	0.0783
3	0.600	0.6735	0.3522	0.9117	0.0751
4	0.400	0.5182	0.4339	0.8855	0.0730
5	0.200	0.4667	0.4766	0.8703	0.0717
6	0.000	0.4514	0.4891	0.8657	0.0713

TABLE 3.3

Catalyst is poisoned for the reaction A $\longrightarrow$ B only .

$\theta = 0.1204$ $h_B = 1.0$ $h_A = 2.5$ $h_P = 1.0$

NO.	RADIAL POSITION	ϕ_A	ϕ_B	ϕ_P	ψ
1	1.000	1.0000	0.0000	1.0000	0.1134
2	0.800	0.7724	0.2110	0.9511	0.1079
3	0.600	0.6218	0.3450	0.9142	0.1037
4	0.400	0.5273	0.4258	0.8887	0.1000
5	0.200	0.4763	0.4681	0.8739	0.0992
6	0.000	0.4612	0.4805	0.8694	0.0986

TABLE 3.4

Catalyst is poisoned for the reaction $A \longrightarrow B$ only .

$\theta = 0.1548$ $h_B = 1.0$ $h_A = 2.5$ $h_P = 1.0$

NO	RADIAL POSITION	ϕ_A	ϕ_B	ϕ_P	ψ
1	1.000	1.0000	0.0000	1.0000	0.1434
2	0.800	0.7776	0.2062	0.9525	0.1367
3	0.600	0.6296	0.3379	0.9167	0.1315
4	0.400	0.5364	0.4176	0.8918	0.1280
5	0.200	0.4860	0.4595	0.8775	0.1259
6	0.000	0.4710	0.4718	0.8730	0.1253

TABLE 3.5

Catalyst is poisoned for the reaction $A \longrightarrow B$ only .

$\theta = 0.0516$ $h_B = 1.0$ $h_A = 2.5$ $h_P = 4.0$

NO	RADIAL POSITION	ϕ_A	ϕ_B	ϕ_P	ψ
1	1.000	1.0000	0.0000	1.0000	0.5645
2	0.800	0.8218	0.1645	0.6685	0.4007
3	0.600	0.6845	0.2876	0.4499	0.2782
4	0.400	0.5905	0.3697	0.3202	0.2004
5	0.200	0.5373	0.4153	0.2543	0.1596
6	0.000	0.5212	0.4289	0.2354	0.1477

TABLE 3.6

Catalyst is poisoned for the reaction A$\longrightarrow$B only.

$\theta = 0.0860$ $h_B = 1.0$ $h_A = 2.5$ $h_P = 4.0$

NO	RADIAL POSITION	ϕ_A	ϕ_B	ϕ_P	ψ
1	1.000	1.0000	0.0000	1.0000	0.7498
2	0.800	0.8615	0.1275	0.7315	0.5930
3	0.600	0.7440	0.2332	0.5293	0.4488
4	0.400	0.6578	0.3095	0.3971	0.3433
5	0.200	0.6070	0.3538	0.3259	0.2830
6	0.000	0.5913	0.3674	0.3049	0.2648

TABLE 3.7

Catalyst is poisoned for the reaction A ⟶ B only.

$\theta = 0.1204$ $h_B = 1.0$ $h_A = 2.5$ $h_P = 4.0$

NO	RADIAL POSITION	ϕ_A	ϕ_B	ϕ_P	ψ
1	1.000	1.0000	0.0000	1.0000	0.8562
2	0.800	0.8960	0.0954	0.7893	0.7327
3	0.600	0.8003	0.1818	0.6119	0.5976
4	0.400	0.7255	0.2487	0.4849	0.4846
5	0.200	0.6793	0.2895	0.4122	0.4144
6	0.000	0.6648	0.3023	0.3902	0.3923

TABLE 3.8

Catalyst is poisoned for the reaction A ⟶ B only.

$\theta = 0.1548$ $h_B = 1.0$ $h_A = 2.5$ $h_P = 4.0$

NO	RADIAL POSITION	ϕ_A	ϕ_B	ϕ_P	ψ
1	1.000	1.0000	0.0000	1.0000	0.9174
2	0.800	0.9248	0.0687	0.8407	0.8298
3	0.600	0.8511	0.1355	0.6939	0.7194
4	0.400	0.7900	0.1905	0.5800	0.6156
5	0.200	0.7507	0.2256	0.5109	0.5456
6	0.000	0.7381	0.2368	0.4893	0.5227

TABLE 3.9

Catalyst is poisoned for the reaction A$\longrightarrow$B only.

$\theta = 0.0516$ $h_B = 1.0$ $h_A = 2.5$ $h_P = 10.0$

NO	RADIAL POSITION	ϕ_A	ϕ_B	ϕ_P	ψ
1	1.000	1.0000	0.0000	1.0000	0.9954
2	0.800	0.8861	0.1034	0.5373	0.8398
3	0.600	0.7487	0.2289	0.1716	0.3647
4	0.400	0.6364	0.3305	0.0432	0.1003
5	0.200	0.5712	0.3886	0.0130	0.0307
6	0.000	0.5515	0.4060	0.0078	0.0186

TABLE 3.10

Catalyst is poisoned for the reaction $A \longrightarrow B$ only.

$\theta = 0.0860$ $h_B = 1.0$ $h_A = 2.5$ $h_P = 10.0$

NO	RADIAL POSITION	ϕ_A	ϕ_B	ϕ_P	ψ
1	1.000	1.0000	0.0000	1.0000	0.9998
2	0.800	0.9387	0.0548	0.7244	0.9831
3	0.600	0.8477	0.1379	0.3655	0.7430
4	0.400	0.7462	0.2318	0.1209	0.3060
5	0.200	0.6768	0.2959	0.0401	0.1070
6	0.000	0.6547	0.3162	0.0249	0.0666

TABLE 3.11

Catalyst is poisoned for the reaction A$\longrightarrow$B only.

$\theta = 0.1204$ $h_B = 1.0$ $h_A = 2.5$ $h_P = 10.0$

NO	RADIAL POSITION	ϕ_A	ϕ_B	ϕ_P	ψ
1	1.000	1.0000	0.0000	1.0000	0.9999
2	0.800	0.9720	0.0247	0.8425	0.9989
3	0.600	0.9275	0.0651	0.5977	0.9522
4	0.400	0.8618	0.1266	0.3013	0.6506
5	0.200	0.8014	0.1836	0.1273	0.3086
6	0.000	0.7797	0.2042	0.0851	0.2082

TABLE 3.12

Catalyst is poisoned for the reaction A$\longrightarrow$B only.

$\theta = 0.1548$ $h_B = 1.0$ $h_A = 2.5$ $h_P = 10.0$

NO	RADIAL POSITION	ϕ_A	ϕ_B	ϕ_P	ψ
1	1.000	1.0000	0.0000	1.0000	0.9999
2	0.800	0.9921	0.0068	0.9297	0.9999
3	0.600	0.9795	0.0182	0.8162	0.9960
4	0.400	0.9578	0.0386	0.6285	0.9277
5	0.200	0.9296	0.0655	0.4197	0.7023
6	0.000	0.9167	0.0781	0.3388	0.5744

TABLE 3.13

Catalyst is poisoned for the reaction A $\longrightarrow$ B only.

$\theta = 0.0516$ $h_B = 1.0$ $h_A = 5.0$ $h_P = 1.0$

NO	RADIAL POSITION	ϕ_A	ϕ_B	ϕ_P	ψ
1	1.000	1.0000	0.0000	1.0000	0.0503
2	0.800	0.4786	0.4876	0.9481	0.0477
3	0.600	0.2442	0.6898	0.9091	0.0457
4	0.400	0.1385	0.7709	0.8822	0.0443
5	0.200	0.0937	0.8007	0.8666	0.0436
6	0.000	0.0820	0.8078	0.8618	0.0433

TABLE 3.14

Catalyst is poisoned for the reaction A$\longrightarrow$B only.

$\theta = 0.0860$ $h_B = 1.0$ $h_A = 5.0$ $h_P = 1.0$

NO	RADIAL POSITION	ϕ_A	ϕ_B	ϕ_P	ψ
1	1.000	1.0000	0.0000	1.0000	0.0824
2	0.800	0.4860	0.4805	0.9496	0.0783
3	0.600	0.2516	0.6830	0.9117	0.0751
4	0.400	0.1446	0.7656	0.8855	0.0730
5	0.200	0.0988	0.7965	0.8703	0.0717
6	0.000	0.0868	0.8039	0.8657	0.0713

TABLE 3.15

Catalyst is poisoned for the reaction A$\longrightarrow$B only.

$\theta = 0.1204$ $h_B = 1.0$ $h_A = 5.0$ $h_P = 1.0$

NO	RADIAL POSITION	ϕ_A	ϕ_B	ϕ_P	ψ
1	1.000	1.0000	0.0000	1.0000	0.1134
2	0.800	0.4934	0.4735	0.9511	0.1079
3	0.600	0.2592	0.6762	0.9142	0.1037
4	0.400	0.1509	0.7601	0.8887	0.1008
5	0.200	0.1042	0.7921	0.8739	0.0992
6	0.000	0.0918	0.7998	0.8694	0.0986

TABLE 3.16

Catalyst is poisoned for the reaction $A \longrightarrow B$ only.

$\theta = 0.1548$ $h_B = 1.0$ $h_A = 5.0$ $h_P = 1.0$

NO	RADIAL POSITION	ϕ_A	ϕ_B	ϕ_P	ψ
1	1.000	1.0000	0.0000	1.0000	0.1434
2	0.800	0.5009	0.4664	0.9525	0.1367
3	0.600	0.2668	0.6692	0.9167	0.1315
4	0.400	0.1573	0.7545	0.8918	0.1280
5	0.200	0.1097	0.7875	0.8775	0.1259
6	0.000	0.0970	0.7956	0.8730	0.1253

TABLE 3.17

Catalyst is poisoned for the reaction A ⟶ B only.

$\theta = 0.0516$ $h_B = 1.0$ $h_A = 5.0$ $h_P = 4.0$

NO	RADIAL POSITION	ϕ_A	ϕ_B	ϕ_P	ψ
1	1.000	1.0000	0.0000	1.0000	0.5645
2	0.800	0.5795	0.3914	0.6685	0.4007
3	0.600	0.3341	0.6079	0.4499	0.2782
4	0.400	0.2046	0.7145	0.3202	0.2004
5	0.200	0.1448	0.7602	0.2543	0.1596
6	0.000	0.1285	0.7721	0.2354	0.1477

TABLE 3.18

Catalyst is poisoned for the reaction A⟶B only.

$\theta = 0.0860$ $h_B = 1.0$ $h_A = 5.0$ $h_P = 4.0$

NO	RADIAL POSITION	ϕ_A	ϕ_B	ϕ_P	ψ
1	1.000	1.0000	0.0000	1.0000	0.7498
2	0.800	0.6521	0.3226	0.7315	0.5930
3	0.600	0.4140	0.5349	0.5293	0.4488
4	0.400	0.2727	0.6551	0.3971	0.3433
5	0.200	0.2024	0.7122	0.3259	0.2830
6	0.000	0.1826	0.7279	0.3049	0.2648

TABLE 3.19

Catalyst is poisoned for the reaction $A \longrightarrow B$ only.

$\theta = 0.1204$ $h_B = 1.0$ $h_A = 5.0$ $h_P = 4.0$

NO	RADIAL POSITION	ϕ_A	ϕ_B	ϕ_P	ψ
1	1.000	1.0000	0.0000	1.0000	0.8562
2	0.800	0.7206	0.2580	0.7893	0.7327
3	0.600	0.5017	0.4545	0.6119	0.5976
4	0.400	0.3567	0.5809	0.4849	0.4846
5	0.200	0.2788	0.6469	0.4122	0.4144
6	0.000	0.2560	0.6658	0.3902	0.3923

TABLE 3.20

Catalyst is poisoned for the reaction $A \longrightarrow B$ only.

$\theta = 0.1548$ $h_B = 1.0$ $h_A = 5.0$ $h_P = 4.0$

NO	RADIAL POSITION	ϕ_A	ϕ_B	ϕ_P	ψ
1	1.000	1.0000	0.0000	1.0000	0.9174
2	0.800	0.7833	0.1993	0.8407	0.8298
3	0.600	0.5939	0.3702	0.6939	0.7194
4	0.400	0.4552	0.4930	0.5800	0.6156
5	0.200	0.3751	0.5628	0.5109	0.5456
6	0.000	0.3508	0.5837	0.4893	0.5227

TABLE 3.21

Catalyst is poisoned for the reaction $A \longrightarrow B$ only.

$\theta = 0.0516$ $h_B = 1.0$ $h_A = 5.0$ $h_P = 10.0$

NO	RADIAL POSITION	ϕ_A	ϕ_B	ϕ_P	ψ
1	1.000	1.0000	0.0000	1.0000	0.9954
2	0.800	0.7342	0.2431	0.5373	0.8398
3	0.600	0.4499	0.5025	0.1716	0.3647
4	0.400	0.2651	0.6659	0.0432	0.1003
5	0.200	0.1792	0.7382	0.0130	0.0307
6	0.000	0.1563	0.7568	0.0078	0.0186

TABLE 3.22

Catalyst is poisoned for the reaction A⟶B only.

$\theta = 0.0860$ $h_B = 1.0$ $h_A = 5.0$ $h_P = 10.0$

NO	RADIAL POSITION	ϕ_A	ϕ_B	ϕ_P	ψ
1	1.000	1.0000	0.0000	1.0000	0.9998
2	0.800	0.8469	0.1375	0.7244	0.9831
3	0.600	0.6273	0.3386	0.3655	0.7430
4	0.400	0.4122	0.5364	0.1209	0.3060
5	0.200	0.2887	0.6481	0.0401	0.1070
6	0.000	0.2536	0.6793	0.0249	0.0666

TABLE 3.23

Catalyst is poisoned for the reaction A $\longrightarrow$ B only.

$\theta = 0.1204$ $h_B = 1.0$ $h_A = 5.0$ $h_P = 10.0$

NO	RADIAL POSITION	ϕ_A	ϕ_B	ϕ_P	ψ
1	1.000	1.0000	0.0000	1.0000	0.9999
2	0.800	0.9207	0.0701	0.8425	0.9989
3	0.600	0.7952	0.1843	0.5977	0.9522
4	0.400	0.6188	0.3491	0.3013	0.6506
5	0.200	0.4728	0.4864	0.1273	0.3086
6	0.000	0.4245	0.5318	0.0851	0.2082

TABLE 3.24

Catalyst is poisoned for the reaction $A \longrightarrow B$ only.

$\theta = 0.1548$ $h_B = 1.0$ $h_A = 5.0$ $h_P = 10.0$

NO	RADIAL POSITION	ϕ_A	ϕ_B	ϕ_P	ψ
1	1.000	1.0000	0.0000	1.0000	0.9999
2	0.800	0.9731	0.0235	0.9297	0.9999
3	0.600	0.9297	0.0626	0.8162	0.9960
4	0.400	0.8556	0.1321	0.6285	0.9277
5	0.200	0.7628	0.2211	0.4197	0.7023
6	0.000	0.7216	0.2608	0.3388	0.5744

TABLE 3.25

Catalyst is poisoned for the reaction A$\longrightarrow$B only.

$\theta = 0.0512$ $h_B = 1.0$ $h_A = 10.0$ $h_P = 1.0$

NO	RADIAL POSITION	ϕ_A	ϕ_B	ϕ_P	ψ
1	1.000	1.0000	0.0000	1.0000	0.0503
2	0.800	0.1861	0.7677	0.9481	0.0477
3	0.600	0.0371	0.8772	0.9091	0.0457
4	0.400	0.0084	0.8779	0.8822	0.0443
5	0.200	0.0025	0.8675	0.8666	0.0436
6	0.000	0.0015	0.8635	0.8618	0.0433

TABLE 3.26

Catalyst is poisoned for the reaction A$\longrightarrow$B only.

$\theta = 0.0860$ $h_B = 1.0$ $h_A = 10.0$ $h_P = 1.0$

NO	RADIAL POSITION	ϕ_A	ϕ_B	ϕ_P	ψ
1	1.000	1.0000	0.0000	1.0000	0.0824
2	0.800	0.1919	0.7621	0.9496	0.0783
3	0.600	0.0394	0.8752	0.9117	0.0751
4	0.400	0.0091	0.8774	0.8855	0.0730
5	0.200	0.0028	0.8675	0.8703	0.0717
6	0.000	0.0017	0.8636	0.8657	0.0713

TABLE 3.27

Catalyst is poisoned for the reaction A ⟶ B only.

$\theta = 0.1204$ $h_B = 1.0$ $h_A = 10.0$ $h_P = 1.0$

NO	RADIAL POSITION	ϕ_A	ϕ_B	ϕ_P	ψ
1	1.000	1.0000	0.0000	1.0000	0.1134
2	0.800	0.1978	0.7564	0.9511	0.1079
3	0.600	0.0418	0.8730	0.9142	0.1037
4	0.400	0.0100	0.8769	0.8887	0.1008
5	0.200	0.0031	0.8674	0.8739	0.0992
6	0.000	0.0019	0.8636	0.8694	0.0986

TABLE 3.28

Catalyst is poisoned for the reaction A⟶B only.

$\theta = 0.1548$ $h_B = 1.0$ $h_A = 10.0$ $h_P = 1.0$

NO	RADIAL POSITION	ϕ_A	ϕ_B	ϕ_P	ψ
1	1.000	1.0000	0.0000	1.0000	0.1434
2	0.800	0.2038	0.7506	0.9525	0.1367
3	0.600	0.0443	0.8708	0.9167	0.1315
4	0.400	0.0109	0.8763	0.8918	0.1280
5	0.200	0.0035	0.8674	0.8775	0.1259
6	0.000	0.0022	0.8637	0.8730	0.1253

TABLE 3.29

Catalyst is poisoned for the reaction A$\longrightarrow$B only.

$\theta = 0.0516$ $h_B = 1.0$ $h_A = 10.0$ $h_P = 4.0$

NO	RADIAL POSITION	ϕ_A	ϕ_B	ϕ_P	ψ
1	1.000	1.0000	0.0000	1.0000	0.5645
2	0.800	0.2846	0.6727	0.6685	0.4007
3	0.600	0.0744	0.8446	0.4499	0.2782
4	0.400	0.0200	0.8712	0.3202	0.2004
5	0.200	0.0068	0.8682	0.2543	0.1596
6	0.000	0.0043	0.8656	0.2354	0.1477

TABLE 3.30

Catalsyt is poisoned for the reaction A$\longrightarrow$B only.

$\theta = 0.0860$ $h_B = 1.0$ $h_A = 10.0$ $h_P = 4.0$

NO	RADIAL POSITION	ϕ_A	ϕ_B	ϕ_P	ψ
1	1.000	1.0000	0.0000	1.0000	0.7498
2	0.800	0.3681	0.5923	0.7315	0.5930
3	0.600	0.1187	0.8049	0.5293	0.4488
4	0.400	0.0377	0.8584	0.3971	0.3433
5	0.200	0.0145	0.8655	0.3259	0.2830
6	0.000	0.0099	0.8652	0.3049	0.2648

TABLE 3.31

Catalyst is poisoned for the reaction A $\longrightarrow$ B only.

$\theta = 0.1204$ $h_B = 1.0$ $h_A = 10.0$ $h_P = 4.0$

NO	RADIAL POSITION	ϕ_A	ϕ_B	ϕ_P	ψ
1	1.000	1.0000	0.0000	1.0000	0.8562
2	0.800	0.4565	0.5075	0.7893	0.7327
3	0.600	0.1803	0.7489	0.6119	0.5976
4	0.400	0.0684	0.8342	0.4849	0.4846
5	0.200	0.0304	0.8563	0.4122	0.4144
6	0.000	0.0220	0.8597	0.3902	0.3923

TABLE 3.32

Catalyst is poisoned for the reaction A$\longrightarrow$B only.

$\theta = 0.1548$ $h_B = 1.0$ $h_A = 10.0$ $h_P = 4.0$

NO	RADIAL POSITION	ϕ_A	ϕ_B	ϕ_P	ψ
1	1.000	1.0000	0.0000	1.0000	0.9174
2	0.800	0.5457	0.4224	0.8407	0.8298
3	0.600	0.2603	0.6758	0.6939	0.7194
4	0.400	0.1183	0.7924	0.5800	0.6156
5	0.200	0.0613	0.8340	0.5109	0.5456
6	0.000	0.0474	0.8430	0.4893	0.5227

TABLE 3.33

Catalyst is poisoned for the reaction A ⟶ B only.

$\theta = 0.0516$ $h_B = 1.0$ $h_A = 10.0$ $h_P = 10.0$

NO	RADIAL POSITION	ϕ_A	ϕ_B	ϕ_P	ψ
1	1.000	1.0000	0.0000	1.0000	0.9954
2	0.800	0.5373	0.4285	0.5373	0.8398
3	0.600	0.1716	0.7591	0.1716	0.3647
4	0.400	0.0432	0.8601	0.0432	0.1003
5	0.200	0.0130	0.8740	0.0130	0.0307
6	0.000	0.0078	0.8741	0.0078	0.0186

TABLE 3.34

Catalyst is poisoned for the reaction A$\longrightarrow$B only

$\theta = 0.0860$ $h_B = 1.0$ $h_A = 10.0$ $h_P = 10.0$

NO	RADIAL POSITION	ϕ_A	ϕ_B	ϕ_P	ψ
1	1.000	1.0000	0.0000	1.0000	0.9998
2	0.800	0.7244	0.2500	0.7244	0.9831
3	0.600	0.3655	0.5798	0.3655	0.7430
4	0.400	0.1209	0.7990	0.1209	0.3060
5	0.200	0.0401	0.8637	0.0401	0.1070
6	0.000	0.0249	0.8740	0.0249	0.0666

TABLE 3.35

Catalyst is poisoned for the reaction $A \longrightarrow B$ only.

$\theta = 0.1203$ $h_B = 1.0$ $h_A = 10.0$ $h_P = 10.0$

NO	RADIAL POSITION	ϕ_A	ϕ_B	ϕ_P	ψ
1	1.000	1.0000	0.0000	1.0000	0.9999
2	0.800	0.8425	0.1402	0.8425	0.9989
3	0.600	0.5977	0.3640	0.5977	0.9522
4	0.400	0.3013	0.6397	0.3013	0.6506
5	0.200	0.1273	0.7991	0.1273	0.3086
6	0.000	0.0851	0.8366	0.0851	0.2082

TABLE 3.36

Catalyst is poisoned for the reaction A⟶B only

$\theta = 0.1548$ $h_B = 1.0$ $h_A = 10.0$ $h_P = 10.0$

NO	RADIAL POSITION	ϕ_A	ϕ_B	ϕ_P	ψ
1	1.000	1.0000	0.0000	1.0000	0.9999
2	0.800	0.9297	0.6172	0.9297	0.9999
3	0.600	0.8162	0.1643	0.8162	0.9960
4	0.400	0.6285	0.3403	0.6285	0.9277
5	0.200	0.4197	0.5396	0.4197	0.7023
6	0.000	0.3388	0.6170	0.3388	0.5744

CHAPTER VI

DISCUSSION OF RESULTS

A. General

The intraparticle concentration equations (29-48) for the 'Modified Homogeneous Poisoning Model' were integrated on an IBM 360-40 computer. The total computer time consumed was about two hours. Numerical solutions were tested for convergence by decreasing the step size along the θ axis as well as along the ξ axis. A step size of o.o2 along the dimensionless space coordinate and a step size of o.00086 along the demensionless time coordinate were found to be satisfactory. All calculations were done in double precision arithmetic.

The intraparticle concentration profiles of the species A, B, P and the deactivation profile ψ in the catalyst particle are tabulated in Tables (3.1 - 3.36 and R.1 - R.36*). Tables (3.1 - 3.36) are for the case when the catalyst is poisoned for the reaction A ⟶ B only, and tables (R.1 - R.36) are for the case when the catalyst is poisoned for the reaction A ⟶ B as well as the reaction B ⟶ F. The concentration and deactivation profiles were calculated for various values of the ratio (h_A/h_B), θ, and

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*Tables (R.1-R.36) constitute Appendix I.

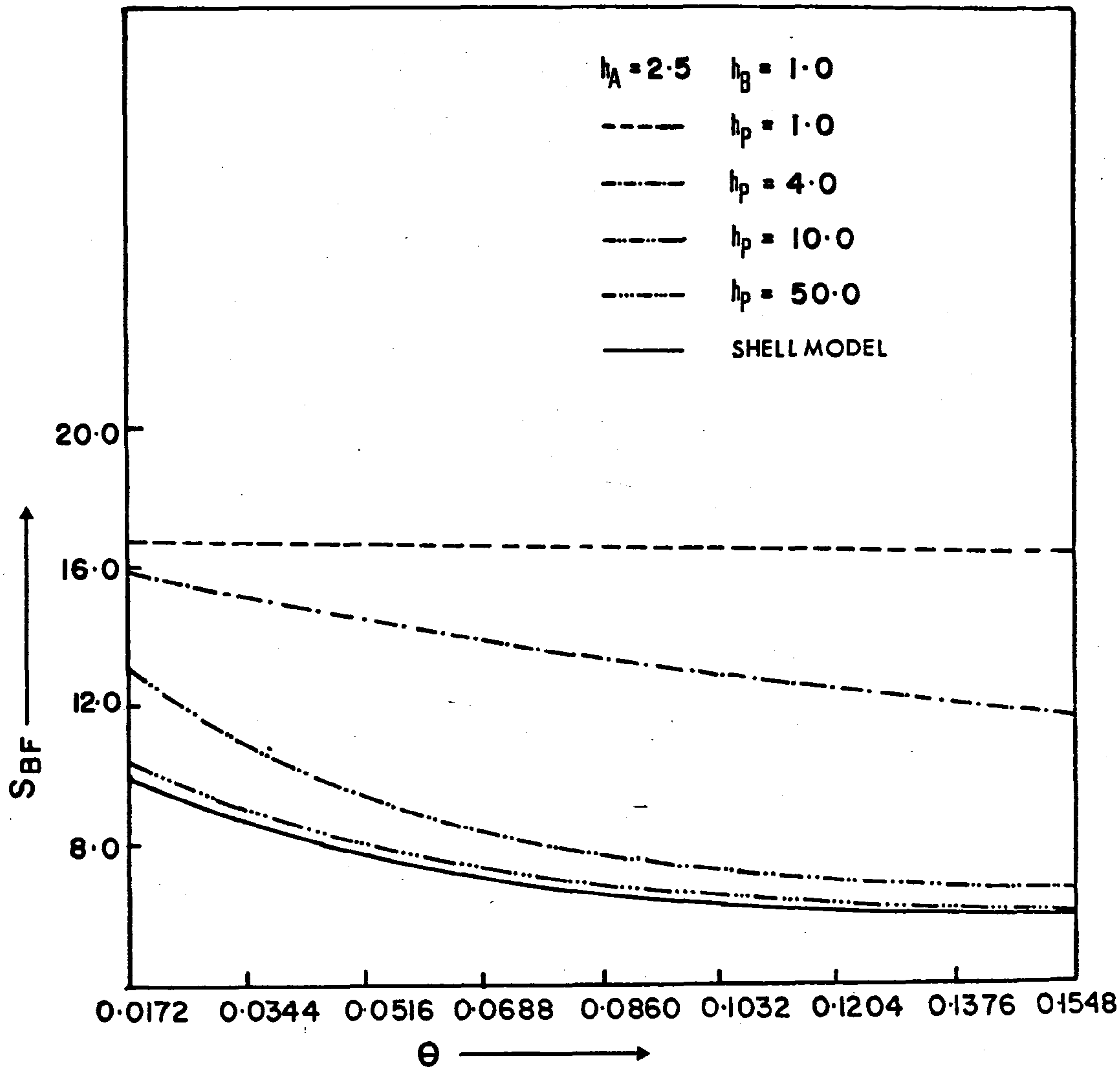


FIG 1·1 EFFECT OF h_p ON S_{BF}. CATALYST POISONED FOR REACTION A ⟶ B ONLY

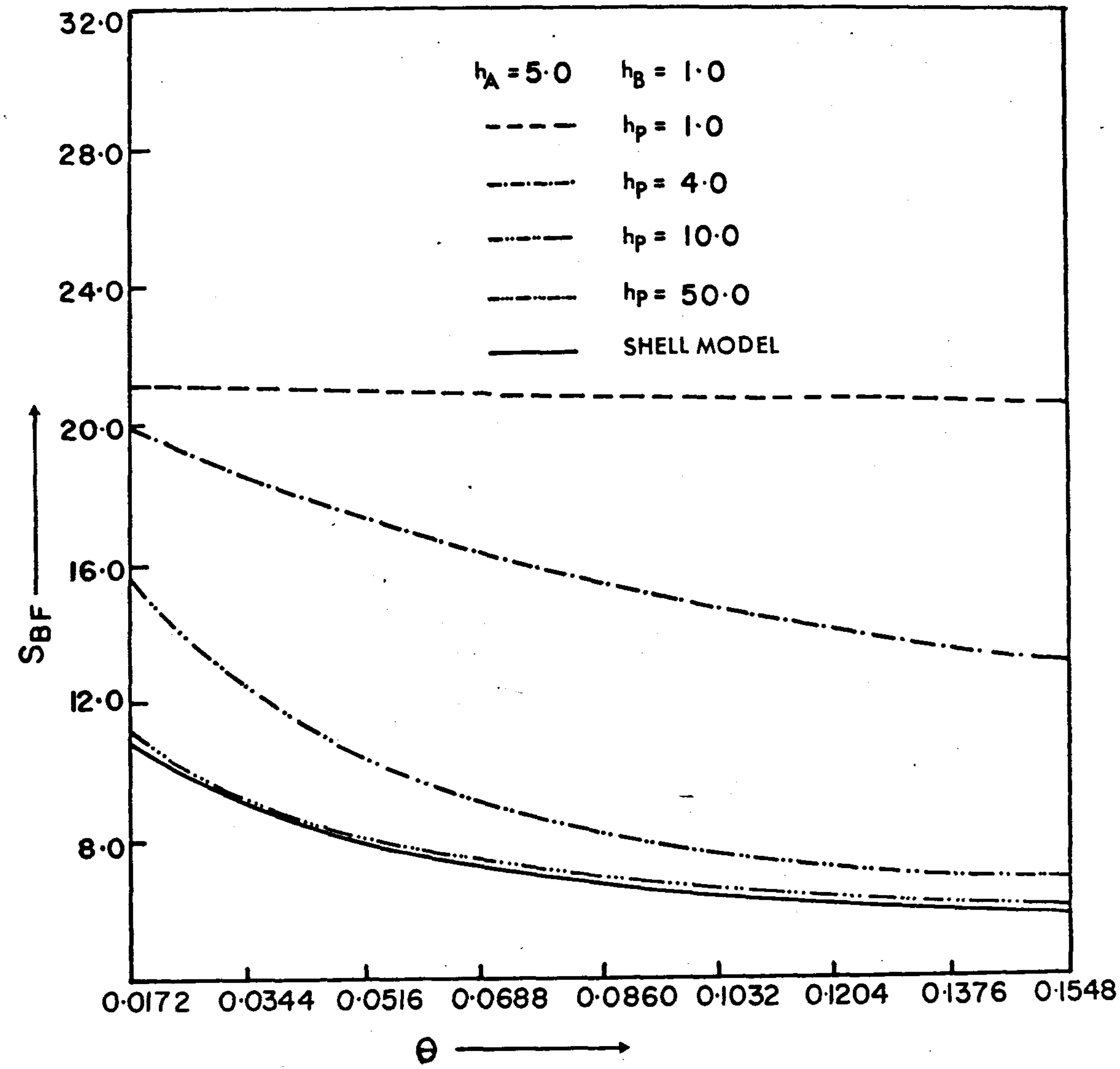


FIG 1·2 EFFECT OF h_p ON S_{BF}. CATALYST POISONED FOR REACTION A ⟶ B ONLY

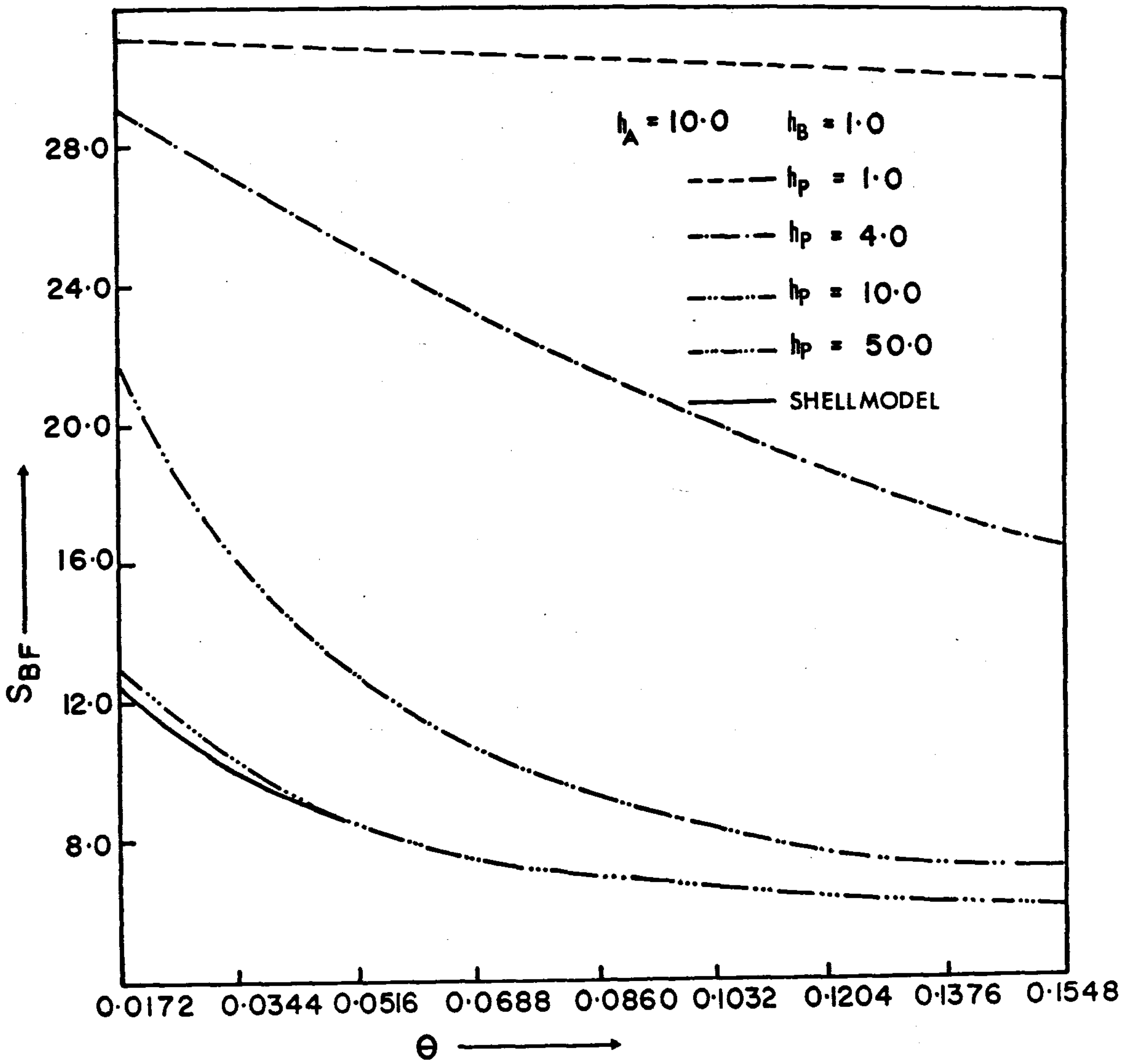


FIG 1·3 EFFECT OF h_P ON S_{BF}. CATALYST POISONED FOR REACTION A ⟶ B ONLY

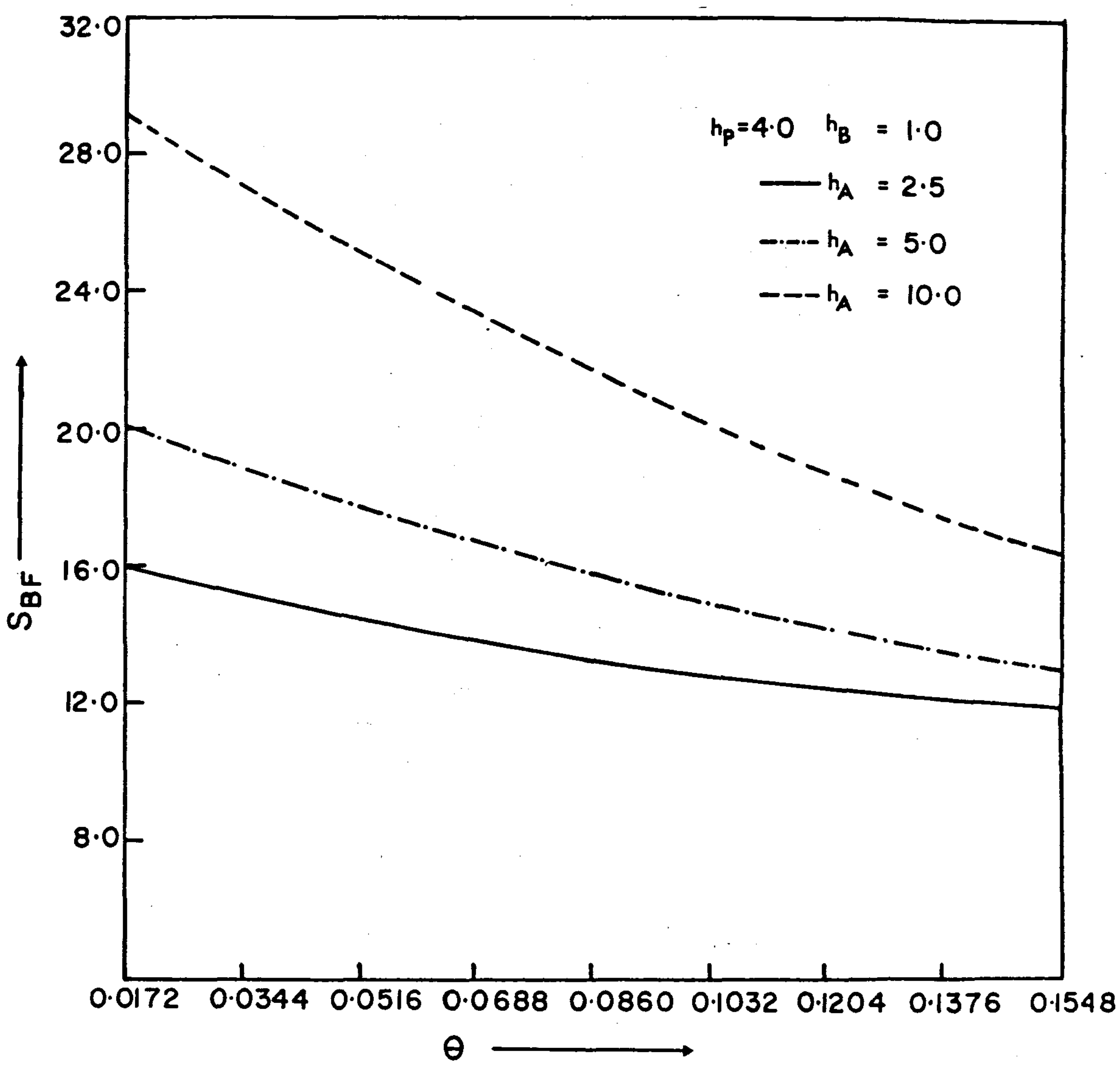


FIG 1·4 EFFECT OF (h_A/h_B) ON S_{BF}. CATALYST POISONED FOR REACTION A ⟶ B ONLY

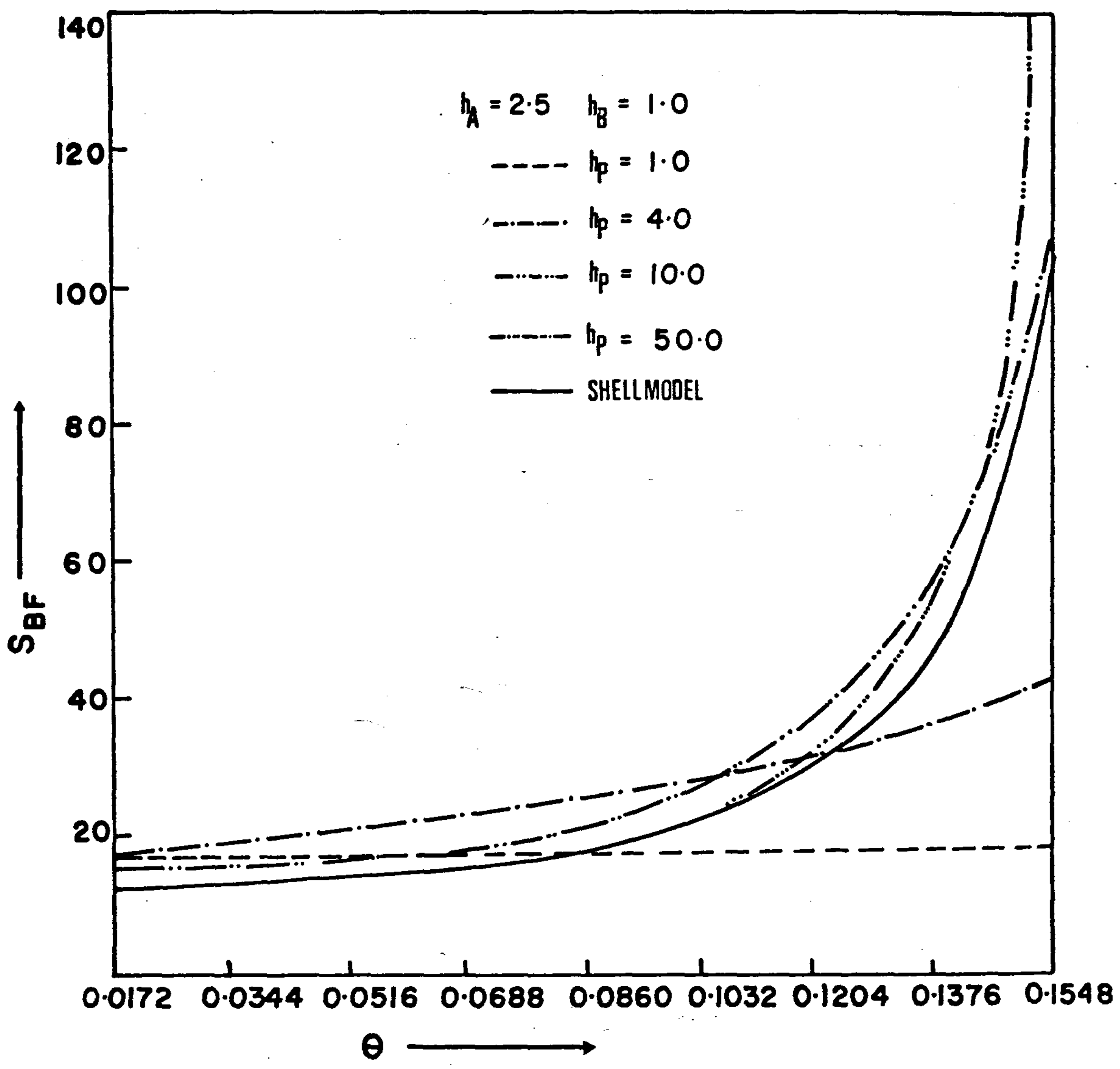


FIG 2·1 EFFECT OF h_P ON S_{BF}. CATALYST POISONED FOR BOTH REACTIONS A ⟶ B AND B ⟶ F

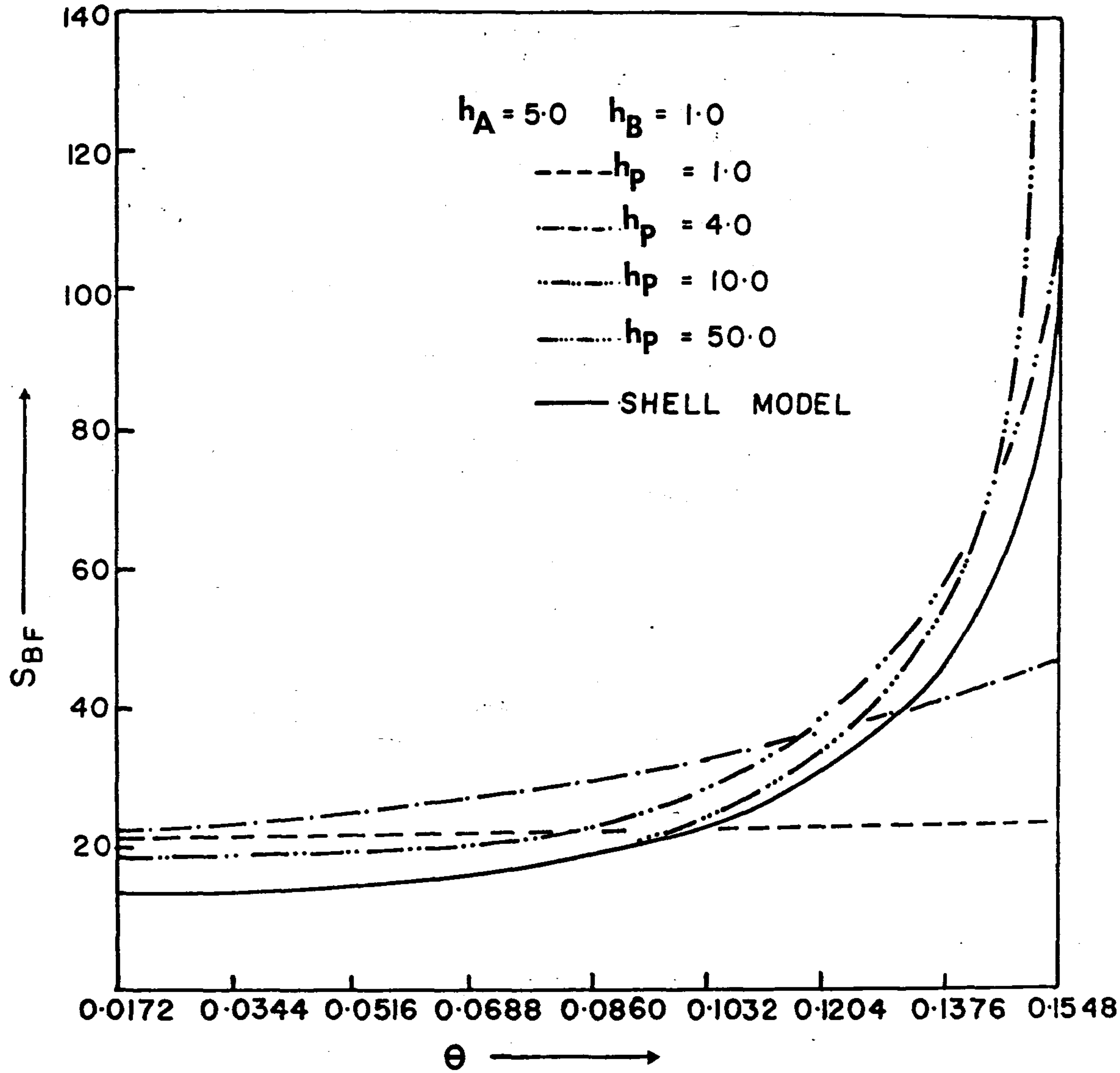


FIG 2·2 EFFECT OF h_p ON S_{BF}. CATALYST POISONED FOR BOTH REACTIONS A⟶B AND B⟶F

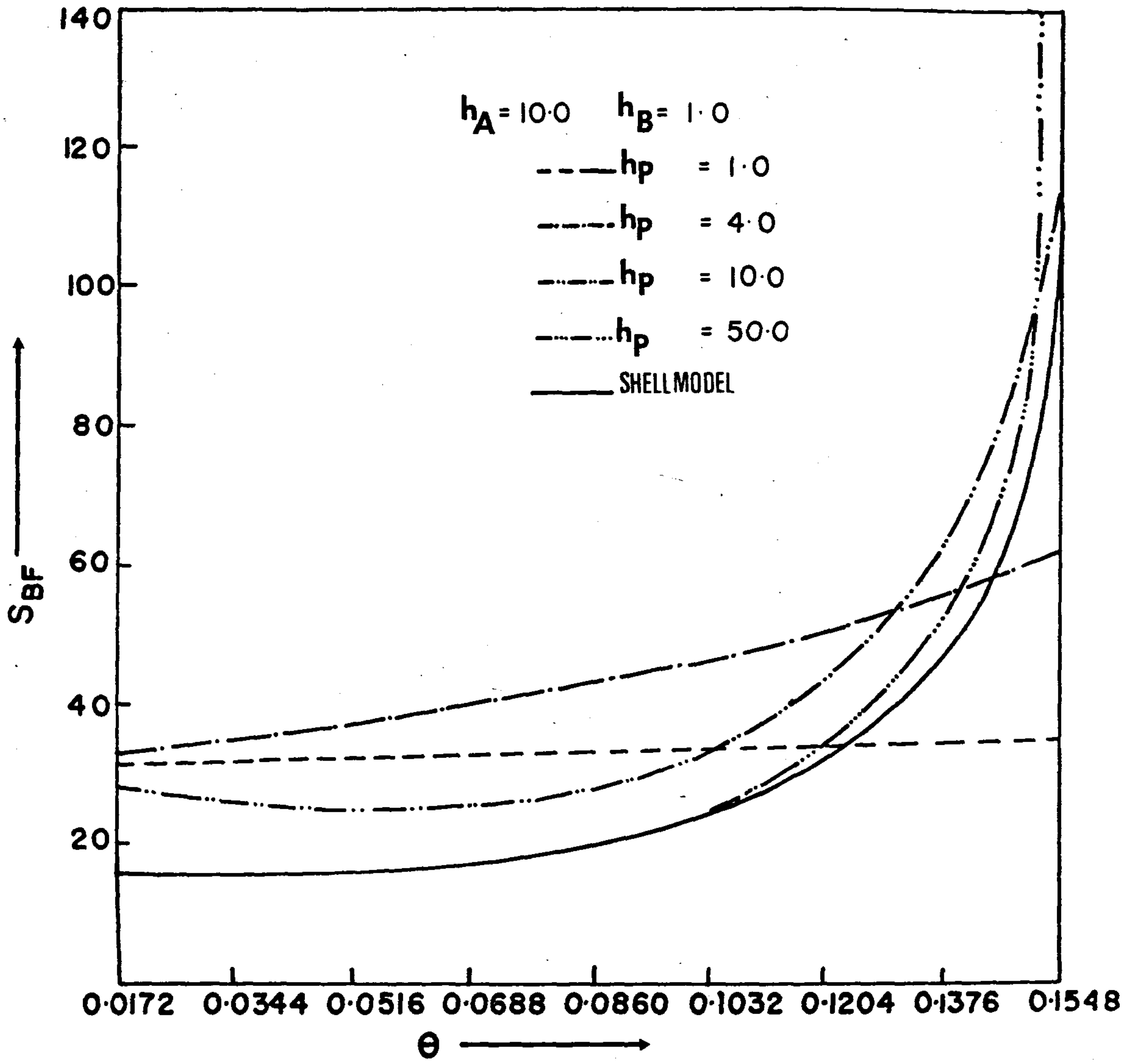


FIG 2·3 EFFECT OF h_P ON S_{BF}. CATALYST POISONED FOR BOTH REACTIONS A ⟶ B AND B ⟶ F

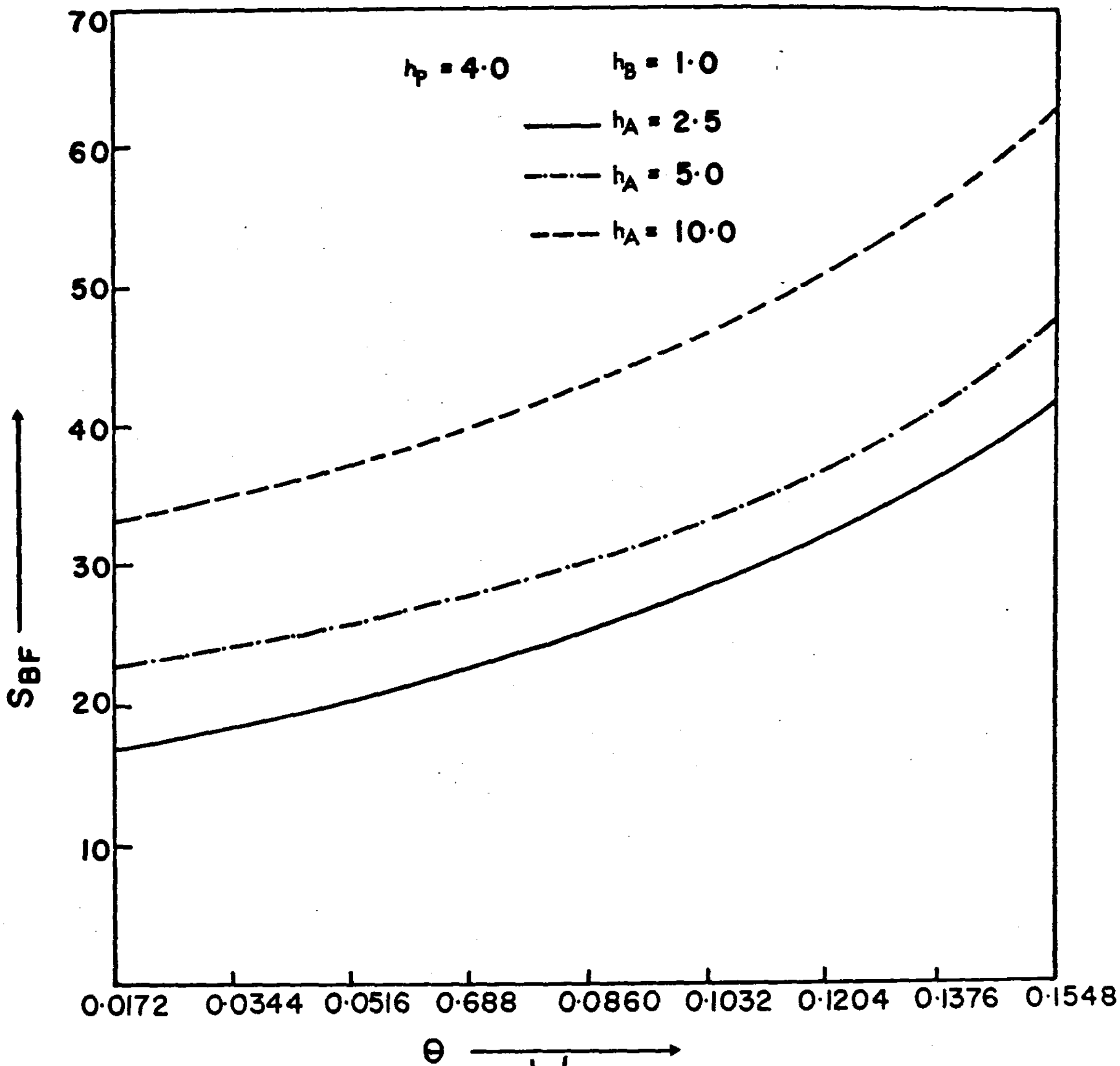


FIG 2·4 EFFECT OF (h_A/h_B) ON S_{BF}. CATALYST POISONED FOR BOTH REACTIONS A⟶B AND B⟶F

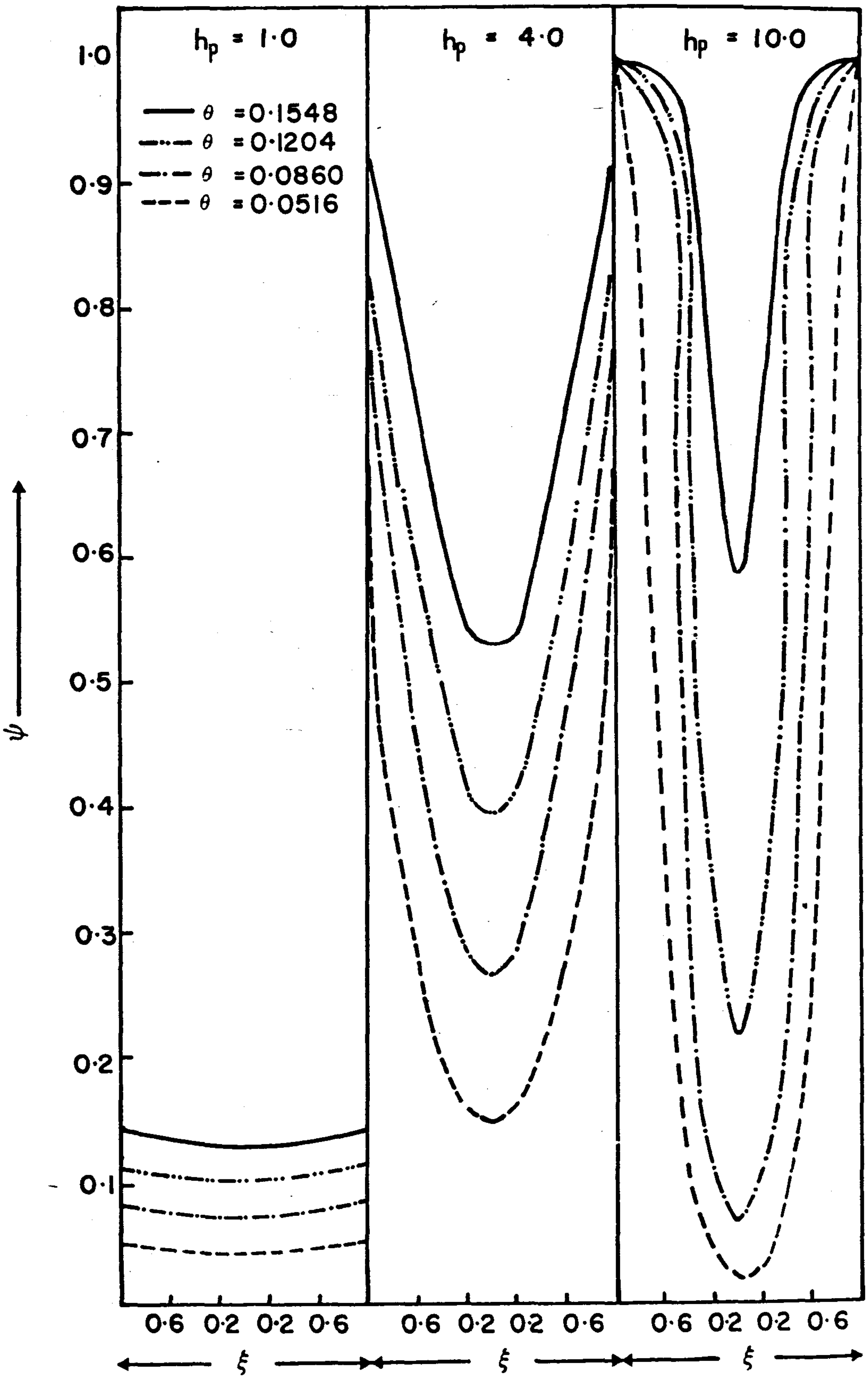


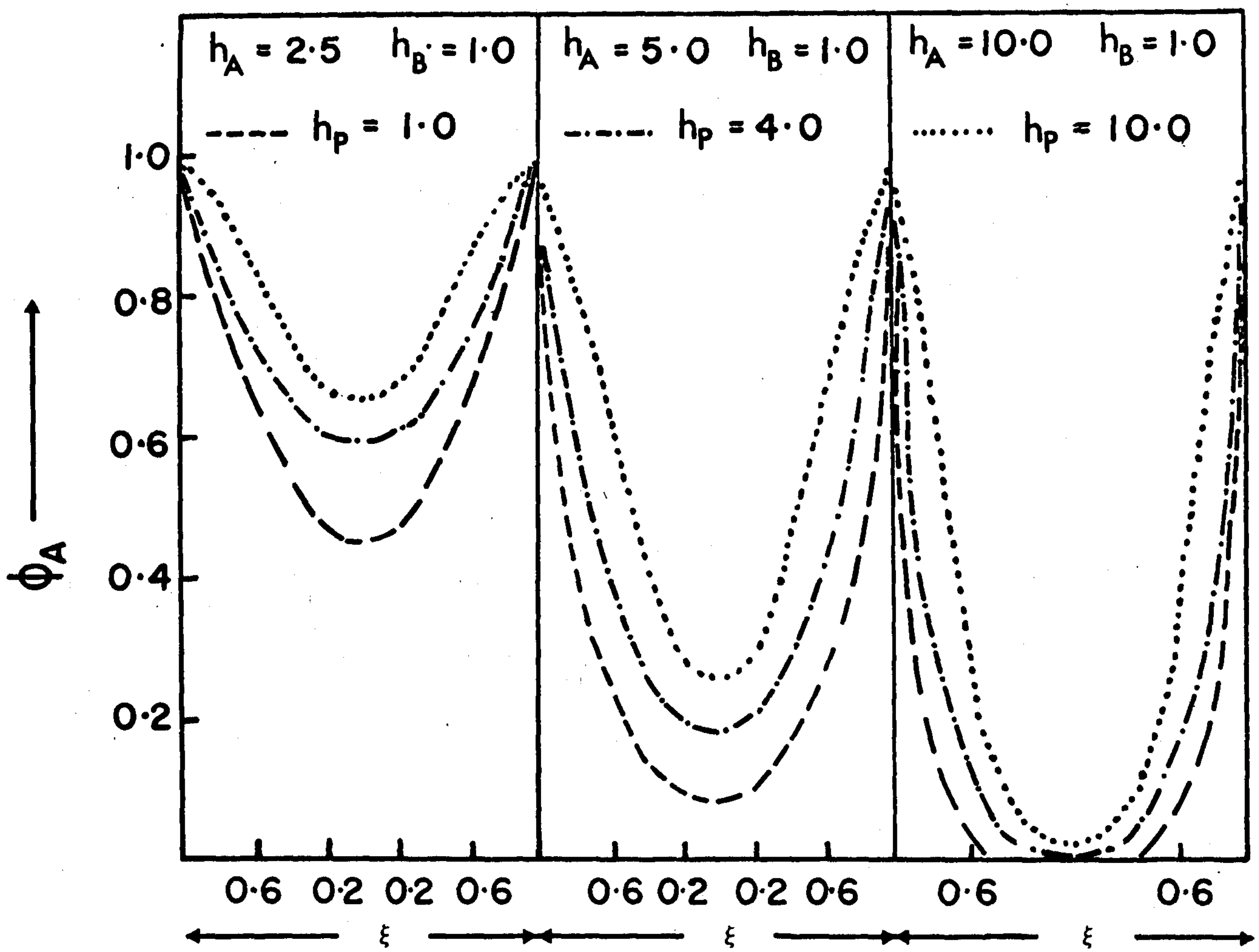
FIG 3·1 DEACTIVATION PROFILE

'h_P'.

Tables (1.1 - 1.15) and figures (1.1 - 1.4) show the effects of 'θ', 'h_P' and the ratio (h_A/h_B), on the selectivity parameter 'S_{BF}', for the case when the catalyst is poisoned for the reaction A ⟶ B only. Corresponding results for the case when the catalyst is poisoned for the reaction A ⟶ B as well as the reaction B ⟶ F are shown in tables (2.1 - 2.15) and figures (2.1 - 2.4).

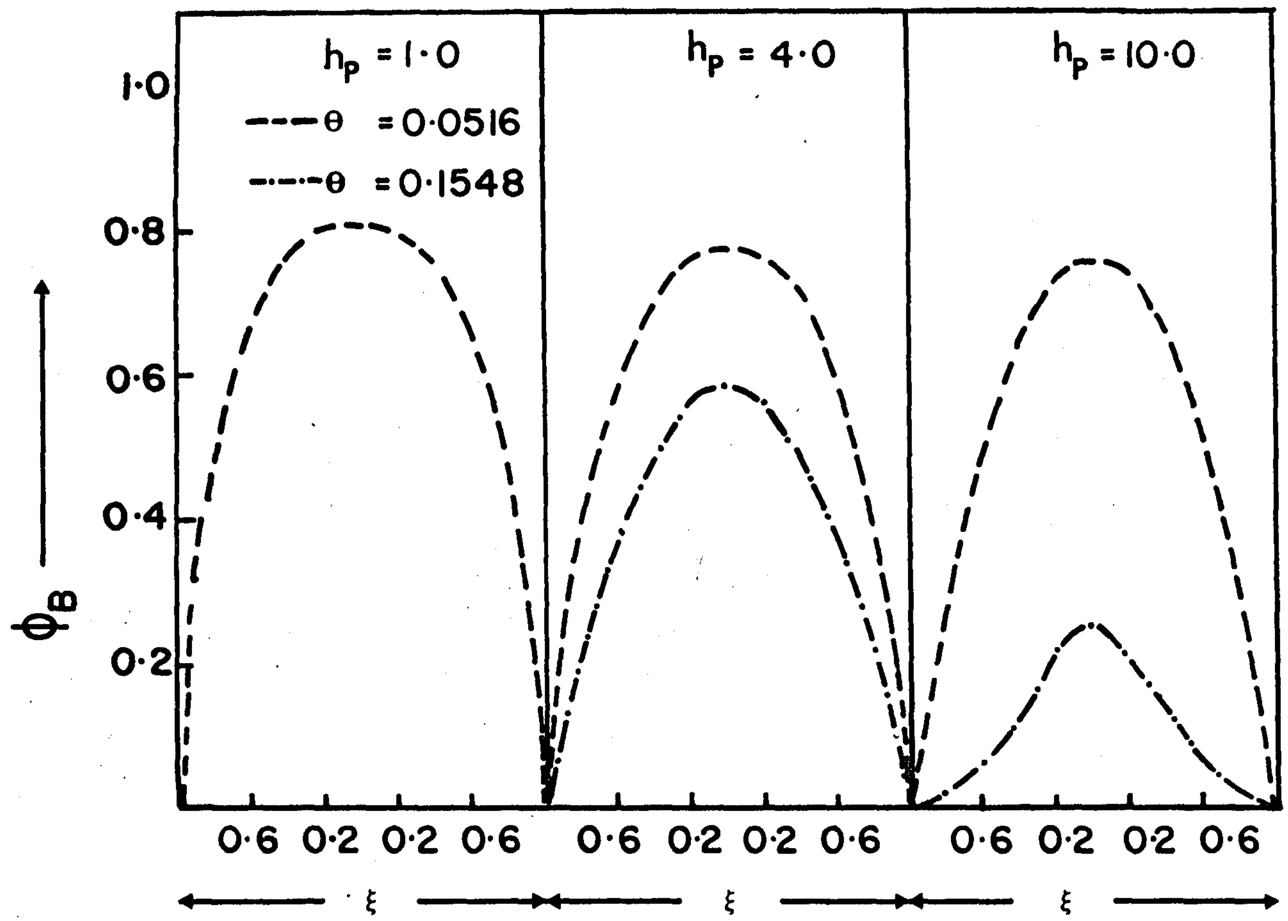
B. Catalyst Poisoned for the Reaction A ⟶ B Only.

From a consideration of figures (1.1 - 1.3), it is apparent that when the catalyst is poisoned for the reaction A ⟶ B only, an increase in pellet poisoning (resulting from an increase in θ) either causes an insignificant change in the value of the parameter 'S_{BF}' or causes a fall in the magnitude of the selectivity 'S_{BF}'. For a small value of 'h_P' (Thiele Modulus for the poison species P) i.e. $h_P = 1$, the decrease in the value of 'S_{BF}' is insignificant, but for higher values of 'h_P' i.e: $h_P \geq 4$, 'S_{BF}' decreases appreciably as the poisoning of the pellet progresses. Figure (3.1) helps to explain why this is so. For $h_P = 1$, the catalyst deactivation is insignificant over the range of 'θ' shown; whereas, for $h_P \geq 4$, the catalyst deactivation is considerable and increases significantly with time. Increasing deactivation of the catalyst pellet



PARAMETER $\theta = 0.086$

FIG 3·2 CONCENTRATION PROFILE FOR A



PARAMETERS $h_A = 5{\cdot}0$, $h_B = 1{\cdot}0$

FIG 3·3 CONCENTRATION PROFILE OF B CATALYST POISONED FOR REACTION A——B ONLY causes a fall in the rate of formation of 'B' (the rate of decompostion of 'B', being completely unaffected), thus, lowering the selectivity of 'S_{BF}'. Figure (3.3) which shows the concentration profile of 'B' for various values of 'h_P', confirms this explanation. It is to be noted that the curves for $\theta = 0.0516$ and $\theta = 0.1548$ at $h_P = 1$ are almost identical (hence only one of them can be shown).

Figure (3.2) displays the concentration profile of species 'A'. It is clear from this figure that as 'h_P' increases, the concentration of 'A' inside the particle also increases. But a look at figure (3.1), reveals that the catalyst activity has also fallen significantly. Since selectivity 'S_{BF}' falls with increasing 'h_P' (figures 1.1 - 1.3), it seems that a fall in the activity of the catalyst more than compensates for the increased concentration of 'A' in the pellet.

Figure (1.4) displays the effect of the ratio (h_A/h_B) on the parameter 'S_{BF}'. For $\nu = 1$, the ratio (h_A/h_B) is an index of the ratio (k_A/k_B). Thus the higher the (k_A/k_B) ratio is, the higher would be the value of the parameter 'S_{BF}'.

At high values of 'h_P', the 'Modified Homogeneous Poisoning Model' is expected to resemble the 'Shell Poisoning Model'. Thus, in figures (1.1 - 1.3) the 'Shell Poisoning Model' plot and the plot for $h_P = 50$, are almost identical.

C. Catalyst Poisoned For the Reaction A ⟶ B as Well as For the Reaction B ⟶ F.

Figures (2.1 - 2.4) lead one to conclude that when the catalyst is poisoned for the reaction A ⟶ B as well as for the reaction B ⟶ F, the selectivity parameter 'S_{BF}' either increases with the passage of process time, or there is no significant change in the value of this parameter. The insensitivity of 'S_{BF}' to the age of the catalyst particle operating at low values of 'h_p', has already been explained in subsection B. The increase in the selectivity of the desired product, with the aging (increased poisoning) of the catalyst appears to be paradoxical. However, as Maxted (28) has mentioned, such a conclusion has been found to be experimentally true in a number of cases (1,2,20,and 36). With the passage of time (and increase in deactivation) the rate of formation of the intermediate 'B' falls in the outer shell of the pellet. Since the catalyst is deactivated more on the outside than it is on the inside, the concentration of the reactant 'A' in the inner core of the pellet increases with the passage of time θ (deactivation of the core also increases but this process is not so fast). Consequently, whereas, with increasing θ, the rate of formation of 'B' decreases in the outer shell of the pellet, this same rate increases in the inside core of the particle as the pellet ages. If the catalyst particle is poisoned for the reaction A ⟶ B only, the effect of this increased rate of formation of 'B' in the inner core of the pellet is negligible. This however, is not the case when the catalyst is poisoned for both the reactions. The increasing deactivation of the catalyst decreases the rate of decomposition of the intermediate 'B' in the inside core as well as in the outer shell. The combination of increased rate of formation 'B' in the inside core and a decreased rate of decomposition of 'B' throughout the catalyst gives a higher value for the parameter 'S_{BF}'. In the case when the catalyst is poisoned for the reaction A ⟶ B as well as for the reaction B ⟶ F, the selectivity parameter 'S_{BF}' is not affected in a straightforward manner by changes in 'h_P'. Thus, as is clear from figures (2.1 - 2.3), the value of the parameter 'S_{BF}' can decrease or increase with increasing 'h_P', depending upon the magnitude of 'h_P' and 'θ'. It seems to be virtually impossible to draw a general conclusion.

When the catalyst is poisoned for both reactions, increasing the ratio (h_A/h_B) at $\nu = 1$, results in higher selectivity 'S_{BF}' for the intermediate 'B'. This is well displayed by figure (2.4). Figure (1.4) displays similar trends for the case when the catalyst is poisoned for the reaction A ⟶ B only.

As was the case in subsection B (catalyst poisoned for the reaction $A \longrightarrow B$ only), the 'Shell Poisoning Model' plot and the 'M.H.P. Model' plot for $h_p = 50$ are identical over the greater part of the range of 'θ'. As 'θ' approaches 0.15, the value of 'S_{BF}' predicted by the curve for $h_p = 50$ is much higher than the one predicted by the curve for the 'Shell Poisoning Model'. It is likely that at this high value of 'h_p', the size of the unpoisoned core predicted by the $h_p = 50$ curve is slightly larger than the size predicted by the 'Shell Poisoning Model'. This difference can explain the gap found between the values of 'S_{BF}' predicted by the 'Shell Poisoning Model' and the 'M.H.P. Model' with $h_p = 50$. However, it should be mentioned that the 'Shell Poisoning Model' plot represents a closed analytical solution, whereas the plot for $h_p = 50$, represents a numerical solution subject to discritisation and other errors. Since the region over which the differences appear is so narrow, a final conclusion concerning the exact cause of this difference seems to be very difficult to arrive at.

CHAPTER VII

CONCLUSIONS

For a heterogeneous consecutive reaction $A \longrightarrow B \longrightarrow F$, catalysed by porous spherical particles subject to poisoning by impurities in the feed stream, the selectivity 'S_{BF}' as predicted by the 'Modified Homogeneous Poisoning Model' behaves differently, depending on whether one or both reactions in the kinetic scheme are affected by the poisoning. When only the reaction $A \longrightarrow B$ is poisoned, the selectivity either does not change significantly or decreases as the catalyst pellets age. At lower values of h_P, aging does not produce any significant change in the magnitude of 'S_{BF}', whereas, appreciable decrease is observed at higher values of h_P. On the other hand if both the reactions in the scheme $A \longrightarrow B \longrightarrow F$ are poisoned, the 'M.H.P. Model' predicts, that 'S_{BF}' will either remain constant or increase.

The effect, increasing values of h_P have on 'S_{BF}', also differentiates the two cases. For the case where the catalyst is poisoned for the reaction $A \longrightarrow B$ only, selectivity decreases considerably as the Thiele Modulus h_P for the species P increases. This conclusion suggests that selectivity 'S_{BF}' can be increased by the use of smaller spherical pellets. The effect of increasing h_P on 'S_{BF}'

for the case when the catalyst is poisoned for both the reactions, is more complex, and not subject to easy qualitative interpretation.

There are some common features in the selectivity behavior for the two cases. The selectivity is seen to increase markedly as the ratio (k_A/k_B) increases. Also, at higher values of h_p selectivity values predicted by the 'M.H.P. Model' are in almost complete agreement with values of 'S_{BF}' predicted by the 'Shell Poisoning Model'.

Useful, though the conclusions from this study are, they have been arrived at on the basis of the assumption that isothermal conditions prevail inside the pellet. As has been pointed out in a number of studies (11,12,38,48), such an assumption is very seldom true in actual practice. Temperature gradients are usually found to exist in the catalyst pellets and a thorough study of poisoning should take into account the temperature gradients prevailing inside the pellet. Because a study along these suggested lines will require very difficult and lengthy numerical calculations, it can be justified only if it is done for an actual reaction scheme, rather than for a hypothetical scheme.

APPENDIX I

*TABLE R.1

Catalyst is poisoned for the reaction A ⟶ B as well as the reaction B ⟶ P.

$\theta = 0.0516$ $h_B = 1.0$ $h_A = 2.5$ $h_P = 1.0$

NO	RADIAL POSITION	ϕ_A	ϕ_B	ϕ_P	ψ
1	1.000	1.0000	0.0000	1.0000	0.0503
2	0.800	0.7619	0.2216	0.9481	0.0477
3	0.600	0.6059	0.3609	0.9091	0.0457
4	0.400	0.5090	0.4441	0.8822	0.0443
5	0.200	0.4571	0.4875	0.8666	0.0436
6	0.000	0.4417	0.5001	0.8618	0.0433

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*Tables (R.1-R.36) show results based on the 'M.H.P. Model'

TABLE R.2

Catalyst is poisoned for the reaction A ⟶ B as well as the reaction B ⟶ F.

$\theta = 0.0860$ $h_B = 1.0$ $h_A = 2.5$ $h_P = 1.0$

NO	RADIAL POSITION	ϕ_A	ϕ_B	ϕ_P	ψ
1	1.000	1.0000	0.0000	1.0000	0.0824
2	0.800	0.7672	0.2171	0.9496	0.0783
3	0.600	0.6139	0.3545	0.9117	0.0751
4	0.400	0.5182	0.4372	0.8855	0.0730
5	0.200	0.4667	0.4804	0.8703	0.0717
6	0.000	0.4514	0.4931	0.8657	0.0713

TABLE R.3

Catalyst is poisoned for the reaction A$\longrightarrow$B as well as the reaction B$\longrightarrow$F.

$\theta = 0.1204$ $h_B = 1.0$ $h_A = 2.5$ $h_P = 1.0$

NO	RADIAL POSITION	ϕ_A	ϕ_B	ϕ_P	ψ
1	1.000	1.0000	0.0000	1.0000	0.1134
2	0.800	0.7724	0.2126	0.9511	0.1079
3	0.600	0.6218	0.3481	0.9142	0.1037
4	0.400	0.5273	0.4302	0.8887	0.1008
5	0.200	0.4763	0.4732	0.8739	0.0992
6	0.000	0.4612	0.4859	0.8649	0.0986

TABLE R.4

Catalyst is poisoned for the reaction A $\longrightarrow$ B as well as the reaction B $\longrightarrow$ F.

$\theta = 0.1548$ $h_B = 1.0$ $h_A = 2.5$ $h_P = 1.0$

NO	RADIAL POSITION	ϕ_A	ϕ_B	ϕ_P	ψ
1	1.000	1.0000	0.0000	1.0000	0.1434
2	0.800	0.7776	0.2082	0.9525	0.1367
3	0.600	0.6296	0.3418	0.9167	0.1315
4	0.400	0.5364	0.4231	0.8918	0.1280
5	0.200	0.4860	0.4660	0.8775	0.1259
6	0.000	0.4710	0.4786	0.8730	0.1253

TABLE R.5

Catalyst is poisoned for the reaction A $\longrightarrow$ B as well as the reaction B $\longrightarrow$ P.

$\theta = 0.0516$ $h_B = 1.0$ $h_A = 2.5$ $h_P = 1.0$

NO	RADIAL POSITION	ϕ_A	ϕ_B	ϕ_P	ψ
1	1.000	1.0000	0.0000	1.0000	0.5645
2	0.800	0.8218	0.1683	0.6685	0.4007
3	0.600	0.6845	0.2946	0.4499	0.2782
4	0.400	0.5905	0.3788	0.3202	0.2004
5	0.200	0.5373	0.4255	0.2543	0.1596
6	0.000	0.5212	0.4394	0.2354	0.1477

TABLE R.6

Catalyst is poisoned for the reaction A $\longrightarrow$ B as well as the reaction B $\longrightarrow$ F.

$\theta = 0.0860$ $h_B = 1.0$ $h_A = 2.5$ $h_P = 4.0$

NO	RADIAL POSITION	ϕ_A	ϕ_B	ϕ_P	ψ
1	1.000	1.0000	0.0000	1.0000	0.7498
2	0.800	0.8615	0.1323	0.7315	0.5930
3	0.600	0.7440	0.2424	0.5293	0.4488
4	0.400	0.6578	0.3217	0.3971	0.3433
5	0.200	0.6070	0.3678	0.3259	0.2830
6	0.000	0.5913	0.3819	0.3049	0.2648

TABLE R.7

Catalyst is poisoned for the reaction A ⟶ B as well as the reaction B ⟶ F.

$\theta = 0.1204$ $h_B = 1.0$ $h_A = 2.5$ $h_P = 4.0$

NO	RADIAL POSITION	ϕ_A	ϕ_B	ϕ_P	ψ
1	1.000	1.0000	0.0000	1.0000	0.8562
2	0.800	0.8960	0.1003	0.7893	0.7327
3	0.600	0.8003	0.1915	0.6119	0.5976
4	0.400	0.7255	0.2620	0.4849	0.4846
5	0.200	0.6793	0.3049	0.4122	0.4144
6	0.000	0.6648	0.3183	0.3902	0.3923

TABLE R.8

Catalyst is poisoned for the reaction A $\longrightarrow$ B as well as the reaction B $\longrightarrow$ F.

$\theta = 0.1584$ $h_B = 1.0$ $h_A = 2.5$ $h_P = 4.0$

NO	RADIAL POSITION	ϕ_A	ϕ_B	ϕ_P	ψ
1	1.000	1.0000	0.0000	1.0000	0.9174
2	0.800	0.9248	0.0731	0.8407	0.8298
3	0.600	0.8511	0.1444	0.6939	0.7194
4	0.400	0.7900	0.2029	0.5800	0.6156
5	0.200	0.7507	0.2402	0.5109	0.5456
6	0.000	0.7381	0.2521	0.4893	0.5227

TABLE R.9

Catalyst is poisoned for the reaction $A \longrightarrow B$ as well as the reaction $B \longrightarrow F$.

$\theta = 0.0516$ $h_B = 1.0$ $h_A = 2.5$ $h_P = 10.0$

NO	RADIAL POSITION	ϕ_A	ϕ_B	ϕ_P	ψ
1	1.000	1.0000	0.0000	1.0000	0.9954
2	0.800	0.8861	0.1074	0.5373	0.8398
3	0.600	0.7487	0.2355	0.1716	0.3647
4	0.400	0.6364	0.3381	0.0432	0.1003
5	0.200	0.5712	0.3963	0.0130	0.0307
6	0.000	0.5515	0.4136	0.0078	0.0186

TABLE R.10

Catalyst is poisoned for the reaction A $\longrightarrow$ B as well as the reaction B $\longrightarrow$ F.

$\theta = 0.0860$ $h_B = 1.0$ $h_A = 2.5$ $h_P = 10.0$

NO	RADIAL POSITION	ϕ_A	ϕ_B	ϕ_P	ψ
1	1.000	1.0000	0.0000	1.0000	0.9998
2	0.800	0.9387	0.0586	0.7244	0.9831
3	0.600	0.8477	0.1454	0.3655	0.7430
4	0.400	0.7462	0.2412	0.1209	0.3060
5	0.200	0.6768	0.3059	0.0401	0.1070
6	0.000	0.6547	0.3262	0.0249	0.0666

TABLE R.11

Catalyst is poisoned for the reaction A ⟶ B as well as the reaction B ⟶ F.

$\theta = 0.1204$ $h_B = 1.0$ $h_A = 2.5$ $h_P = 10.0$

NO	RADIAL POSITION	ϕ_A	ϕ_B	ϕ_P	ψ
1	1.000	1.0000	0.0000	1.0000	0.9999
2	0.800	0.9720	0.0272	0.8425	0.9989
3	0.600	0.9275	0.0705	0.5977	0.9522
4	0.400	0.8618	0.1343	0.3013	0.6506
5	0.200	0.8014	0.1924	0.1273	0.3086
6	0.000	0.7797	0.2132	0.0851	0.2082

TABLE R.12

Catalyst is poisoned for the reaction $A \longrightarrow B$ as well as the reaction $B \longrightarrow F$

$\theta = 0.1548$ $h_B = 1.0$ $h_A = 2.5$ $h_P = 10.0$

NO	RADIAL POSITION	ϕ_A	ϕ_B	ϕ_P	ψ
1	1.000	1.0000	0.0000	1.0000	0.9999
2	0.800	0.9921	0.0077	0.9297	0.9999
3	0.600	0.9795	0.0202	0.8162	0.9960
4	0.400	0.9578	0.0417	0.6285	0.9277
5	0.200	0.9296	0.0695	0.4197	0.7023
6	0.000	0.9167	0.0823	0.3388	0.5744

TABLE R.13

Catalyst is poisoned for the reaction A $\longrightarrow$ B as well as the reaction B $\longrightarrow$ F.

$\theta = 0.0516$ $h_B = 1.0$ $h_A = 5.0$ $h_P = 1.0$

NO	RADIAL POSITION	ϕ_A	ϕ_B	ϕ_P	ψ
1	1.000	1.0000	0.0000	1.0000	0.0503
2	0.800	0.4786	0.4890	0.9481	0.0477
3	0.600	0.2442	0.6926	0.9091	0.0457
4	0.400	0.1385	0.7746	0.8822	0.0443
5	0.200	0.0937	0.8051	0.8666	0.0436
6	0.000	0.0820	0.8123	0.8618	0.0433

TABLE R.14

Catalyst is poisoned for the reaction A$\longrightarrow$B as well as the reaction B$\longrightarrow$F

$\theta = 0.0860$ $h_B = 1.0$ $h_A = 5.0$ $h_P = 1.0$

NO	RADIAL POSITION	ϕ_A	ϕ_B	ϕ_P	ψ
1	1.000	1.0000	0.0000	1.0000	0.0824
2	0.800	0.4860	0.4828	0.9496	0.0783
3	0.600	0.2516	0.6875	0.9117	0.0751
4	0.400	0.1446	0.7717	0.8855	0.0730
5	0.200	0.0988	0.8036	0.8703	0.0717
6	0.000	0.0868	0.8113	0.8657	0.0713

TABLE R.15

Catalyst is poisoned for the reaction A ⟶ B as well as the reaction B ⟶ F.

$\theta = 0.1204$ $h_B = 1.0$ $h_A = 5.0$ $h_P = 1.0$

NO	RADIAL POSITION	ϕ_A	ϕ_B	ϕ_P	ψ
1	1.000	1.0000	0.0000	1.0000	0.1134
2	0.800	0.4934	0.4767	0.9511	0.1079
3	0.600	0.2592	0.6823	0.9142	0.1037
4	0.400	0.1509	0.7085	0.8887	0.1008
5	0.200	0.1042	0.8018	0.8739	0.0992
6	0.000	0.0918	0.8099	0.8694	0.0986

TABLE B 16

Catalyst is poisoned for the reaction A ⟶ B as well as the reaction B ⟶ F.

$\theta = 0.1548$ $h_B = 1.0$ $h_A = 5.0$ $h_P = 1.0$

NO	RADIAL POSITION	ϕ_A	ϕ_B	ϕ_P	ψ
1	1.000	1.0000	0.0000	1.0000	0.1434
2	0.800	0.5009	0.4705	0.9525	0.1367
3	0.600	0.2668	0.6769	0.9167	0.1315
4	0.400	0.1573	0.7650	0.8918	0.1280
5	0.200	0.1097	0.7997	0.8775	0.1259
6	0.000	0.9708	0.8083	0.8730	0.1253

TABLE R.17

Catalyst is poisoned for the reaction A⟶B as well as the reaction B⟶F.

$\theta = 0.0516$ $h_B = 1.0$ $h_A = 5.0$ $h_P = 4.0$

NO	RADIAL POSITION	ϕ_A	ϕ_B	ϕ_P	ψ
1	1.000	1.0000	0.0000	1.0000	0.5645
2	0.800	0.5795	0.3997	0.6685	0.4007
3	0.600	0.3341	0.6228	0.4499	0.2782
4	0.400	0.2046	0.7334	0.3202	0.2004
5	0.200	0.1448	0.7812	0.2543	0.1596
6	0.000	0.1285	0.7936	0.2354	0.1477

TABLE R.18

Catalyst is poisoned for the reaction A ⟶ B as well as the reaction B ⟶ F.

$\theta = 0.0860$ $h_B = 1.0$ $h_A = 5.0$ $h_P = 4.0$

NO	RADIAL POSITION	ϕ_A	ϕ_B	ϕ_P	ψ
1	1.000	1.0000	0.0000	1.0000	0.7498
2	0.800	0.6521	0.3338	0.7315	0.5930
3	0.600	0.4140	0.5560	0.5293	0.4488
4	0.400	0.2727	0.6827	0.3971	0.3433
5	0.200	0.2024	0.7433	0.3259	0.2830
6	0.000	0.1826	0.7599	0.3049	0.2648

TABLE R.19

Catalyst is poisoned for the reaction A ⟶ B as well as the reaction B ⟶ F.

$\theta = 0.1204$ $h_B = 1.0$ $h_A = 5.0$ $h_P = 4.0$

NO	RADIAL POSITION	ϕ_A	ϕ_B	ϕ_P	ψ
1	1.000	1.0000	0.0000	1.0000	0.8562
2	0.800	0.7206	0.2705	0.7893	0.7327
3	0.600	0.5017	0.4786	0.6119	0.5976
4	0.400	0.3567	0.6134	0.4849	0.4846
5	0.200	0.2788	0.6840	0.4122	0.4144
6	0.000	0.2560	0.7043	0.3902	0.3923

TABLE R.20

Catalyst is poisoned for the reaction A$\longrightarrow$B as well as the reaction B$\longrightarrow$F.

$\theta = 0.1548$ $h_B = 1.0$ $h_A = 5.0$ $h_P = 4.0$

NO	RADIAL POSITION	ϕ_A	ϕ_B	ϕ_P	ψ
1	1.000	1.0000	0.0000	1.0000	0.9174
2	0.800	0.7833	0.2114	0.8407	0.8298
3	0.600	0.5939	0.3943	0.6939	0.7194
4	0.400	0.4552	0.5263	0.5800	0.6156
5	0.200	0.3751	0.6015	0.5109	0.5456
6	0.000	0.3508	0.6241	0.4893	0.5227

TABLE R.21

Catalyst is poisoned for the reaction A⟶B as well as the reaction B⟶F.

θ - 0.0516 $h_B = 1.0$ $h_A = 5.0$ $h_P = 10.0$

NO	RADIAL POSITION	ϕ_A	ϕ_B	ϕ_P	ψ
1	1.000	1.0000	0.0000	1.0000	0.9954
2	0.800	0.7343	0.2521	0.5374	0.8398
3	0.600	0.4499	0.5174	0.1716	0.3648
4	0.400	0.2651	0.6825	0.0432	0.1003
5	0.200	0.1792	0.7550	0.0130	0.0307
6	0.000	0.1563	0.7736	0.0078	0.0186

TABLE R.22

Catalyst is poisoned for the reaction A $\longrightarrow$ B as well as the reaction B $\longrightarrow$ F.

$\theta = 0.0860$ $h_B = 1.0$ $h_A = 5.0$ $h_P = 10.0$

NO	RADIAL POSITION	ϕ_A	ϕ_B	ϕ_P	ψ
1	1.000	1.0000	0.0000	1.0000	0.9998
2	0.800	0.8469	0.1469	0.7244	0.9831
3	0.600	0.6274	0.3568	0.3655	0.7430
4	0.400	0.4122	0.5590	0.1209	0.3060
5	0.200	0.2887	0.6719	0.0402	0.1070
6	0.000	0.2536	0.7032	0.0249	0.0666

TABLE R.23

Catalyst is poisoned for the reaction A$\longrightarrow$B as well as the reaction B$\longrightarrow$P.

$\theta = 0.1204$ $h_B = 1.0$ $h_A = 5.0$ $h_P = 10.0$

NO	RADIAL POSITION	ϕ_A	ϕ_B	ϕ_P	ψ
1	1.000	1.0000	0.0000	1.0000	0.9999
2	0.800	0.9207	0.0772	0.8425	0.9989
3	0.600	0.7952	0.1994	0.5977	0.9522
4	0.400	0.6188	0.3705	0.3013	0.6506
5	0.200	0.4728	0.5106	0.1273	0.3086
6	0.000	0.4245	0.5566	0.0851	0.2082

TABLE R.24

Catalyst is poisoned for the reaction A $\longrightarrow$ B as well as the reaction B $\longrightarrow$ F.

$\theta = 0.1548$ $h_B = 1.0$ $h_A = 5.0$ $h_P = 10.0$

NO	RADIAL POSITION	ϕ_A	ϕ_B	ϕ_P	ψ
1	1.000	1.0000	0.0000	1.0000	0.9999
2	0.800	0.9731	0.0265	0.9297	0.9999
3	0.600	0.9297	0.0695	0.8162	0.9961
4	0.400	0.8556	0.1429	0.6285	0.9277
5	0.200	0.7628	0.2346	0.4198	0.7023
6	0.000	0.7216	0.2752	0.3388	0.5744

TABLE R.25

Catalyst is poisoned for the reaction A $\longrightarrow$ B as well as the reaction B $\longrightarrow$ F.

$\theta = 0.0512$ $h_B = 1.0$ $h_A = 10.0$ $h_P = 1.0$

NO	RADIAL POSITION	ϕ_A	ϕ_B	ϕ_P	ψ
1	1.000	1.0000	0.0000	1.0000	0.0503
2	0.800	0.1861	0.7696	0.9481	0.0477
3	0.600	0.0371	0.8808	0.9091	0.0457
4	0.400	0.0084	0.8826	0.8822	0.0443
5	0.200	0.0025	0.8728	0.8666	0.0436
6	0.000	0.0015	0.8690	0.8618	0.0433

TABLE R.26

Catalyst is poisoned for the reaction A ⟶ B as well as the reaction B ⟶ F.

$\theta = 0.0860$ $h_B = 1.0$ $h_A = 10.0$ $h_P = 1.0$

NO	RADIAL POSITION	ϕ_A	ϕ_B	ϕ_P	ψ
1	1.000	1.0000	0.0000	1.0000	0.0824
2	0.800	0.1919	0.7653	0.9496	0.0783
3	0.600	0.0394	0.8811	0.9117	0.0751
4	0.400	0.0091	0.8851	0.8855	0.0730
5	0.200	0.0028	0.8762	0.8703	0.0717
6	0.000	0.0017	0.8726	0.8657	0.0713

TABLE R.27

Catalyst is poisoned for the reaction A $\longrightarrow$ B as well as the reaction B $\longrightarrow$ F

$\theta = 0.1204$ $h_B = 1.0$ $h_A = 10.0$ $h_P = 1.0$

NO	RADIAL POSITION	ϕ_A	ϕ_B	ϕ_P	ψ
1	1.000	1.0000	0.0000	1.0000	0.1134
2	0.800	0.1978	0.7608	0.9511	0.1079
3	0.600	0.0418	0.8812	0.9142	0.1037
4	0.400	0.1003	0.8875	0.8887	0.1008
5	0.200	0.0031	0.8795	0.8739	0.0992
6	0.000	0.0099	0.8761	0.8694	0.0987

TABLE R.28

Catalyst is poisoned for the reaction A $\longrightarrow$ B as well as the reaction B $\longrightarrow$ P.

θ = 0.1548 h_B = 1.0 h_A = 10.0 h_P = 1.0

NO	RADIAL POSITION	ϕ_A	ϕ_B	ϕ_P	ψ
1	1.000	1.0000	0.0000	1.0000	0.1434
2	0.800	0.2038	0.7563	0.9525	0.1367
3	0.600	0.0443	0.8811	0.9167	0.1315
4	0.400	0.0109	0.8898	0.8918	0.1280
5	0.200	0.0035	0.8827	0.8775	0.1260
6	0.000	0.0026	0.8796	0.8730	0.1253

TABLE R.29

Catalyst is poisoned for the reaction A ⟶ B as well as the reaction B ⟶ P.

$\theta = 0.0516$ $h_B = 1.0$ $h_A = 10.0$ $h_P = 4.0$

NO	RADIAL POSITION	ϕ_A	ϕ_B	ϕ_P	ψ
1	1.000	1.0000	0.0000	1.0000	0.5645
2	0.800	0.2846	0.6854	0.6685	0.4007
3	0.600	0.0744	0.8663	0.4499	0.2782
4	0.400	0.0200	0.8977	0.3202	0.2004
5	0.200	0.0068	0.8969	0.2543	0.1596
6	0.000	0.0043	0.8950	0.2354	0.1477

TABLE R.30

Catalyst is poisoned for the reaction A $\longrightarrow$ B as well as the reaction B $\longrightarrow$ P.

$\theta = 0.0860$ $h_B = 1.0$ $h_A = 10.0$ $h_P = 4.0$

NO	RADIAL POSITION	ϕ_A	ϕ_B	ϕ_P	
1	1.000	1.0000	0.0000	1.0000	0.7498
2	0.800	0.3681	0.6107	0.7315	0.5930
3	0.600	0.1187	0.8373	0.5293	0.4488
4	0.400	0.0377	0.8994	0.3971	0.3433
5	0.200	0.0145	0.9105	0.3259	0.2830
6	0.000	0.0099	0.9113	0.3049	0.2648

TABLE R.31

Catalyst is poisoned for the reaction A$\longrightarrow$B as well as the reaction B$\longrightarrow$F.

$\theta = 0.1204$ $h_B = 1.0$ $h_A = 10.0$ $h_P = 4.00$

NO	RADIAL POSITION	ϕ_A	ϕ_B	ϕ_P	ψ
1	1.000	1.0000	0.0000	1.0000	0.8562
2	0.800	0.4565	0.5291	0.7893	0.7327
3	0.600	0.1803	0.7888	0.6119	0.5976
4	0.400	0.0684	0.8860	0.4849	0.4846
5	0.200	0.0304	0.9142	0.4122	0.4144
6	0.000	0.0220	0.9194	0.3902	0.3923

TABLE R.32

Catalyst is poisoned for the reaction $A \longrightarrow B$ as well as the reaction $B \longrightarrow P$.

$\theta = 0.1548$ $h_B = 1.0$ $h_A = 10.0$ $h_P = 4.0$

NO	RADIAL POSITION	ϕ_A	ϕ_B	ϕ_P	ψ
1	1.000	1.0000	0.0000	1.0000	0.9174
2	0.800	0.5457	0.4450	0.8407	0.8298
3	0.600	0.2603	0.7193	0.6939	0.7194
4	0.400	0.1183	0.8506	0.5800	0.6156
5	0.200	0.6132	0.9002	0.5109	0.5456
6	0.000	0.4745	0.9116	0.4893	0.5227

TABLE R.33

Catalyst is poisoned for the reaction A$\longrightarrow$B as well as the reaction B$\longrightarrow$F.

$\theta = 0.0516$ $h_B = 1.0$ $h_A = 10.0$ $h_P = 10.0$

NO	RADIAL POSITION	ϕ_A.	ϕ_B	ϕ_P	ψ
1	1.000	1.0000	0.0000	1.0000	0.9954
2	0.800	0.5373	0.4434	0.5373	0.8398
3	0.600	0.1716	0.7828	0.1716	0.3647
4	0.400	0.0432	0.8860	0.0432	0.1003
5	0.200	0.0130	0.9000	0.0130	0.0307
6	0.000	0.0078	0.9001	0.0078	0.0186

TABLE R.34

Catalyst is poisoned for the reaction $A \longrightarrow B$ as well as the reaction $B \longrightarrow F$.

$\theta = 0.0860$ $h_B = 1.0$ $h_A = 10.0$ $h_P = 10.0$

NO	RADIAL POSITION	ϕ_A	ϕ_B	ϕ_P	ψ
1	1.000	1.0000	0.0000	1.0000	0.9998
2	0.800	0.7244	0.2661	0.7244	0.9831
3	0.600	0.3655	0.6104	0.3655	0.7430
4	0.400	0.1209	0.8363	0.1209	0.3060
5	0.200	0.0401	0.9026	0.0401	0.1070
6	0.000	0.0249	0.9130	0.0249	0.0666

TABLE B.35

Catalyst is poisoned for the reaction A $\longrightarrow$ B as well as the reaction B $\longrightarrow$ P.

$\theta = 0.1203$ $h_B = 1.0$ $h_A = 10.0$ $h_P = 10.0$

NO	RADIAL POSITION	ϕ_A	ϕ_B	ϕ_P	ψ
1	1.000	1.0000	0.0000	1.0000	0.9999
2	0.800	0.8425	0.1539	0.8425	0.9989
3	0.600	0.5977	0.3929	0.5977	0.9522
4	0.400	0.3013	0.6800	0.3013	0.6506
5	0.200	0.1273	0.8441	0.1273	0.3086
6	0.000	0.8510	0.8825	0.0851	0.2082

TABLE R.36

Catalyst is poisoned for the reaction A$\longrightarrow$B as well as the reaction B$\longrightarrow$P.

$\theta = 0.1548$ $h_B = 1.0$ $h_A = 10.0$ $h_P = 10.0$

NO	RADIAL POSITION	ϕ_A	ϕ_B	ϕ_P	ψ
1	1.000	1.0000	0.0000	1.0000	0.9999
2	0.800	0.9297	0.0696	0.9297	0.9999
3	0.600	0.8162	0.1821	0.8162	0.9960
4	0.400	0.6285	0.3680	0.6285	0.9277
5	0.200	0.4197	0.5740	0.4197	0.7023
6	0.000	0.3388	0.6535	0.3388	0.5744

NOMENCALTURE

Latin Letters

C_i = concentration of species i in the pores of the catalyst, gm moles/cc

D_i = effective diffusivity for the species i

M = number of increments + 1, along the ξ axis

N = number of increments + 1, along the θ axis

$\overset{*}{S}$ = active sites

$S_{ji\ell}$ = j = A,B,C,D, ℓ = A,B,P coefficients used in Gaussian elimination

g_1, g_2, g_3, g_4 = defined by equations (143), (145), (147) and (149) respectively

h_i = Thiele Modulus for the species i

$$\sqrt{\frac{k_i \ \rho \ r_0^2}{D_i}}, \quad i = A,B,P$$

k_i = specific reaction rate constant, $cc \Big/ \langle sec, gm\ catalyst \rangle$

i = A,B,P

q = concentration of poisoned sites (gm moles/gm catalyst)

q_0 = concentration of sites corresponding to complete deactivation

r = radial position in the catalyst pellet

r_0 = radius of catalyst particles cms .

t = time (secs)

Greek Letters

Δ = Laplace Operator

$\Delta\theta$ = increment along θ axis

$\Delta\xi$ = increment along ξ axis

∇ = gradient operator

ϕ_i = $i = A, B$, dimensionless concentration $C_i/\overset{*}{C}_A$

ϕ_P = dimensionless concentration $C_P/\overset{*}{C}_P$

ψ = q/q_0

Ω = $1 - \psi$

β_1 β_2 = defined by equations (151) and (153) respectively

δ = small time, sec.

ϵ_P = void fraction in the catalyst pellet

θ = dimensionless time $\left[\dfrac{t\,\overset{*}{C}_P\,D_P}{r_0^2\,q_0\,\rho}\right]$

ν = (D_A / D_B)

ξ = dimensionless distance (r/r_0)

ξ_P = position of the poison front in the 'Shell Poisoning Model'

ρ = density of the catalyst (gms/cc)

Superscripts

$'$ = refers to conditions in the non-poisoned core in the 'Shell Poisoning Model'

$*$ = refers to bulk

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PART III

SELECTIVITY OPTIMISATION FOR COMPLEX NON-LINEAR REACTION SCHEMES

ABSTRACT

Selectivity optimisation for a complex reaction scheme has been investigated. From single reactor considerations, conditions under which selectivity maxima occur at conversions greater than zero are determined. For a cascade of c.s.t.rs. the discrete version of Pontryagin's Maximum Principle has been employed to establish the optimal conditions. The results indicate that the requirements for maximum selectivity are frequently at variance with those for maximum yield. The need for the use of selectivity as a performance criterion different from the yield is thus established.

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CHAPTER I

INTRODUCTION

An important consideration in the performance of chemical reactors for multiple reaction schemes is selectivity with respect to the desired product. In as much as the economics of the operation is affected by wastage of raw materials as well as by separation costs, selectivity considerations can occasionally be the key factors in reactor design and operation. This aspect of reactor design has not received the attention it deserves, primarily because most of the kinetic schemes that have been studied thus far are relatively simple first order schemes, and for first order schemes, maximum selectivity occurs at zero conversion of the key reactant. Reactor design based on selectivity maximisation was thus not a feasible objective.

In many situations, however, the reaction schemes are more complex and one or more steps are of an order other than one. Information about the behavior of selectivity in such cases is virtually nonexistent and the criteria for reactor design are yield oriented. It is conceivable that for such complex non-linear reaction schemes, maximum selectivity might not occur at zero conversion of the key reactant, in which case the criteria for designing a reactor, with yield as the objective, can be different from the criteria for a selectivity oriented design.

The present study was undertaken to establish whether or not for complex non-linear kinetic schemes:

i. selectivity maxima can occur at conversion levels greater than zero

ii. optimal policies for selectivity maximisation are the same as the ones for yield maximisation.

CHAPTER II

REVIEW OF LITERATURE

A. Yield Studies

A review of literature in the field of design of chemical reactors for carrying out complex chemical reactions must begin with K.G. Denbigh's work (9). He showed that for a given conversion the stirred tank required a much greater volume than the tubular reactor because of the lower reaction rate that prevails in the presence of complete mixing. The use of a multistage tank reactor system was therefore suggested to effect a saving in the reactor volume. Denbigh (9) also described design criteria for selection of reactor systems to carry out various complex reactions. By assuming that the yield of a product depended on the concentration of a single reactant and the reactor operating temperature, Denbigh (9) had concluded that in order to achieve the optimum yield, a reaction parameter such as temperature should be varied continuously along a reaction path. He recommended that the parameter should be adjusted to maximise the local reaction rate. Denbigh's (9) conclusion regarding adjustment of a parameter to maximise the local reaction rate (the so-called disjoint policy) is valid only for single reactions. For multiple reactions, where the yield is a function of the concentration of a number of reactants and the reactor operating temperature, such a conclusion is not necessarily true. Both Amundson (1) and Horn (22) have pointed this out.

Bilous and Amundson's (4) work points out the pitfalls encountered during optimisation for reactor design. In their study of the consecutive reaction

$A \xrightarrow[r_1]{E_1} B \xrightarrow[r_2]{E_2} D$, occuring in a tubular reactor, they concluded

that no matter what the ratio (E_1/E_2) is, the temperature profile should have a negative gradient. This is a justifiable conclusion for the case when $(E_1/E_2) < 1$, but is incongruous for the case $(E_1/E_2) > 1$. Amundson et al (4) had expressed doubts about the validity of the conclusion as regards the case $(E_1/E_2) > 1$, and pointed out that their conclusions were based on the properties of the first derivative, and that their optima might not be global optima. As Aris (3) later showed, Amundson et al (4) had run into a local extremum in dealing with the case $(E_1/E_2) > 1$.

A landmark in the history of optimum reactor design was Denbigh's (10) paper at the first European

Symposium on Chemical Reaction Engineering. He considered the complex first order scheme:

$$\begin{tikzcd}
A \arrow[r, "k_1", "E_1"'] \arrow[d, "E_2"', "k_2"] & X \arrow[r, "k_3", "E_3"'] \arrow[d, "E_4"', "k_4"] & Y \\
P & Q &
\end{tikzcd}$$

in which Y is the desirable product, X is an intermediate and P and Q are waste products. For different values of the ratios (E_2/E_1) and (E_4/E_3) Denbigh showed how to choose optimum temperature profiles for two equal sized c.s.t.rs.

Piret and Trambouze (28) used graphical methods for the determination of the preferred type (or combination of types) and optimum sizes of the reactors needed for the desired level of conversion of some key reactant. The triangular diagrams Piret et al (28) used for this purpose could deal with reaction systems such as

$$\begin{tikzcd}
A \arrow[r] \arrow[d] & \text{B(desired)} \arrow[r, shift left] & Q \arrow[l, shift left] \\
D & &
\end{tikzcd}$$

(first order scheme) (i)

$$\begin{tikzcd}
A \arrow[r, "r_1"] \arrow[d, "r_2"] & \text{B(desired)} \\
D &
\end{tikzcd}$$

(ii)

In scheme (ii) one of the reactions was of the first order and the other was of the second order. Piret and Trambouze (28) dealt only with those reactions which needed three or less than three chemical species to characterise them. Moreover, temperature effects were completely ignored.

From 1959 onwards, the interest in reactor design for multiple reactions shifted towards the application of newly developed optimisation techniques . With the help of these techniques far more complex systems could be analysed than had been possible before. Using Dynamic programming, Aris (2) optimised the yield for Denbigh's reaction. Aris used interpolation and tabulation to find the maximum for each stage. Dynamic programming is based on the concept of imbedding the given problem in a class of similar problems and choosing a particular solution from the general solution. This requires a computer system with an exceptionally large memory and thus the utility of this algorithm is rather limited. Aris (2) had assumed that the minimisation of the unwanted products and the maximisation of the desirable products can be achieved by the same design. This probably is true in the case of Denbigh's reaction but can not be considered a valid principle in general. Pis'man and Ioffe (29) used Dynamic Programming to compute the optimum temperature and sizes for a complex first order reaction scheme occurring in a series of c.s.t.rs. They used the properties of the first derivative to maximise the objective function at each stage. This procedure does save core space, but it is based on the assumption that there is only one stationary point for each stage and this point is a maximum.

Denbigh (11) developed the concepts of instantaneous yield and the overall yield in a paper presented at the Second Symposium on Chemical Reaction Engineering. He showed how the relationship between the instantaneous yield and the extent of the reaction could be used graphically for the optimum design of a series of c.s.t.rs. However, as Zwietering (36) pointed out, the method is useful as long as the extent of reaction can be expressed as a function of the concentration of a single species. Obviously the applicability of the method is rather limited.

Katz (24) developed the discrete version of Pontryagin's maximum principle* and later (25) showed how to optimise the operating conditions for the production of an intermediate B formed in the reaction,

$$A \rightleftharpoons B \longrightarrow \text{(unwanted products)}$$

taking place in a cascade of N tanks. Katz (25), in his later paper, extended the discrete version of the maximum principle to cover many new situations. Fan et al (16) generalised the 'D.M.P.' to cover arbitrary and complex topologies. Almost all of Fan et al's (16) work deals

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*Abbreviated as 'D.M.P.'

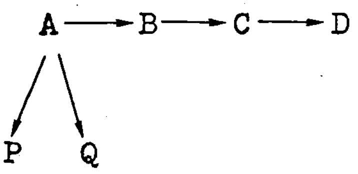
with systems in which the objective function is linear in state variables. Denn and Aris (12) have derived a weak version of the 'Discrete Maximum Principle' using Green's function. They determined the optimum temperature policy for a train of three equal sized c.s.t.rs in which a second order complex reaction, $A \longrightarrow B \longrightarrow C$, was taking place.

Katz's (24) version of the 'D.M.P.' has been severly criticised by Horn and Jackson (23). Denn (13), Holtzman (19) and Holtzman and Halkin (20) have also criticised Katz's version. Horn et al (23) pointed out that Katz (24) and Fan et al (16) had deduced the nature of the stationary values from a consideration of first order variations only. Thus, Katz's (24) sufficient conditions were actually only the necessary conditions. Holtzman (19) and Holtzman and Halkin (20) have stated the conditions under which 'D.M.P.' can be used. Instead of considering the evolution of the system in a discrete manner with stage number, Gurel and Lapidus (18) considered the simultaneous evolution of all stages in the time domain. Variables from each stage are thus transformed into elements of an overall state vector at a given time.

By treating the optimal policy for the discrete system as the optimal steady-state policy for the transformed problem, the 'Continuous Maximum Principle' can be used. Gurel et al (18) have thus used the time and its evolution as a continuum to avoid the difficulties arising out of the essentially discontinuous nature of the 'D.M.P.'. It is apparent that the number of state and control variables (n stage process) which must be handled in the continuous form are not s and q, but (s x n) and (q x n) respectively.

The applicability of 'D.M.P.' is limited not only by the very restrictive conditions under which it can be used, but the algorithm also suffers from convergence difficulties. The 'Maximum Principle' poses a two point boundary value problem and when the objective function is not linear in its arguments, matching the boundary conditions can be a very difficult task. Denn (14) and Paynter and Bankoff (27) have reported serious convergence difficulties encountered by them in applying the 'Maximum Principle'.

A number of other techniques have been used in yield optimisation studies. Storey and Rosenbrock (33) have compared various optimisation techniques and have recommended the use of Rosenbrock's (31) direct search technique. They used as a test case the problem of finding the optimum operating conditions for the production of the species C formed by the first order scheme:



Reed and Stevens (30) used a gradient method (another direct technique) to study the yield optimisation problem for a system which had a tank reactor as its reaction unit. Later DiBella and Stevens (15) used 'Non-Linear Programming' to solve the same problem. Most direct search methods are time consuming, occupy a lot of core space and do not guarantee the global nature of the computed optimum. Recently Fine and Bankoff (17) have used a second variational technique to optimise the yield of an intermediate in a consecutive reaction. This technique was first suggested by Merriam (26). Because the treatment is based on the considerations of second variations, it is apparent that both necessary and sufficient conditions have been fulfilled in locating the optimum.

B. Selectivity Studies

Denbigh (11) plotted differential selectivity 'ϕ' against the extent of reaction (degree of conversion) to obtain 'ϕ' curves which he used to optimise the reactor sizes for a series of c.s.t.rs. From a consideration of the 'ϕ' curves he concluded that if the 'ϕ' curve had a negative gradient, better selectivity could be obtained by lowering the concentration of the key reactant, as slowly as possible. On the other hand if the 'ϕ' curve had a positive slope, concentration of the key reactant should be lowered as quickly as possible, in order to obtain better selectivity. As has been pointed out before, Denbigh's (11) treatment is valid for only those reactions which can be characterised by the degree of conversion of a single species. Also the treatment is based on the assumption that the reactors are operated at the same temperature. Chermin and Van Krevelen (7) plotted the maximum yield of an intermediate B against a parameter

'S' $\left[S = C_{A0}^{m-n} \frac{k_1}{k_2} \right]$

---called the selectivity parameter---for a consecutive reaction

$$A \xrightarrow[k_1]{\text{mth order}} B \xrightarrow[k_2]{\text{nth order}} D \qquad m = 0,1,2, \quad n = 0,1,2.$$

Chermin et al (7) found that the maximum yield of B increased with the increasing values of 'S'. Since for a consecutive reaction, yield and selectivity design criteria are the same, Chermin et al's (7) work is useful as a selectivity study; otherwise their study is of a limited value. Van de Vusse and Voetter (34) did a study with the aim of deciding the optimum operating conditions for carrying out the reaction:

$$A + B \xrightarrow[k_1]{} D \text{ (desirable)}$$

$$A + A \xrightarrow[k_2]{} X \text{ (undesirable)}$$

They studied the effects of the selectivity parameter,

$q\left(q = \frac{F_B k_2}{F_A k_1}^{*}\right)$, on the yield of D at a given level of conversion for various types of reactors, and concluded that at higher values of conversion, yield is optimum if the selectivity is optimum, whereas at lower levels of conversion, the yield is more and more determined by conversion and is less dependent on selectivity.

Van de Vusse (35) has also discussed the relative merits of a plug flow and a tank reactor for the reaction scheme:

$$A \xrightarrow{k_1} B \xrightarrow{k_2} D$$

$$A + A \xrightarrow[k_3]{} X \, .$$

It is apparent that for high yields of B, a reactor with a short residence time is the best choice and hence a plug flow reactor should be chosen. However, the concentration of A in the plug flow reactor will be relatively high and this should favour the undesirable reaction. Thus, higher yield can be obtained only at the cost of selectivity. On the other hand in a tank reactor, where the concentration of A is relatively low and selectivity for B is much better, longer residence time will help the decomposition of B

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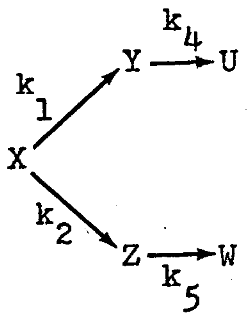
*F_B and F_A are flow rates of A and B.

and thus lower the yield of B. Van de Vusse (35) has shown that for $k_3C_A^o / k_1 > k_2/k_1$, the selectivity of B will be maximum at conversions greater than zero. Though Van de Vusse's (35) paper does not specify the conversions at which the yield and selectivity optima occur, the treatment does lead one to suspect that perhaps the yield and selectivity maxima do not occur at the same level of conversion of A. Also, one is tempted to speculate about the use of a series of c.s.t.rs to overcome the dilemma of the choice between a c.s.t.r and a plug flow reactor. Van de Vusse's study also gives rise to the following questions:

i. How many tanks are needed in a series of c.s.t.rs and what should be their sizes. Carberry and Gillespie (5 , 6) have suggested that for selectivity sensitive reactions (such as the Van de Vusse scheme), the use of a plug flow reactor with product recirculation can provide a way out of the dilemma of the choice between a plug flow reactor and a c.s.t.r. From a study of the 'Recirculation Model Reactor', Carberry et al (5, 6) conjectured that a 2-3 tank train of c.s.t.rs should suffice.

ii. Does maximum selectivity occur at meaningful levels of yield and if it does, are the same policies (tank sizes and operating temperatures) needed for yield and selectivity optimisation?

In addition to these theoretical studies, a number of experimental studies dealing with selectivity have also been done. Demaria, Longfield and Butler (8) conducted an experimental study to investigate selectivity of phthalic anhydride in the napthalene oxidation reaction. Spielman (32) did an experimental study of the oxidation of hydrocarbons according to the following schemes:



and $A \longrightarrow B \longrightarrow D$

(U, Y and Z) are the desirable products in the first scheme and B is the desirable one in the second scheme. Spielman (32) concluded that if the desirable products are degradable intermediates in a sequence of first order irreversible reactions, then

i. Selectivity in batch or plug flow reactors is higher than in a continuous stirred tank reactor for any conversion level.

ii. High conversion operation may be useless. An optimum practical yield of intermediate is obtained at relatively low conversion.

In case the desired products are terminal ones in a sequence of first order irreversible reactions, the above mentioned conclusions are reversed. It should be mentioned here that maximum selectivity in either of Spielman's (32) schemes occurs at zero conversion of the key reactant.

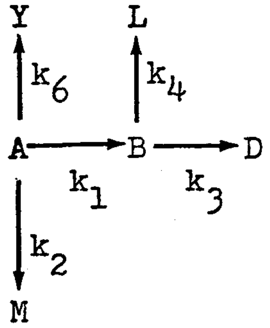
It is apparent that selectivity oriented reaction design has not received much attention thus far. Existence of optimal conditions for selectivity maxima as different from yield maxima has not been established. It is conceivable that optimal policies for selectiivty differ from those for yield. In this study certain complex schemes are explored for such possibilities.

CHAPTER III

SYSTEM DESCRIPTION

A. Kinetic Considerations

The reaction scheme,*



was chosen because it is complex enough to include most of the irreversible reactions met in industrial practice. B is the desired product in the scheme. Yield and selectivity with respect to B are defined by the following equations:

$$\eta_B \equiv \text{yield of B} \equiv \frac{\text{Amount of B Produced}}{\text{Amount of A Fed}} \qquad (1)$$

$$\sigma_B \equiv \text{selectivity for B} \equiv \frac{\text{Amount of B Produced}}{\text{Amount of A Consumed}} \qquad (2).$$

The effect of operating conditions on the selectivity and yield of B is first considered in a single reactor and then in a cascade of c.s.t.rs. Temperature and space time are the control variables. The objective is the optimisation

---

System parameters k_{oi} and E_i are listed in Appendix A of yield/selectivity. In addition, the order of certain reactions in the reaction scheme is varied to study its effect on the optimal conditions. It was decided to try first, ordinary calculus methods, and in case they failed, to use the 'Discrete Maximum Principle'. Because Halkin (20) and Holtzman's (19) criteria for using 'D.M.P.' are rather complicated, it was decided not to make an a priori check, but to verify the 'D.M.P.' optima by comparing them with optima obtained by a direct search method. The Hooke and Jeeves (21) method was chosen for this purpose.

For the sake of analytical simplicity, the following assumptions were made:

i. The tank reactors are ideal back mix reactors. Each can be maintained at any required temperature.

ii. The feed to the first tank consists of pure A. Initial feed concentration of A is = 1.0 gm moles/liter.

iii. There are no volume changes as a result of chemical reactions.

iv. There is no bypassing or recirculation of any stream.

B. Optimal Considerations

Case 1, reaction A ⟶ Y is of the second order. All the other reactions are of the first order.

a. Single c.s.t.r:

For a single reactor with feed consisting

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* Derivation of 'D.M.P.' (the weak version) as stated by Denn (12) is given in Appendix B .

of pure A, selectivity and yield of B are given by equations (3) and (4) respectively,

$$\sigma_B = \frac{k_1 x_1}{(k_1+k_2)x_1 + k_6(x_1)^2 + (k_3+k_4)(\overset{0}{x}_1 - x_1)} \qquad (3)$$

$$\eta_B = \frac{k_1 x_1(\overset{0}{x}_1 - x_1)}{\overset{0}{x}_1\left[(k_1+k_2)x_1 + k_6(x_1)^2 + (k_3+k_4)(\overset{0}{x}_1 - x_1)\right]} \qquad (4)$$

Maximum selectivity is given by equation (5) and the space time corresponding to this selectivity value is given by equation (7).

$$\left[\sigma_B\right]_{max} = \left[\frac{k_1}{(k_1+k_2) + k_6\overset{0}{x}_1\psi(2-\psi)}\right] \qquad (5)$$

where, $(\psi)^2 = (k_3+k_4)/(k_6\overset{0}{x}_1)$ (6)

$$\tau_{\left[\sigma_B\right]_{max}} = \frac{1-\psi}{(k_1+k_2)\psi + k_6\overset{0}{x}_1(\psi)^2} \qquad (7).$$

The maximum selectivity occurs at a conversion of A $>$ 0 if and only if

$$k_6\overset{0}{x}_1 > (k_3+k_4) \qquad (8).$$

The conversion of A corresponding to maximum σ_B is given as

$$x_1 = \overset{0}{x}_1 \psi \qquad (9).$$

The maximum yield of B is obtained when

$$x_1 = \lambda \overset{0}{x}_1 \qquad (10)$$

where,

$$\lambda = \frac{\sqrt{k_3 + k_4}}{\sqrt{k_3+k_4} + \sqrt{k_1+k_2+k_6\overset{0}{x}_1}} \qquad (11).$$

The corresponding expressions for $\left[\eta_B\right]_{\max}$ and ${}^{T}\left[\eta_B\right]_{\max}$ are:

$$\left[\eta_B\right]_{\max} \quad \frac{k_1\lambda(1-\lambda)}{(k_1+k_2)\lambda + k_6\overset{0}{x}_1(\lambda)^2+(k_3+k_4)(1-\lambda)} \qquad (12)$$

and,

$${}^{T}\left[\eta_B\right]_{\max} = \frac{1-\lambda}{\lambda\left\{(k_1+k_2) + k_6\overset{0}{x}_1\lambda\right\}} \qquad (13).$$

b. Series of c.s.t.rs:

1. System equations: The material balance for the nth reactor of the cascade is given by the following set of non-linear difference equations:

i. Component A

$$\overset{n-1}{x}_1 = \overset{n}{x}_1 + \left[(\overset{n}{k}_1+\overset{n}{k}_2)\overset{n}{x}_1 + k_6(\overset{n}{x}_1)^2\right]\overset{n}{\tau} \qquad (14)$$

ii. Component B

$$\overset{n-1}{x}_2 = \overset{n}{x}_2 + \left[(\overset{n}{k}_3+\overset{n}{k}_4)\overset{n}{x}_2 - \overset{n}{k}_1\overset{n}{x}_1\right]\overset{n}{\tau} \qquad (15)$$

where,

$$\overset{n}{k}_i = k_{oi}\, e^{-E_i/(R\overset{n}{T})} \qquad (16).$$

Equations (17) and (18) based on equations (14) and (15) respectively describe the evolution of the system:

$$\overset{n}{X}_1 = \left[\frac{-\left\{1+\overset{n}{\tau}(\overset{n}{k}_1+\overset{n}{k}_2)\right\} + \sqrt{\left\{1+\overset{n}{\tau}(\overset{n}{k}_1+\overset{n}{k}_2)\right\}^2 + 4\overset{n}{K}_6\overset{n}{\tau}\overset{n-1}{X}_1}}{2\overset{n}{K}_6\overset{n}{\tau}}\right] \qquad n=1,2,\ldots \quad (17)$$

$$\overset{n}{X}_2 = \left[\frac{2\overset{n}{K}_6\overset{n-1}{X}_2 + \overset{n}{k}_1 * \left\{-\left[1+\overset{n}{\tau}\left(\overset{n}{k}_1+\overset{n}{k}_2\right)\right] + \sqrt{\left[1+\overset{n}{\tau}(\overset{n}{k}_1+\overset{n}{k}_2)\right]^2 + 4\overset{n}{K}_6\overset{n}{\tau}\overset{n-1}{X}_1}\right\}}{2\overset{n}{K}_6\left(1+\overset{n}{\tau}(\overset{n}{k}_3+\overset{n}{k}_4)\right)}\right] \quad ,n=1,2,\ldots \quad (18).$$

Equation (19) redefines selectivity in a form useful for stage wise calculations,

$$\overset{n}{X}_3 = \frac{\overset{n}{X}_2}{1-\overset{n}{X}_1}, \qquad n=1,2,\ldots \quad (19)$$

It should be mentioned here that equation (18) gives yield of B according to equation (1).

2. Statement of the'Discrete Maximum Principle':

In the operation and design of a cascade of tank reactors, the two important parameters are the holding time and the operating temperature for the reactors. In order to compute these control variables for the optimal performance of the tank reactor train, two objective functions can be chosen. The selectivity'σ_B' is one and the yield'η_B'is the other. The 'Discrete Maximum Principle' described in the following pages can be used to decide the optimal policies for both of these objective functions.

For an N stage sequential process characterised by the transformation equations (20) and (21)

$$\overset{n}{\vec{x}} = \overset{n}{f}\,(\overrightarrow{\overset{n-1}{x}}, \overset{n}{\vec{q}}) \qquad n = 1,2,\dots N \quad (20),$$

$$\overset{o}{\vec{x}} = \vec{a}_o \quad (21),$$

the optimisation problem consists of maximisation (or minimisation) of a specified objective function.

$$\overset{T}{\vec{c}}\,\overset{N}{\vec{x}} = \sum_{i=1}^{S} c_i \overset{N}{x}_i \quad (22)$$

For an optimal choice of the nth stage decision vector $\overset{n}{\vec{q}}$, the stage wise Hamiltonian $\overset{n}{H}$, should be stationary with respect to the interior components of the vector $\overset{n}{\vec{q}}$ and maximum with respect to the components of $\overrightarrow{\overset{n}{q}}$ that lie on a constraint. This is the so-called weak maximum principle (12, 23). The stage wise Hamiltonian is defined as:

$$\overset{n}{H} = \sum_{i=1}^{S} \overset{n}{x}_i \overset{n}{z}_i \quad , \qquad n = 1,2,3,\dots N \qquad (23)$$

The vector $\overset{n}{z}$ is defined by the adjoint equations

$$\overset{n-1}{z}_i = \frac{\delta \overset{n}{H}}{\delta \overset{n-1}{x}_i} \qquad \begin{array}{l} i = 1,2,\dots S \\ n = 1,2,\dots N \end{array} \qquad (24),$$

with the boundary conditions

$$\overset{N}{z}_i = c_i \qquad (25).$$

The vector $\overrightarrow{\overset{n}{x}} \left[= \overset{n}{f}\,(\overrightarrow{\overset{n-1}{x}}\,,\ \overrightarrow{\overset{n}{q}}\,) \right]$ is usually called a state vector.

3. The 'D.M.P.' algorithm equations for selectivity optimisation:

For the system of c.s.t.rs under consideration, the state equations for selectivity optimisation process are given as

$$\overset{n}{X}_1 = \frac{-\left[1 + \overset{n}{\tau}\,(\overset{n}{k}_1 + \overset{n}{k}_2)\right] + \phi}{2\overset{n}{K}_6\,\overset{n}{\tau}} \qquad n = 1,2,\dots N \qquad (17)$$

$$\overset{n}{X}_2 = \frac{2\overset{n}{K}_6\overset{n-1}{X}_2 + \overset{n}{k}_1 * \left[- \left\{ 1 + \overset{n}{\tau}(\overset{n}{k}_1 + \overset{n}{k}_2) \right\} + \phi \right]}{2\overset{n}{K}_6 \left[1 + \overset{n}{\tau}(\overset{n}{k}_3 + \overset{n}{k}_4) \right]} \qquad n = 1,2,\ldots N \quad (18)$$

and

$$\overset{n}{X}_3 = \frac{2\overset{n}{K}_6\overset{n}{\tau}\,\overset{n-1}{X}_3(1-\overset{n-1}{X}_1) + \overset{n}{k}_1\overset{n}{\tau} * \left[- \left(1 + \overset{n}{\tau}(\overset{n}{k}_1 + \overset{n}{k}_2) \right) + \phi \right]}{\left[1 + \overset{n}{\tau}(\overset{n}{k}_3 + \overset{n}{k}_4) \right] * \left[2\overset{n}{K}_6\overset{n}{\tau} \left(1 + \overset{n}{\tau}(\overset{n}{k}_1 + \overset{n}{k}_2) - \phi \right) \right]} \qquad n = 1,2,\ldots N \quad (26),$$

where,

$$\phi = \sqrt{\left[1 + \overset{n}{\tau}(\overset{n}{k}_1 + \overset{n}{k}_2) \right]^2 + 4\overset{n}{K}_6\overset{n}{\tau}\,\overset{n-1}{X}_1} \qquad n = 1,2,\ldots N \quad (27).$$

The initial conditions for these state vectors are:

$$\overset{o}{X}_1 = 1.0 \qquad (28)$$

$$\overset{o}{X}_2 = 0.0 \qquad (29)$$

$$\overset{o}{X}_3 = 0.0 \qquad (30).$$

Condition (30) though not mathematically correct $\left(\frac{0}{0} \text{ form}\right)$ is physically reasonable.

The Hamiltonian is

$$\overset{n}{H}_{sel} = \overset{n}{X}_1\overset{n}{Z}_1 + \overset{n}{X}_2\overset{n}{Z}_2 + \overset{n}{X}_3\overset{n}{Z}_3 \qquad n = 1,2,\ldots N \quad (31).$$

The performance index is $\overset{N}{X}_3$, and the adjoint vector components are:

$$\overset{n}{Z}_1 = \overset{n-1}{Z}_1 \phi - \overset{n-1}{Z}_2 (\overset{n}{k}_1 \overset{n}{\tau}) - \left(\overset{n-1}{Z}_3 \Big/ (1-\overset{n-1}{X}_1)\right) * \left[(\overset{n}{k}_1 \overset{n}{\tau}) - \overset{n-1}{X}_3 \phi + \left(\frac{2\overset{n}{K}_6 \overset{n}{\tau}\, \overset{n-1}{X}_3 (1-\overset{n-1}{X}_1) - \overset{n}{k}_1 \overset{n}{\tau} \left[1+ \overset{n}{\tau}(\overset{n}{k}_1+\overset{n}{k}_2)\right] + \overset{n}{k}_1 \overset{n}{\tau} \phi}{2\overset{n}{K}_6 \overset{n}{\tau} + \left[1+\overset{n}{\tau}(\overset{n}{k}_1+\overset{n}{k}_2)\right] - \phi} \right)\right]$$

$$n = 1,2,\ldots N \qquad (32)$$

$$\overset{n}{Z}_2 = \overset{n-1}{Z}_2 \left[1+ \overset{n}{\tau}(\overset{n}{k}_3+\overset{n}{k}_4)\right] \qquad n = 1,2,\ldots N \qquad (33)$$

$$\overset{n}{Z}_3 = \overset{n-1}{Z}_3 \frac{\left(\left[1+ \overset{n}{\tau}(\overset{n}{k}_3+\overset{n}{k}_4)\right] * \left[2\overset{n}{K}_6 \overset{n}{\tau} + 1+\overset{n}{\tau}(\overset{n}{k}_1+\overset{n}{k}_2) - \phi\right]\right)}{2\overset{n}{K}_6 \overset{n}{\tau} (1-\overset{n-1}{X}_1)} \qquad n = 1,2,\ldots N \qquad (34)$$

The boundary conditions for these adjoint vector components are

$$\overset{N}{Z}_1 = 0 \qquad (35),$$

$$\overset{N}{Z}_2 = 0 \qquad (36),$$

and

$$\overset{N}{Z}_3 = 1 \qquad (37).$$

The decision variables are $\overset{n}{\tau}$ and $\overset{n}{T}$. $\overset{n}{T}$ enters the equations as $\overset{n}{k}_i = k_{oi}\, e^{-Ei/(R\overset{n}{T})}$. (16)

4. 'D.M.P. algorithm for yield optimisation:

Equations (17) and (18) are the only state equations needed for yield optimisation. The initial conditions for these equations are

$$\overset{o}{X}_1 = 1.0 \qquad (38)$$

$$\overset{o}{X}_2 = 0 \qquad (39).$$

The Hamiltonian for this case is

$$\overset{n}{H}_{yie} = \overset{n}{X}_1\overset{n}{Z}_1 + \overset{n}{X}_2\overset{n}{Z}_2 \qquad n = 1,2,\ldots N \qquad (40).$$

The performance index is $\overset{N}{X}_2$ and the adjoint vector components are

$$\overset{n}{Z}_1 = \phi\,\overset{n-1}{Z}_1 - (\overset{n}{k}_1\,\overset{n}{\tau})\overset{n-1}{Z}_2 \qquad n = 1,2,\ldots N \qquad (41)$$

and

$$\overset{n}{Z}_2 = \overset{n-1}{Z}_2\left[1+\overset{n}{\tau}(\overset{n}{k}_3+\overset{n}{k}_4)\right] \quad n = 1,2,\ldots N \qquad (42).$$

The boundary conditions for these adjoint vector components are

$$\overset{N}{Z}_1 = 0 \qquad (43)$$

$$\overset{N}{Z}_2 = 1 \qquad (44).$$

The control vector components are again $\overset{n}{\tau}$and $\overset{n}{T}$.

5. Computational procedure for determination of

$\overset{n}{\tau}$ and $\overset{n}{T}$.

In order to determine the optimum reactor policies for the various objectives (selectivity or yield), it is necessary to find the stationary points for the stage wise Hamiltonian as defined in equations (31) and (40) with the help of the corresponding state and adjoint equations. It is apparent that this involves the solution of a two point non-linear boundary value problem. Whereas the state vectors are known at $n = 0$, the adjoint vectors are known at $n = N$.

The optimal policies have meaning only if the control vector components do not exceed certain practical limits. For example the operating temperatures are usually limited by the nature of the material used in equipment construction. Therefore, it was decided to limit the operating temperature such that

$$50\overset{o}{K} \leq T \leq 1{,}000\ \overset{o}{K}.$$

Restrictions on the size of the reactors were also placed. However it should be mentioned that in the case of reactor size, optimal policies were determined for various upper limits of the reactor size. (A negligible holding time was taken as the lower limit for the reactor size). These upper limits on the holding size of the reactors are listed in tables (1-6).

The non linear two point boundary value problem can be solved by the boundary condition iteration technique.

A brief description of this method is given below:

i. Initial values $\overset{o}{Z}_i$, for the components of the adjoint vector are assumed.

ii. The available decision space is divided into a grid.

iii. The first stage Hamiltonian $\overset{1}{H}$ is calculated at various grid points. The values of $\overset{1}{T}$ and $\overset{1}{\tau}$ at which $\overset{1}{H}$ attains its maximum, are stored. The step (ii) and (iii) can be replaced by any other steps permitting calculation of the maximum of a function in a constrained decision space.

iv. The tentative optimal policies $(\overset{\bar{n}}{T}, \overset{\bar{n}}{\tau} --- \overset{\bar{N}}{T}, \overset{\bar{N}}{\tau})$ and the corresponding adjoint vector components $\overset{n}{Z}_i --- \overset{N}{Z}_i$ are computed and stored similarly.

v. If the computed $\overset{N}{Z}_i$ match the given values of $\overset{N}{Z}_i$ (for selectivity optimisation, equations (35-37) and for yield optimisation, equations (43-44)), the optimal policies are$(\overset{\bar{n}}{T}, \overset{\bar{n}}{\tau}\ \ n = 1,2,...N)$, and in case the computed values of $\overset{N}{Z}_i$and the given values of $\overset{N}{Z}_i$ do not match, an error function G,

$$G = \sum_{i=1}^{i=2\text{or}3} \left[\overset{N}{Z}_i(\text{computed}) - \overset{N}{Z}_i(\text{given}) \right]^2 \qquad (45),$$

is minimised by any of the direct search techniques. In this study the Hooke-Jeeves (21) pattern search method was used, and when $G \leq \epsilon$, the iteration on the boundary conditions was stopped. The results are tabulated in tables (1-6).

Case 2, Reaction $A \longrightarrow B$ is of the second order. All other reactions are of the first order. For a single reactor, the selectivity with respect to B is given by equation (46)

$$\sigma_B = \frac{k_1 x_1^2}{(k_2+k_6)x_1 + k_1 x_1^2 + (\overset{o}{x}_1 - x_1)(k_3+k_4)} \qquad (46).$$

In order that σ_B is maximum at a conversion of $A > 0$, it is necessary that

$$(k_3+k_4) + (k_2+k_6) < 0 \qquad (47).$$

It is obvious that it is impossible to physically fulfill condition (47). This case was therefore not investigated any further.

CHAPTER IV

RESULTS

TABLE I

Optimal policies for selectivity optimisation, single c.s.t.r.

$T_{U-L} = 1{,}000\,^{\circ}K$ $T_{L-L} = 50\,^{\circ}K$

τ_{U-L}(min)	$\overset{1}{T}$($^{\circ}$K)	$\frac{1}{\tau}$ (min)	%$(\sigma_B)_{max}$
512.000	229.843	442.055	99.506
64.000	240.000	58.035	99.350
32.000	245.468	31.264	99.275
16.000	249.062	15.439	99.208
8.000	256.250	7.624	99.055

TABLE 2

Optimal policies for selectivity optimisation, two c.s.t.rs.

$T_{U-L} = 1{,}000\,^\circ K$ $\quad$ $T_{L-L} = 50\,^\circ K$

τ_{U-L}(min)	$\overset{1}{T}$ ($^\circ$K)	$\overset{1}{\tau}$(min)	$\overset{2}{T}$ ($^\circ$K)	$\overset{2}{\tau}$(min)	$\%(\sigma_B)_{max}$
512.000	233.700	512.000	247.225	102.366	99.409
64.000	249.877	61.337	253.522	40.814	99.202
32.000	251.578	29.668	262.521	6.543	99.054
16.000	257.433	15.856	265.370	3.256	98.978
8.000	245.066	2.583	256.226	4.306	97.524

Table 3

Optimal policies for selectivity optimisation, three c.s.t.rs.

$T_{U-L} = 1{,}000\,^{\circ}K$ $T_{L-L} = 50\,^{\circ}K$

τ_{U-L} (min)	$\overset{1}{T}$ ($^{\circ}K$)	$\overset{1}{\tau}$(min)	$\overset{2}{T}$ ($^{\circ}K$)	$\overset{2}{\tau}$(min)	$\overset{3}{T}$($^{\circ}K$)	$\overset{3}{\tau}$(min)	%$(\sigma_B)_{max}$
512.000	236.704	300.800	242.236	209.408	244.151	103.680	99.375
64.000	242.422	60.441	251.834	38.013	250.988	37.984	99.237
32.000	253.062	28.800	257.903	22.000	260.778	24.400	99.104
16.000	253.373	15.284	262.472	15.390	261.607	15.266	99.041
8.000	259.139	7.250	253.375	6.600	264.726	6.600	98.913

TABLE 4

Optimal policies for yield optimisation, single c.s.t.r.

$T_{U-L} = 1{,}000\,^{\circ}K$ $T_{L-L} = 50\,^{\circ}K$

τ_{U-L} (min)	$\frac{1}{T}$ ($^{\circ}K$)	$\frac{1}{\tau}$ (min)	$\%(\eta_B)_{max}$
512.000	275.000	512.000	93.929
64.000	296.953	63.981	89.664
32.000	304.921	31.991	87.658
16.000	313.359	15.997	85.282
8.000	322.187	8.000	82.475

TABLE 5

Optimal policies for yield optimisation, two c.s.t.rs.

$T_{U-L} = 1{,}000\overset{o}{K}$ $\quad$ $T_{L-L} = 50\overset{o}{K}$

τ_{U-L} (min)	$\overset{1}{T}$ ($\overset{o}{K}$)	$\overset{1}{\tau}$(min)	$\overset{2}{T}$ ($\overset{o}{K}$)	$\overset{2}{\tau}$(min)	$\%(\eta_B)_{max}$
512.000	261.170	509.107	265.613	447.213	97.787
64.000	285.689	61.542	285.051	61.656	95.804
32.000	293.363	32.000	292.794	31.986	94.776
16.000	302.401	15.776	301.954	15.300	93.318
8.000	310.381	7.872	310.023	7.970	91.610

TABLE 6

Optimal policies for yield optimisation, three c.s.t.rs.

$T_{U-L} = 1{,}000\,^{\circ}K$ $T_{L-L} = 50\,^{\circ}K$

τ_{U-L} (min)	$\overset{1}{T}$ (°K)	$\overset{1}{\tau}$(min)	$\overset{2}{T}$ (°K)	$\overset{2}{\tau}$(min)	$\overset{3}{T}$(°K)	$\overset{3}{\tau}$(min)	%$(\eta_B)_{max}$
512.000	253.434	509.911	265.074	189.224	264.616	231.624	98.424
64.000	275.493	63.528	277.165	63.571	278.598	63.255	97.379
32.000	284.338	31.859	285.862	31.846	285.832	31.950	96.657
16.000	293.927	15.946	295.624	15.955	296.035	15.986	95.643
8.000	302.970	7.982	302.317	7.925	301.765	7.974	94.408

CHAPTER V

DISCUSSION OF RESULTS AND CONCLUSIONS

A. Discussion of Results:

The optimal conditions for a single reactor were calculated by the pattern search technique (21). Also, the results obtained by using the 'D.M.P.' were compared with those obtained by direct pattern search. The results obtained through these two different methods were in agreement with each other within 2%. Since reactions are more sensitive to temperature than they are to the size of a reactor , the ratio $(\Delta T/\Delta \tau) = 4.0$ was used in constructing the grid for locating the maximum of a stage wise Hamiltonian. The same ratio was used in pattern search movements. The value of ϵ (p.28) was chosen as $0.1*10^{-7}$. It should be mentioned here that the boundary condition iteration technique was found to be rather an inefficient method. The total IBM 1620 II time consumed for this study was about ten hours.

It is apparent from equations(7) and (13) that different reactor sizes are needed for optimising selectivity as opposed to yield. A consideration of tables (1-6) shows clearly that optimal policies $(T, \tau)$for yield and selectivity optimisation are different from each other.

A consideration of tables (1-6) also shows that whereas the yield with respect to B increases with the increasing number of reactors, the selectivity with respect to B displays an opposite trend. This confirms Van de Vusse's (35) observation that in selectivity sensitive reactions (such as Case 1 of this study), it is good to use a tank reactor for selectivity optimisation and a plug flow reactor for yield optimisation.

B. Conclusions:

1. For a complex reaction scheme, in which the maximum selectivity with respect to an intermediate corresponds to a positive definite conversion of the key reactant; the optimal policies for yield and selectivity maximisation are distinctly different. Thus it is erroneous to consider yield as the sole performance criterion.

2. The boundary condition iteration technique was found to work for the solution of the non linear optimisation problem, but convergence difficulties resulted in the consumption of a large amount of computer time.

APPENDIX A

SYSTEM PARAMETERS

$K_i = K_{oi} e^{-E_i/RT}$

$K_{oi} = \frac{\text{Liters, gm moles}}{\text{Minutes}}$ or $\frac{1}{\text{Minutes}}$

$K_{01} = 28.e^{13.75}$

$E_1 = 11.000$ Kcal

$K_{02} = 0.8e^{16.25}$

$E_2 = 13.000$ Kcal

$K_{03} = 0.84e^{31.25}$

$E_3 = 25.000$ Kcal

$K_{04} = 3.e^{25.}$

$E_4 = 20.000$ Kcal

$K_{06} = 8.e^{22.5}$

$E_6 = 18.000$ Kcal

APPENDIX B

DISCRETE MAXIMUM PRINCIPLE (WEAK VERSION)

$$\text{Let } \overset{n}{x} = \overset{n}{P}(\overset{n-1}{x}, \overset{n}{q}) \qquad n = 1,2,\ldots N \qquad (1A)$$

describe the evolution of a discrete system, x is an s dimensional state vector and q is a t dimensional decision vector. Let $\overset{\overline{n}}{x}$, n = 1,2,...N represent the state resulting from the optimum decisions $\overset{\overline{n}}{q}$, n = 1,2,...N, then

$$\overset{\overline{n}}{x} = \overset{n}{P}(\overset{\overline{n-1}}{x}, \overset{\overline{n}}{q}) \qquad n = 1,2,\ldots N \qquad (2A).$$

If the following independent small perturbations of $\overset{\overline{n}}{q}$ are made at each stage,

$$\overset{n}{q} = \overset{\overline{n}}{q} + \epsilon \overset{n}{\varphi} \qquad n = 1,2,\ldots N \qquad (3A),$$

the disturbance then will alter $\overset{\overline{n}}{x}$ to

$$\overset{n}{x} = \overset{\overline{n}}{x} + \epsilon \overset{n}{y} + 0(\overset{2}{\epsilon}) \qquad (4A),$$

where $\overset{n}{\varphi}$ is a t dimensional vector, $\overset{n}{y}$ is an s dimensional vector, ϵ is a positive parameter of first order smallness, and $0(\overset{2}{\epsilon})$ represents quantities of an order of smallness greater than one. It is also assumed that y and φ are independent of ϵ. From equation (1A), (2A) and (4A) one can write

$$\epsilon \overset{n}{y} = \overset{n}{P}(\overset{n-1}{x}, \overset{n}{q}) - \overset{n}{P}(\overset{\overline{n-1}}{x}, \overset{\overline{n}}{q}) + 0(\overset{2}{\epsilon}) \qquad (5A).$$

Equation (5A) can be expanded in Taylor series to give equation (6A),

$$\epsilon y_i^{n} = \sum_{j=1}^{s} \epsilon y_j^{n-1} \left[\frac{\delta P_i^{n}}{\delta x_j^{n-1}} \left(\overline{x}^{n-1}, \overline{q}^{n} \right) \right] + P_i^{n} \left(\overline{x}^{n-1}, q^{n} \right)$$

$$- P_i^{n} \left(\overline{x}^{n-1}, \overline{q}^{n} \right) + O\left(\epsilon^{2}\right)$$

$i=1,2,\ldots\ s, \quad n=1,2,\ldots N$ (6A).

If the equation (6A) is multiplied by Z_i^{n} (the ith component of an s dimensional vector Z^{n}) and summed up over i=1 to i=s, the resulting equation can be written as

$$\sum_{i=1}^{s} \epsilon y_i^{n} Z_i^{n} = \sum_{i=1}^{s} \sum_{j=1}^{s} \epsilon y_j^{n-1} \frac{\delta P_i^{n}}{\delta x_j^{n-1}} \left(\overline{x}^{n-1}, \overline{q}^{n}, \right) Z_i^{n} + \sum_{i=1}^{s} P_i \left(\overline{x}^{n-1}, q^{n} \right) Z_i^{n}$$

$$\sum_{i=1}^{s} P_i \left(\overline{x}^{n-1}, \overline{q}^{n} \right) Z_i^{n} + O\left(\epsilon^{2}\right) \qquad (7A).$$

If,

$$Z_j^{n-1} \equiv \sum_{i=1}^{s} \frac{\delta P_i^{n}}{\delta x_j} \left(x^{n-1}, q^{n} \right) Z_i^{n} \qquad (8A)$$

Equation (7A) can be written as

$$\sum_{i=1}^{s} \left[\epsilon y_i^{n} Z_i^{n} - \epsilon y_i^{n-1} Z_i^{n-1} \right] = \sum_{i=1}^{s} \left[P_i \left(\overline{x}^{n-1}, q^{n} \right) Z_i^{n} - P_i \left(\overline{x}^{n-1}, \overline{q}^{n} \right) Z_i^{n} \right]$$

$$+ O\left(\epsilon^{2}\right) \qquad (9A).$$

Summing over n=1 to n=N yields

$$\epsilon \sum_{i=1}^{s} \left(y_i^N Z_i^N - y_i^o Z_i^o \right) = \sum_{n=1}^{N} \sum_{i=1}^{s} \left[P_i\left(\overline{x^{n-1}}, q^n\right) - P_i\left(\overline{x^{n-1}}, \overline{q^n}\right) \right] Z_i^n + O\left(\epsilon^2\right) \qquad (10A)$$

Since the initial conditions are fixed, $y_i^o = 0$, equation (10A) becomes

$$\epsilon \sum_{i=1}^{s} y_i^N Z_i^N = \sum_{n=1}^{N} \sum_{i=1}^{s} \left(P_i\left(\overline{x^{n-1}}, q^n\right) - P_i\left(\overline{x^{n-1}}, \overline{q^n}\right) \right) Z_i^n + O\left(\epsilon^2\right) \qquad (11A).$$

It can be postulated that $Z_i^N = c_i$

where c_i is defined as,

$$\text{Objective function O.F.} = \sum_{i=1}^{s} c_i x_i^N \qquad (12A)$$

Equation (12A) when substituted in equation (11A) gives

$$\epsilon \sum c_i y_i^N = \sum_{n=1}^{N} \sum_{i=1}^{s} \left[P_i\left(\overline{x^{n-1}}, q^n\right) - P_i\left(\overline{x^{n-1}}, \overline{q^n}\right) \right] Z_i^n + O\left(\epsilon^2\right) \qquad (13A)$$

The objective function, O.F. as a result of the perturbation described by equation (3A), can be described as

$$\text{O.F.} = \sum_{i=1}^{s} c_i \overline{x_i^N} + \sum_{i=1}^{s} \epsilon c_i y_i^N + O\left(\epsilon^2\right) \qquad n=1,2,\ldots N \qquad (14A).$$

Since $\overline{q^n}$, $n=1,2,\ldots N$ is the optimal trajectory i.e. it maximizes O.F. the effect of perturbation represented by equation (3A) can only be to make

$$\sum_{i=1}^{s} \epsilon c_i y_i^N \le 0 \qquad (15A)$$

If equation (13A) is expanded in Taylor series and combined with equation (15A) one can obtain

$$\left\{ \sum_{n=1}^{N} \sum_{j=1}^{t} \left(\epsilon \overset{n}{\varphi}_j\right) \sum_{i=1}^{s} \overset{n}{Z}_i \frac{\delta \overset{n}{P}_i\left(\overline{\overset{n-1}{x}}, \overset{\bar{n}}{q}\right)}{\delta \overset{\bar{n}}{q}_j} + 0\left(\overset{2}{\epsilon}\right) \right\} \leq 0$$

n=1,2,... N (16A)

Equation (16A) can also be written as

$$\sum_{n=1}^{N} \sum_{j=1}^{t} \left(\overset{n}{q}_j - \overset{\bar{n}}{q}_j\right) \sum_{i=1}^{s} \overset{n}{Z}_i \frac{\delta \overset{n}{P}_i\left(\overline{\overset{n-1}{x}}, \overset{\bar{n}}{q}\right)}{\delta \overset{\bar{n}}{q}_j} + 0\left(\overset{2}{\epsilon}\right) \leq 0$$

n=1,2,... N (17A)

Since the perturbated decision vectors $\overset{n}{q}$, n=1,2,... N are assumed to be independent of each other, therefore,

$$\left\{ \sum_{j=1}^{t} \left(\overset{n}{q} - \overset{\bar{n}}{q}\right) \sum_{i=1}^{s} \overset{n}{Z}_i \frac{\delta \overset{n}{P}_i\left(\overline{\overset{n-1}{x}}, \overset{\bar{n}}{q}\right)}{\delta \overset{\bar{n}}{q}_j} + 0\left(\overset{2}{\epsilon}\right) \right\} \leq 0$$

n=1,2,... N (18A)

If $\overset{n}{H} \equiv \sum_{i=1}^{s} \overset{n}{Z}_i P_i\left(\overset{n-1}{x}, \overset{n}{q}\right)$ (19A),

equation (18A) can be written as

$$\left[\sum_{j=1}^{t} \epsilon \overset{n}{\varphi}_j \frac{\delta \overset{n}{H}}{\delta \overset{n}{q}_j} + 0\left(\overset{2}{\epsilon}\right) \right] \leq 0 \qquad (20A).$$

For the stage where the condition $\left(\delta \overset{n}{H} \big/ \delta \overset{n}{q}\right) = 0$ gives the value of $\overset{\bar{n}}{q}$ outside the admissable region, the optimal decision policy usually occurs at the boundary points. Since $\frac{\delta \overset{n}{H}}{\delta \overset{n}{q}} \not\leq 0$, the sign of the ℓ.h.s. of the equation

(20A) is decided by the term $\sum_{j=1}^{t} \epsilon \overset{n}{\varphi}_j \frac{\delta \overset{n}{H}}{\delta \overset{n}{q}_j}$ which is of the order ϵ. It is obvious therefore, that the condition $\sum_{j=1}^{t} \epsilon \varphi \left(\frac{\delta \overset{n}{H}}{\delta \overset{n}{q}}\right)_j < 0$ is equivalent to the condition $\overset{n}{H}=$ maximum.

When the Hamiltonian $\overset{n}{H}$ is stationary i.e. $\frac{\delta \overset{n}{H}}{\delta \overset{n}{q}} = 0$, the sign of the ℓ.h. side of the equation (20A) is decided by the term $0\left(\overset{2}{\epsilon}\right)$, which can be negative , zero or positive. However, it is apparent that a stationary value of $\overset{n}{H}$ corresponds to a stationary value of the Objective Function. This conclusion led Jackson et al(23) to state "- in general the nature of the stationary values of the O.F. and the $\overset{n}{H}$ are unrelated; in other words it is not generally true that $\overset{n}{H}$ must be maximised to maximise the O.F."

NOMENCLATURE

Latin Letters

E_i = energy of activation, K. cal.

H = Hamiltonian, defined in equation (23)

K_6 = $k_6 \overset{o}{x}_1$

N = maximum number of stages in a sequential process

X_i = $(x/ \overset{o}{x}_i)$ $i=1,2$

X_3 = selectivity component of the state vector, defined in equation (19)

T = temperature $\overset{o}{K}$

Z = adjoint vector, defined in equation (24)

k_i = specific reaction rate constant

k_{oi} = pre-exponential factor

q = decision vector

Greek Letters

ϵ = a small number

η_B = yield of B, defined in equation (1)

λ = dimensionless parameter, defined in equation (11)

σ_B = selectivity with respect to B, defined in equation (2)

τ = reactor space time, minutes

ϕ = dimensionless parameter, defined in equation (27)

ψ = dimensionless parameter, defined in equation (6)

Superscripts

T = transpose of a vector

n = nth stage

0 = initial condition

s = number of components in a vector

t = number of components in a vector

Subscripts

sel = selectivity

yie = yield

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PART IV

REACTOR SIMULATION FOR THE HYDROGEN FLOURIDE REACTION——FLOURSPAR + SULPHURIC ACID → PRODUCTS.

ABSTRACT

A model has been proposed to simulate the Hydrogen Flouride reaction— Flourspar + H_2SO_4 — occurring in an externally heated, centrally stirred, rotary tubular reactor. The model takes into account the diffusional transport of Mass and Heat inside flourspar particles of various sizes. It is proposed to compare the theoretically predicted consumption of H_2SO_4 with the experimentally determined consumption of the sulphuric acid.

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CHAPTER I

INTRODUCTION

Although the Hydrogen Flouride reaction— Flourspar + H_2SO_4 — is of commercial importance, there is very little information available about it in the published literature. An experimental investigation is being carried out with the objective of establishing the optimal design conditions required for the production of HF from this reaction.

The reaction is usually carried out in a rotary tubular reactor fitted with a central stirrer. The externally heated reactor is continuously fed at one end with finely ground flourspar and preheated sulphuric acid. At the other end, the products of the reaction are taken out; the gaseous products being sent to the HF Scrubber and the solid ones being dumped.

As a preliminary step in establishing the optimum conditions for the production of HF, it was decided to simulate the reactor mathematically, and to compare the predicted consumption of H_2SO_4 with the experimentally deterimed consumption of the sulphuric acid. In case an agreement is achieved between the theoretical and experimental consumption of H_2SO_4, the simulation process can be extended to predict the yield of HF and finally to establish the optimum operating conditions required for the production of HF.

CHAPTER II

REACTOR SIMULATION

A. Kinetic Considerations

The commercial Hydrogen Flouride reaction can be written as,

$$CaF_2 + H_2SO_4 \longrightarrow CaSO_4 + 2HF + \Delta H_1 \qquad (1)$$

$$CaCO_3 + H_2SO_4 \longrightarrow CaSO_4 + H_2O + CO_2 + (-\Delta H_2) \qquad (2)$$

$$4HF + SiO_2 \longrightarrow SiF_4 + 2H_2O + (-\Delta H_3) \qquad (3)$$

The reactions (2) and (3) are exothermic, whereas (1) is endothermic. The heats of reaction data are available in (2). It has been established (1) that reactions (1) and (2) are of first order with respect to H_2SO_4 and are of zero order with respect to the solids involved. It is assumed that flourspar is present in the form of porous spherical particles of various sizes* and that the reaction is not limited to any reaction front, but takes place throughout the body of the particle. The last assumption provides the theoretical investigator considerable flexibility in fitting the experimental data to theoretical models, by simply varying the required Thiele modulus.

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* For size analysis, see (2).

B. Thermal Considerations

The design of the experimental set-up does not lend itself to a detailed sketching of the thermal regime prevailing inside the reactor. However, after examining the experimental data available, the following assuptions can be made:

i. The ambient temperature across a cross-section of the reactor is constant but thermal gradients exist inside the porous solids. This assumption can be justified on the ground that the rotary movement of the reactor produces a thorough mixing of the materials across any cross-section of the tubular reactor.

ii. The axial variation of temperature along the reactor length can be represented by a step function.

C. Reactor Model

Residence time studies (3) reveal that the reactor behavior falls in between the ideal plug flow reactor and an ideal c.s.t.r. behavior. It was decided therefore to use an axial diffusion model for simulating the reactor, and to adjust the Peclet number to conform with the actual behavior of the reactor.

D. Mass and Heat Balance Equations for the Reactor

With these assumptions, the mass balance for a differential length of the reactor under steady state conditions can be written as,

$$\underset{\text{Convective transport}}{\frac{\delta}{\delta Z}\left(UC_A\right)} - \underset{\text{axial diffusion}}{\frac{\delta}{\delta Z}\left(D_{Aax}\frac{\delta C_A}{\delta Z}\right)} + \underset{\text{chemical reaction}}{\tilde{R}} = 0 \qquad (4),$$

where $\tilde{R}$ is given as

$$\tilde{R} = 4\pi N \sum_{i=1}^{m} D_{Ai} n_i r_{io}^2 \left.\frac{\delta C_A}{\delta r}\right|_{r=r_{io}} \qquad (5)$$

and

$$\sum_{i=1}^{m} n_i = 1 \qquad (6)$$

The boundary conditions for equation (4) have been suggested by Wehner and Wilhelm (4) to be

$$Z = 0, \qquad UC_A(o_-) = UC_A(o_+) - D_{Aax}\left(\frac{\delta C_A}{\delta Z}\right)_{Z=o_+}$$

and,

$$Z = L, \qquad UC_A(L_-) - D_{Aax}\left(\frac{\delta C_A}{\delta Z}\right)_{Z=L} = UC_A(L_+)$$

For all practical purposes these boundary conditions can be written as

$$Z = 0\ ; \qquad C_A = \overset{o}{C}_A \qquad (7)$$

$$Z = L\ , \qquad \left.\frac{\delta C_A}{\delta Z}\right|_{Z=L} = 0 \qquad (8)$$

The term $\tilde{R}$ in equation (4) can be evaluated with the help of mass and heat balances over the various spherical particles. The resulting equations for steady state conditions are given on the next page:

$$* \quad \frac{\delta^2 C_A}{\delta r_i^2} + \frac{2}{r_i}\frac{\delta C_A}{\delta r_i} - \sum_{j=1}^{2}\rho \frac{k_j}{D_{Aj}} C_A = 0 \qquad i=1,2,\ldots \quad m \qquad (9),$$

$$C_A = C_A(Z) \; ; \qquad r_i = r_{io} \qquad i=1,2,\ldots \quad m \qquad (10)$$

$$\frac{\delta C_A}{\delta r} = 0 \quad \text{or,} \quad C_A = \text{finite at } r_i = 0 \qquad i=1,2,\ldots \quad m \qquad (11).$$

Equation (10) states the assumption that there is no resistance to diffusion of H_2SO_4 to the outer surface of the particles.

The specific reaction rate constants k_j, j=1,2 are defined as

$$k_j = k_{oj}e^{-E_j/(RT)} \qquad (12)$$

where $T = T(r_i, Z)$

A differential heat balance can be written for the spherical particle as follows:

$$K_{ci}\frac{\delta^2 T}{\delta r_i^2} + K_{ci}\frac{2}{r_i}\frac{\delta T}{\delta r_i} - \sum_{j=1}^{2}\rho\Delta H_j\left(k_{oj}e^{\left(-E_j/RT\right)}\right)C_A = 0$$

$$i=1,2,\ldots \quad m \qquad (13)$$

The boundary conditions for equation (13) are

$$T = T(Z) \qquad r = r_{io}$$

$$i=1,2,\ldots \quad m \qquad (14)$$

$$\frac{\delta T}{\delta r} = 0 \quad \text{or } T = \text{finite at } r_i = 0$$

$$i=1,2,\ldots \quad m \qquad (15)$$

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* Although ρ has been assumed to be constant in this analysis it could very well be a function of reactor length in the actual case.

E. Non-dimensional Equations for Reactor Simulation

If the coefficient for axial diffusion, D_{Aax} and the effective diffusivities (D_{Ai}) and effective conductivities (K_{ci}) can be assumed constant, equations (4 - 15) can be non-dimensionalised. These non-dimensionalised equations are listed below.

1. Overall Reactor Mass Balance

Equations (16 - 19) describe the over-all mass balance for the reactor

$$\frac{\delta\Phi_A}{\delta X} - N_{Pe}\frac{\delta^2\Phi_A}{\delta X^2} + 4\pi(ND_A L\tau)\sum_{i=1}^{m} n_i y_{io}^2 \left.\frac{\delta\Phi_A}{\delta y_i}\right|_{y=y_{io}} = 0 \qquad (16)$$

$$\sum_{i=1}^{m} n_i = 1 \qquad (17)$$

$$\Phi_A = 1 \qquad X = 0 \qquad (18)$$

$$\frac{\delta\Phi}{\delta X} = 0 \qquad X = 1 \qquad (19).$$

2. Mass Balances for Individual Particles:

Equations (20 - 22) represent the mass balance over individual particles.

$$\frac{\delta^2\Phi_A}{\delta y_i^2} + \frac{2}{y_i}\frac{\delta\Phi_A}{\delta y_i} - \sum_{j=1}^{2} h_j^2\,\Phi_A = 0 \qquad i=1,2,\ldots\ m \quad (20)$$

$$\phi_A = \phi_A(X) \quad ; \quad y_i = y_{io} \qquad i=1,2,\dots \quad m \qquad (21)$$

and

$$\frac{\delta \phi_A}{\delta y_i} = 0 \quad \text{or} \quad \phi_A = \text{finite} \quad \text{at } y_i = 0, \quad i=1,2,\dots \quad m \qquad (22)$$

3. Heat Balance Equations for Individual Particles:

Equations (23 - 25) give the heat balance over individual particles in non-dimensional form.

$$\frac{\delta^2\theta}{\delta y_i^2} + \frac{2}{y_i}\,\frac{\delta \theta}{\delta y_i} - \sum_{j=1}^{2} \phi_A \left(\frac{\overset{o}{C}_A \, \rho \Delta H_j \, k_{oj} \, L^2}{\overset{o}{T} \, K_{ci}} \right) \text{EXP}\left[- \left(E_j \Big/ R\overset{o}{T} \right) \Big/ \theta \right] = 0$$

$$i=1,2,\dots \quad m \qquad (23)$$

$$\theta = \theta(X) \qquad y_i = y_{io} \qquad (24)$$

$$\theta = \text{finite} \;, \quad \frac{\delta\theta}{\delta y} = 0 \quad \text{at } y_i = 0$$

$$i=1,2,\dots \quad m \qquad (25).$$

F. Solution of the Non-dimensional Equations:

Solution of equations (16 - 19) with the help of equations (20 - 25) can be attempted numerically. Such a solution can predict the exit concentration of H_2SO_4 from the reactor. A comparison with the experimental results can then be used for the validification of the theoretical model. It should be mentioned here that if the energy balance equations (23 - 25) are neglected, the solution for the resulting isothermal case can be found easily by using the standard finite difference techniques (5). The simultaneous solution of equations (16 - 25) is however much more difficult.

The theoretical considerations presented in this part will form the basis for the interpretation of the forthcoming experimental data.

NOMENCLATURE

C_A = Concentration of H_2SO_4 (gm moles/cm^3 of the bed material)

D_{Aax} = Axial diffusion coefficient (cm^2/sec)

D_{Ai} = Effective diffusivity of 'A' in the spherical particles (cm^2/sec)

E_j = Energy of activation for the jth reaction (Cal/gm moles)

H_j = Heat of reaction for the jth reaction (Cal/gm moles)

K_c = Effective thermal conductivity of 'A' in the solid particle Cal/(cm)(sec)(K^o)

L = Reactor length (cms)

N = Number of particles in a unit volume of the reactor bed (1/cm^3)

N_{Pe} = (D_{Aax}/UL)

R = Chemical reaction term

T = Reactor temperature ^oK

U = Linear velocity of solids in the reactor cm/sec

X = (Z/L) dimensionless coordinate along the reactor length

Z = Coordinate along the reactor length

h_j = Thiele Modulus $L\sqrt{\rho k_j/D_{Aj}}$ for the jth reaction

k_j = Specific reaction rate constant for the jth reaction $cm^3/(sec, gms\ solids)$

k_{0j} = Pre-exponential factor for the jth reaction

n_i = Fraction of a certain size of particles

r_{i0} = Radius of the ith group of particles

y_i = Dimensionless coordinate (r_i/L)

Greek Letters

θ = Dimensionless temperature $(T/\overset{o}{T})$

ρ = Density of the bed (gm/cm^3)

τ = (L/U) the reactor residence time

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