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STUDIES IN GAS – LIQUID REACTIONS

A THESIS SUBMITTED TO THE
UNIVERSITY OF NAGPUR
FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY
IN

CHEMICAL ENGINEERING

[illegible]

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B. D. Kulkarni

SYNOPSIS

The thesis is concerned primarily with gas-liquid reactions. The main objective of the studies is to formulate a generalised procedure for gas-liquid reactions which can also be applied to gas-solid catalytic reactions under certain limiting conditions. In addition, experimental results are presented for a system of practical importance [chlorohydrination of ethylene]. In the last chapter of the thesis a theoretical analysis of the role of catalyst fouling is presented for different situations. The chief features of the theoretical and experimental work presented in the thesis are outlined below.

A detailed analysis of gas-liquid reactions is made and a mathematical model which explains the diffusion-reaction behaviour of heterogeneous systems developed. Gas-solid catalytic reactions represent a limiting situation of this general model. The effectiveness factors for gas-liquid reactions are represented by regions which, under appropriate limiting conditions, degenerate to a line for gas-solid catalytic reactions.

The concept of the effectiveness factor is extended to a p^{th} order reaction and a generalised expression for the effectiveness factor obtained. This expression, under appropriate limiting conditions, is shown to represent the gas-liquid and gas-solid reactions. The results obtained indicate that the generalised approach can be used to formulate a unified diffusion-reaction theory for all heterogeneous systems.

The case of gas absorption under nonisothermal conditions is examined in the light of developments discussed above. A kinetic boundary condition at the interface for the liquid component B is proposed, and qualitative and approximately quantitative features of the system are evaluated. The results indicate that unlike in cases mentioned above, β [the newly defined gas-liquid parameter] alone is not sufficient to generalise the gas-liquid and gas-solid systems, but requires that the Thiele modulus based on the surface rate constant is also zero simultaneously. The surface tension driven instability [Marangoni instabilities] encountered in many gas-liquid systems is impossible under nonisothermal conditions.

A mathematical model is developed to compute the optimum gas phase composition for the case of simultaneous absorption of two gases which react between themselves, so as to get the maximum yield. The constraint of fluxes [for reactants A and B] being present in their stoichiometric amounts at the end of the film is imposed on the governing differential equation and variational methods of calculus are used to get the solution.

An analysis of the complex reaction scheme representing the reactions encountered in the manufacture of propylene oxide was carried out earlier in this Laboratory using the non-linear exponential profile. The exact results could not be obtained then because of the complex mathematical formulation. Suitable methods are devised now to get a more accurate solution [within 3% of the exact solution].

Experiments to get the intrinsic kinetics of the reaction

$$HOCl + C_2H_4[g] \rightarrow C_2H_4OHCl$$

encountered in the manufacture of ethylene oxide [or propylene oxide] have been completed. The data are analysed in terms of the regimes of operation.

As pointed out in the above sections one of the objectives of the present work in gas-liquid reactions is to provide a common basis for the analysis of the role of diffusion in gas-liquid and gas-solid catalytic reactions. Arising out of this, some theoretical studies are also reported on gas-solid catalytic systems.

The design of a fixed bed reactor with a deactivating catalyst is a complex problem, primarily because of the wide variety of deactivation processes involved. A mathematical model is developed for the case of nonisothermal catalyst fouling with no diffusion.

A two-dimensional model for the fixed bed reactor with internal diffusion and catalyst deactivation is then developed for a general order reaction. The effect of the deactivation process on the apparent order of reaction is evaluated for the case of pore mouth poisoning.

The effect of nonuniform deposition of catalyst on the carrier support is then examined for a general order reaction. The governing nonlinear differential equation is transformed into an Emden-Fowler type of equation using suitable transformations,

and its asymptotic solutions are presented, verifying the previously known general conclusions for a first order reaction. The expressions obtained can be used for a wide variety of systems.

CONTENTS

CHAPTER 1

1.1 GENERAL REMARKS

Gas-liquid and gas-solid reactions are usually considered as two distinct classes in chemical engineering. The formulation of the problems and the mathematical approaches are also different for the two cases. While this approach seems justified considering the distinctive physical nature of each of these systems, purely from a design and analytical point of view it seems possible to evolve a common design philosophy. This philosophy is based on the recognition that chemical reaction is the chief occurrence in all reactors, with diffusion very much in the role of an intruder or falsifier of the true kinetics.

While this philosophy has been followed in the design of catalytic reactors, the converse approach has found favour in the case of gas-liquid reactors. Thus one talks of enhancement of the physical absorption due to chemical reaction in gas-liquid systems as against the retardation of the chemical reaction in gas-solid catalytic reactions. A common approach to the two systems is possible by considering diffusion as the intruder in both the cases.

The present work was undertaken with the object of attempting a theoretical analysis of the two systems, partly for examining the feasibility of a common approach, and partly for studying certain specific aspects of the two cases. In all these analyses certain mathematical tools have been employed to get analytical solutions wherever possible. Thus the first chapter of the thesis will be concerned with a brief discussion of the approximate methods used in chemical engineering, particularly those that are pertinent to the problems of diffusion-cum-reaction.

1.2 OBJECTIVES OF THE PRESENT WORK

In the light of what has been stated above the objectives of the present work may be outlined as follows:

[1] To present a mathematical analysis of the problem of diffusion and reaction between two gases in a liquid.

[2] To formulate an approach for determining the optimum bulk phase composition for reaction between two gases in a liquid.

[3] To propose a common approach to the analysis of gas-liquid and gas-solid catalytic reactions.

[4] To determine experimentally the kinetics of an industrially important gas-liquid reaction: chlorohydrination of ethylene, and to verify the model proposed under [1].

[5] To present a rigorous analysis of the role of catalyst fouling in gas-solid catalytic reactions.

It will be noticed that the presentation starts with certain specific problems in gas-liquid reactions, followed by an analogy between gas-liquid and gas-solid catalytic reactions, and ending finally in a theoretical analysis of an important problem in gas-solid catalytic reactions.

As already mentioned in Section 1.1, a brief discussion of the approximate mathematical methods used in the solution of the equations pertinent to the present analyses is also described. Instead of giving brief descriptions of the various problems at this stage, such descriptions are included in the appropriate chapters. A summary of the approximate methods used is however presented below, as these methods are used in all the chapters.

1.3 APPROXIMATE METHODS

The realistic representation of most of the processes often requires the solution of nonlinear equations and resort to finite difference schemes is often envisaged. The numerical methods, though accurate and successful, often involve cumbersome procedures. In engineering practice, where the design of a specific unit is often based on empirical formulation combined with experience and basic understanding of the underlying phenomenon, the accuracy down to this level is often not required. Under such circumstances simple theoretical formulations and approximate solutions are preferable to complicated ones, even though the latter may be more exact. By suitably introducing certain approximations in the basic problem it is often possible to reduce the problem to a stage where analytical solution can be easily obtained. Numerous such approximating techniques have been used in the studies of diffusion [mass or thermal] with or without chemical reaction [or heat source] and are reported in the literature.

In general four types of nonlinearity can be recognised: [i] nonlinear source term caused by chemical reaction; [ii] nonlinearities in the derivative caused mainly ~~be~~ by the dependence of transport coefficients on temperature, etc.; [iii] nonlinear coefficients in the governing equations; and [iv] nonlinear boundary conditions, as for example in some of the heat conduction problems.

The problems encountered in the study of mass transfer in gas-liquid systems can be categorised under either of these classes, and the problems considered, viz. gas absorption with simple and complex reactions [33-45], mass transfer from gas bubbles [46-54], mass transfer across film [55-57] etc., display the methods of solution for each of these classes. The specific approximations used in the case of absorption with simple and complex chemical reactions are compared in Table 1.1 [also see Table 2.1]. The more general methods for obtaining a solution to a variety of problems are briefly considered below.

1.3.1 Orthogonal collocation

The orthogonal collocation method, which is a special case of the collocation method and the method of weighted residuals, was first developed by Villadsen and Stewart [2]. This is a very efficient method in solving the mathematical models describing the combined effects of diffusion and chemical reaction. In this method the unknown exact solution is expanded in a series of known functions, which are chosen to satisfy as many conditions of the problem as is feasible. The unknown coefficients in the series are then determined in a way so as to satisfy the differential equation in some best way. The trial function is substituted into the differential equation which is set to zero at the collocation points and the unknown coefficients in the trial function are determined. More number of terms can be included in the series so as to have a larger number of collocation points thus improving the accuracy. Using first order approximation often gives an analytical solution and is usually sufficient for engineering calculations. Several papers [2-8] have appeared in literature, wherein use of this technique has been made in obtaining solution for various problems, besides an excellent review available [9].

1.3.2 Variational methods

The variational formulations are often useful in finding approximate solutions to a number of problems. The variational format has the structure of an integral which is to be rendered stationary by an appropriate choice of the function appearing in the integrand of the integral. Schechter [10] has described the various approximating techniques to a variety of problems in chemical engineering. In view of the generality of this method it is not considered in greater detail here.

1.3.3 Methods used in heat conduction problems

In heterogeneous systems, the transport of heat or mass by way of conduction or molecular diffusion is often an important factor under consideration. Even for the case of diffusion with no chemical reaction a partial differential equation results for the unsteady state case and only under restricted conditions is an analytical solution to the problem possible. Approximate solutions can however be designed to yield answers in an analytical form. The approximate methods for these types of problems [e.g. heat conduction] are well known and are essentially based on the weighting function or Biot-Langrangian formulation. Thus an analytical expression for the temperature [or concentration] satisfying the boundary conditions of the problem and containing a number of possible time dependent parameters is designed. The various methods [Galerkin's, Biot's and heat balance method] differ only in the manner in which these parameters are obtained. The weighted residual approach has been used with success in solving a variety of important problems, including the boundary layer flows and nonlinear heat and mass transfer problems. Good reviews of weighted residual methods have been given by Ames [11] and Finlayson and Scriven [12] and a number of authors have used it for solution of nonlinear diffusion equations.

The method consists of formulating a solution of the problem which satisfies the partial differential equation, and perhaps some of the boundary conditions, only in some average sense over the region of interest rather than at each and every point of the region as is required in an exact solution.

Boley [13] has summarised the results obtained using these methods for the heat conduction problem with different boundary conditions and concludes that the choice of the method to be used is often a matter of judgement. In order to have an estimate of the error incurred in the approximate solution of the problem, a lower and upper bound for the solution can be found to bracket the approximate solution. The bounds derived for the various problems including the moving boundary value problems have been summarised in reference [13]. The use of superposition in the approximate solutions of the problems with time dependent conditions has been investigated for the heat conduction problems by Boley [14]. The use of Duhamel or convolution integrals on the basis of an approximate solution has been considered in their analysis and a comparison between the solutions with the numerical one is made.

Goodman's integral method is a versatile method that can be used to solve a number of problems containing all the types of nonlinearities. The integral method reduces the nonlinear boundary value problem to an ordinary initial value problem, the solution of which can be often found analytically. The versatility of the method is demonstrated by Goodman [15] by presenting a number of problems in heat conduction. A number of authors [16-18] have used this method to solve heat conduction problems. As far as the analogy between heat conduction and mass diffusion goes, this method can be used to solve diffusion problems also. However apart from a brief mention of these methods they are not considered in any great details here. here.

1.3.4 General approximating methods

In a series of articles, Hlavacek *et al* [19-21] have suggested approximate methods for solving various problems describing heat and mass transfer with chemical reaction. In all these methods, the nonlinear parabolic differential equation which describes a number of systems in chemical engineering is converted into a set of ordinary differential equations which can be solved more easily. In the linearisation technique described for solving a parabolic partial differential equation,

$$\frac{\partial u}{\partial t} = L u + R [x, u] \qquad [1.1]$$

where L is the linear operator containing derivatives up to second order, a solution for u is first obtained with the nonlinear R term removed. This solution is then used to replace the terms under the differential operator. The application of this method has been described by considering a problem of heat and mass transfer with chemical reaction.

1.3.5 Using Fredholm integral equation

A majority of the boundary value problems of chemical engineering can be brought into the form of Fredholm integral equations. The detailed theory of these equations has been discussed in books [22, 23]; once the basic equation is brought in the form

$$\phi [x] - \lambda \int_a^b K [x, y] \, \phi [y] \, dy = f [x] \qquad [1.2]$$

a number of methods can be employed to get the approximate solution. Thus the terms under the integral sign can be replaced by some simple form of expression not involving the integral sign obtained by using any of the formulae for approximate integration. In the method of successive approximations a solution is sought in the form of a series arranged in powers of λ.

$$\phi\,[x] = \phi_0\,[x] + \lambda\,\phi_1\,[x] + \lambda^2\,\phi_2\,[x] + \ldots\ldots \qquad [1.3]$$

For the case when $K\,[x, y]$ is a degenerate kernel, a complete solution to Equation [1.2] can be given. In another instance the kernel $K\,[x, y]$ may be approximately replaced by a degenerate kernel and the resulting equation then solved. These methods are widely used to solve the problems in mathematical physics though their use to chemical engineering problems have not been fully exploited. The process of mass transfer in a tubular reactor which gives rise to a nonlinear equation is considered here to show the applicability of the integral equations of Fredholm to the problem of chemical engineering. The two dimensional partial differential equation along with its boundary conditions can be transformed using the similarity transformations to the following ordinary differential equation:

$$L\,[w] = \frac{d^2 w}{d\,\xi^2} + \frac{\beta_1}{\xi}\,\frac{d\,w}{d\,\xi} = f_1\,[w] = R_1' \qquad [1.4]$$

$$\xi \geq 0, \quad \frac{d\,w}{d\,\xi} = 0, \quad \xi = \frac{1}{\delta\,[x]}, \quad \frac{d\,w}{d\,\xi} = 0$$

$$\xi > 0, \quad w = 1 \qquad [1.5]$$

where β_1 represents an arbitrary constant.

An alternative theorem, which states that Equation [1.4] has a unique solution if the corresponding homogeneous equation has a trivial solution, can be used to establish the uniqueness of the solution. The nontrivial solution of the auxiliary homogeneous equation has the solution

$$v\,[\lambda_m, \eta] = C_1 J_0\,[\sqrt{\lambda_m}, \eta] \qquad [1.6]$$

where λ_m and v_m are the eigenvalues and eigen functions respectively. The eigenvalues λ_m of Equation [1.6] are the squares of the zeros of Bessel function. As regards the existence of these zeros, it is known that each function J_n has, in fact, infinitely many zeros. For Bessel functions of zero order a special treatment based on particular properties of Bessel functions has to be made use of [22]. Accordingly, the eigenvalues of the Bessel problem with boundary condition $v\,[1] = 0$ for $n = 1$ are identical with those for the boundary condition $v'\,[1] = 0$ for $n = 0$ [apart from the first eigenvalue which is zero]. One can thus obtain the asymptotic formula for the zeros λ_m of J_n as

$$\lim_{m \to \infty} \frac{\lambda_m}{m^2 \pi} = 1 \qquad [1.7]$$

where n represents the order of Bessel function. Defining now Equation [1.6] as the kernel, Equation [1.4] can be transformed into its integral representation as

$$W = A_1 W \qquad [1.8]$$

where A_1 is the integral operator given by

$$A_1 w = \int_0^1 v[\lambda_m, \varepsilon] \, f_1[w] \, d\varepsilon \qquad [1.9]$$

Any of the approximate methods described above can now be used to solve this integral equation of Fredholm.

1.3.6 Optimum linearisation technique

The optimum linearisation technique, first introduced by West [24] to solve ordinary differential equations in nonlinear vibration theory and later applied by Vujanovic [25] to heat conduction problems, can be used to solve nonlinear diffusion type of equations. The method is used in the case of simultaneous absorption of two gases which react between themselves [Chapter 3]. It can be applied to problems involving the nonlinearity caused mainly by the dependence of transport coefficients on temperature etc. as well as to problems with nonlinear boundary conditions.

1.3.7 Perturbation method

The perturbation methods can also be used in solving a number of nonlinear problems [59, 60]. The case of longitudinal dispersion in chemical flow reactors [26] is considered here to illustrate the method. The governing differential equation

$$\frac{1}{P_e} \frac{d^2 w}{d x^2} - \frac{d w}{d z} - f[w] = 0 \qquad [1.10]$$

along with the Danckwerts boundary condition represents the physical situation. For a nonlinear f [w] term, analytical solution of the equation is not possible. For solution at high Peclet number Equation [1.10] becomes

$$\frac{d\,w}{d\,z} = - f\,[w] \qquad [1.11]$$

the solution of which w_α can be readily obtained. The concentration profile for $w\,[z, \xi\,]$ for $\xi \neq 0$ is then expressed as a superposition of w_α for $\xi = 0$ and some perturbation terms

$$w\,[z, \xi\,] = w_\alpha\,[z] + \xi\psi_1\,[z] + \xi^2\,\psi_2\,[z] + \dots \qquad [1.12]$$

This series is then substituted into the governing differential Equation [1.10] and like powers of ξ are equated when ordinary differential equations equal to the number of perturbation function retained in Equation [1.12] are obtained, which can be solved to get the functions ψ_1 and ψ_2.

In steady state transport problems the equation $\xi f'' + G\,[z, f, f'] = 0$ often describes the system. In another method [27] the second order term is treated as a singular perturbation on the first order differential equation $G\,[z, f, f'] = 0$. Both these methods have been applied to a nonisothermal, chemically reacting system in the literature [28]. The perturbation technique has also been applied to other problems like bubble dissolution [29], moving boundary problems [30], etc. The same problem of axial dispersion in chemical flow reactor has been considered by Shah and Paraskos [64]. Approximate collocation solutions obtained compare well with the numerical solutions at low and intermediate values of Peclet number. At large values of Peclet number the perturbation solution obtained by Burghardt and Zalesky [27] seems to approximate better and should be preferred.

The perturbation technique can thus be successfully used in obtaining solutions to nonlinear differential equations. A convenient method of obtaining solutions to nonlinear differential equations, which cannot be readily handled by perturbation series, is however the weighted residuals method discussed earlier.

In this chapter the general approximate methods used in the solution of the diffusion-reaction problems have been briefly described. The specific problems in mass transfer, where these techniques are employed, are cited in the references and are not discussed in any detail.

Table 1.2

Enhancement factor for a second order irreversible reaction with various approximations

Approximation	Enhancement factor	Remarks
1	2	3
Von krevelene and Hoftijer [30]	$E = \sqrt{\left[M\left(\frac{E_a - E}{E_a - 1}\right)\right]} \Big/ \tanh \sqrt{\left[M\left(\frac{E_a - E}{E_a - 1}\right)\right]}$	Implicit solution and trial and error method is needed.
Hikita-Asai [32]	$E = \left(\sqrt{\left[M\left(\frac{E_a - E}{E_a - 1}\right)\right]} + \frac{\pi}{8} \Big/ \sqrt{\left[M\left(\frac{E_a - E}{E_a - 1}\right)\right]} \right)$	Implicit solution and trial and error method is needed.
	$\times\, \mathrm{erf}_c \sqrt{\left[\frac{4}{\pi} M\left(\frac{E_a - E}{E_a - 1}\right)\right]} + \frac{1}{2} \exp\left[-\frac{4}{\pi} M\left(\frac{E_a - E}{E_a - 1}\right)\right]$	
Porter [61]	$E = 1 + [E_a - 1]\left[1 - \exp - \left([M - 1]/[E_a - 1]\right)\right]$	Explicit solution. Simpler to use and compares well with the numerical solution when $M >> 2$.

1	2	3
Kishinevskii [62]	$E = 1 + \frac{\sqrt{M}}{\alpha}\left[1 - \exp\left[-0.65\sqrt{M\alpha}\,\right]\right]$ $\alpha = \frac{\sqrt{M}}{E_a - 1} + \exp\left[\frac{0.68}{\sqrt{M}} - \frac{0.45\sqrt{M}}{E_a - 1}\right]$	Explicit solutions. Simpler to use and compare well with the numerical solution in the range of M values. These equations are recommended for design purposes instead of the implicit expressions.
Decoursey [43]	$E = -\frac{M}{2\,[E_a - 1]} + \sqrt{\left[\frac{M^2}{4\,[E_a - 1]^2} + \frac{E_a M}{[E_a - 1]} + 1\right]}$	

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CHAPTER 2

SIMULTANEOUS ABSORPTION OF TWO GASES IN A LIQUID

The analysis of gas-liquid reactions has so far been largely restricted to the absorption of a single gas in a liquid followed by a simple reaction, and the theory pertaining to such systems has been discussed by Danckwerts [1] and Astarita [2]. Attempts have also been made during the last few years to extend the treatment to absorption of a single gas followed by a complex reaction [1 - 12], and also to absorption of two gases each undergoing an independent reaction with the liquid [10 - 18]. Simultaneous absorption of two gases in a liquid with or without chemical reaction is involved in many industrially important processes and the information available in the literature on different aspects of absorption of two gases has been reviewed by Ramachandran and Sharma [13].

In this chapter, the more general situation in which two gases are absorbed in a liquid followed by a complex reaction [between the two gases and the gases with the liquid] will be analysed. The theoretical analysis of such a complex system provides the basic strategy for treating a variety of complex gas-liquid reactions. A typical reaction of industrial importance conforming to the reaction scheme chosen is the chlorohydrination of olefins leading to the corresponding chlorohydrins and subsequently [by lime treatment] to the epoxides.

2.1 THE BASIC EQUATIONS

The complex reaction scheme mentioned is represented by the following set of reactions:

$$z_A\ A + z_B\ B \xrightarrow{k_1} z_x\ X \qquad [i]$$

$$z_B\ B + z_c\ C(l) \underset{k_3}{\overset{k_2}{\rightleftharpoons}} z_E\ E + z_F\ F \qquad [ii]$$

$$z_A\ A + z_E\ E \xrightarrow[k_4]{} z_r\ r \qquad [iii]$$

The concentration profiles for the complex scheme considered are shown in Figure 2.1. The differential equations representing the material balances of the various species involved in the complex scheme may be written [based on the film theory] as follows:

$$D_A \frac{d^2\ C_A}{d\ y^2} = z_A \left[k_1\ C_A^m\ C_B^n + k_4\ C_A^u\ C_E^v\right] \qquad [2.1]$$

$$D_B \frac{d^2\ C_B}{d\ y^2} = z_B \left[k_1\ C_A^m\ C_B^n + k_2\ C_B^p\ C_c^q - k_3\ C_E^{p'}\ C_F^{q'}\right] \qquad [2.2]$$

$$D_C \frac{d^2\ C_c}{d\ y^2} = z_c \left[k_2\ C_B^p\ C_c^q - k_3\ C_E^{p'}\ C_F^{q'}\right] \qquad [2.3]$$

$$D_E \frac{d^2\ C_E}{d\ y^2} = z_E \left[-k_2\ C_B^p\ C_c^q + k_3\ C_E^{p'}\ C_F^{q'} + k_4\ C_A^u\ C_E^v\right] \qquad [2.4]$$

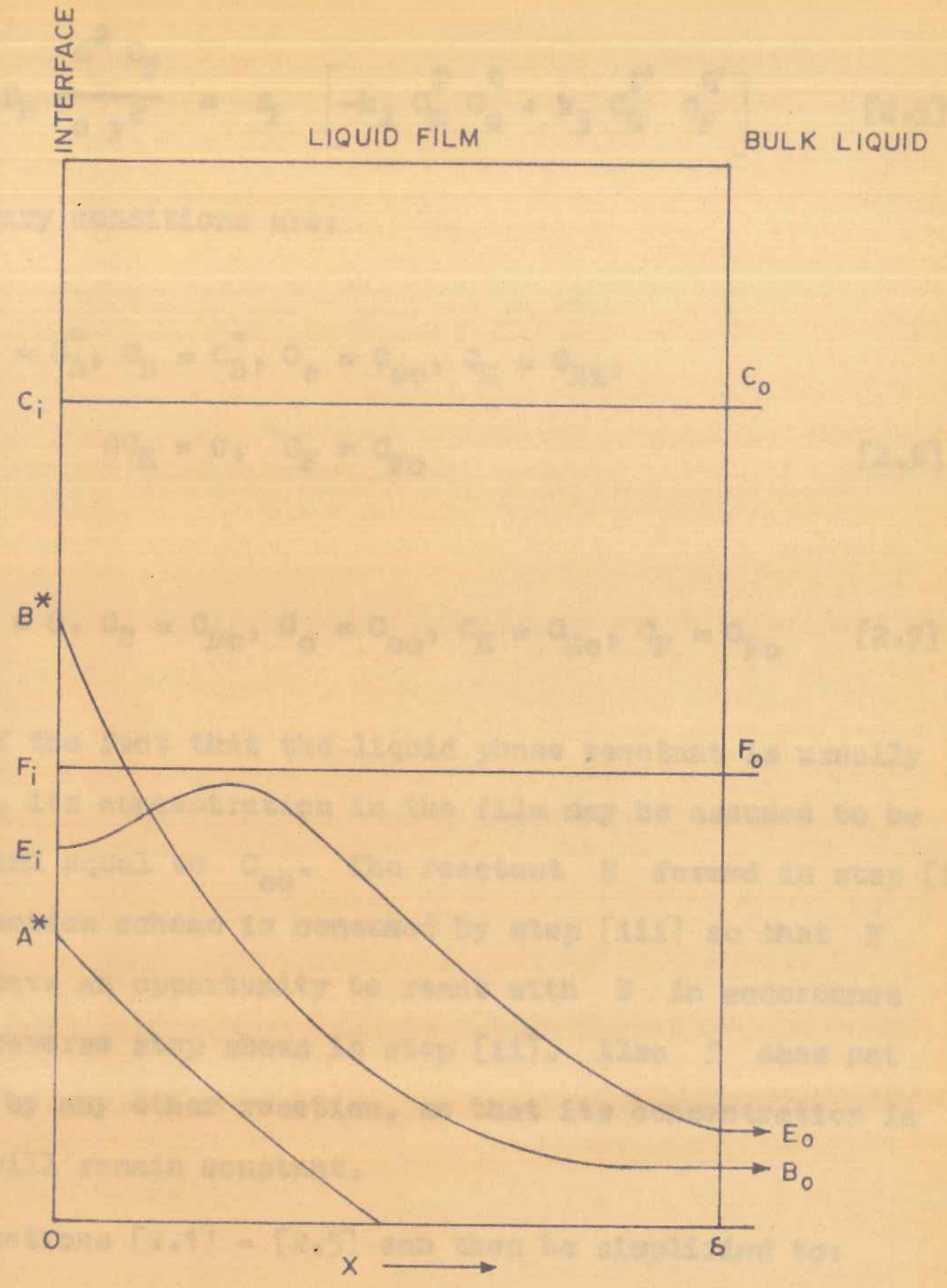

FIGURE 2·1: CONCENTRATION PROFILES OF THE REACTING SPECIES FOR THE FAST REACTION REGIME

$$D_F \frac{d^2 C_F}{d y^2} = z_F \left[-k_2 C_B^p C_c^q + k_3 C_E^{p'} C_F^{q'} \right] \qquad [2.5]$$

The boundary conditions are:

$y = 0$

$$C_A = C_A^*, \; C_B = C_B^*, \; C_c = C_{co}, \; C_E = C_{Ei},$$

$$dC_E = 0, \; C_F = C_{Fo} \qquad [2.6]$$

$y = \delta$

$$C_A = 0, \; C_B = C_{Bo}, \; C_c = C_{co}, \; C_E = C_{Eo}, \; C_F = C_{Fo} \qquad [2.7]$$

In view of the fact that the liquid phase reactant is usually in excess, its concentration in the film may be assumed to be constant and equal to C_{co}. The reactant E formed in step [ii] of the reaction scheme is consumed by step [iii] so that F does not have an opportunity to react with E in accordance with the reverse step shown in step [ii]. Also F does not disappear by any other reaction, so that its concentration in the film will remain constant.

Equations [2.1] - [2.5] can then be simplified to:

$$\frac{d^2 w_A}{d x^2} = M_1 w_A^m w_B^n + M_4 w_A^u w_E^v \qquad [2.8]$$

$$q_B \frac{d^2 w_B}{d x^2} = M_1 w_A^m w_B^n \qquad [2.9]$$

$$q_E \frac{d^2 w_E}{d x^2} = M_4 w_A^u w_E^v \qquad [2.10]$$

with

$$x = 0, \; w_A = 1, \; w_B = 1, \; w_E = w_{Ei}, \; d\,w_E/d\,x = 0 \qquad [2.11]$$

$$x = 1, \; w_A = 0, \; w_B = w_{Bo}, \; w_E = 1 \qquad [2.12]$$

From Equations [2.8] - [2.10] we have

$$\frac{d^2\,w_A}{d\,x^2} = q_B \frac{d^2\,w_B}{d\,x^2} + q_E \frac{d^2\,w_E}{d\,x^2} \qquad [2.13]$$

Equation [2.13] through boundary conditions [2.11] and [2.12] can be solved to establish a relation between w_A, w_B and w_E:

$$w_A = q_B\,w_B + q_E\,w_E + x\left[q_B\,[1-w_{Bo}] + q_E\,[w_{Ei} - 1] - 1\right] +$$

$$[1 - q_B - q_E\,w_{Ei}] \qquad [2.14]$$

Equation [2.14] can now be used to obtain a relation between ϕ_A and ϕ_B, which is given by

$$\phi_A = q_B\,\phi_B - q_B\,[1 - w_{Bo}] - q_E\,[w_{Ei} - 1] + 1 \qquad [2.15]$$

Equation [2.15] is rigorous and does not involve any approximation. The problem however is that, in order to compute ϕ_A and ϕ_B for different values of the various parameters, other expressions for ϕ_A and ϕ_B are also required. These expressions can be obtained by solving Equations [2.8] - [2.10] through boundary conditions [2.11] and [2.12]. The resulting equation may then be solved simultaneously with Equations [2.15] to compute the values of ϕ_A and ϕ_B. An analysis based on this strategy is presented below for the general case.

2.2 ANALYSIS OF THE GENERAL CASE

As mentioned earlier, analytical solution of Equation [2.1] has not been possible, and it is this step where suitable approximations will have to be made in order to linearise Equation [2.1] and enable an approximate solution for ϕ_A. The non-linear exponential profile proposed earlier by Chaudhari and Doraiswamy [19] for components A and B have been used in this work to linearise the problem. The profiles are:

$$w_A = e^{-\phi_A \frac{x}{1-x}} \qquad [2.16]$$

$$w_B = w_{Bo} + [1 - w_{Bo}]\, e^{-\phi_B \frac{x}{1-x}} \qquad [2.17]$$

In addition it has been assumed for the general order reactions considered here that the interfacial concentrations of the liquid phase [non-volatile] components are constant, viz. $w_E = w_{Ei}$. Suggested by Hikita and Asai [9], this assumption has been widely used to linearise problems involving complex reactions, and has been proved to be valid for many gas-liquid systems involving simultaneous diffusion and chemical reaction. This approximation with respect to E envisages the reaction between A and E [reaction iii] to be substantially complete at the interface so that the concentration of E involved is w_{E1}. The second reaction involving the product F does not come into the picture in this analysis.

Linearising Equation [2.8] using the profiles given by Equations [2.16] and [2.17] and solving the resulting equation with boundary conditions [2.11] and [2.12] gives the following expression for the enhancement of A:

$$\phi_A = M' \left[\frac{C_{Bo}}{C_B^*} e^{\phi_A} E_4 [\phi_A] + \left(1 - \frac{C_{Bo}}{C_B^*}\right) e^{\delta\phi_A + \phi_B]} E_4 (\phi_A + \phi_B) \right.$$

$$\left. + 2\,\phi_A\, e^{\phi_A} E_1 [\phi_A] + M'' e^{\phi_A} E_4 [\phi_A] \right] \qquad [2.18]$$

In deriving the expression for ϕ_B, the complication arising out of reaction [ii] should be considered. In addition to the boundary conditions given by Equations [2.11] and [2.12], the kinetic boundary condition explained in Chapter 4 can be written for the component B. Thus

$$-D_B \left.\frac{d\, C_B}{d\, y}\right|_{y = \delta} = \frac{1}{a} \left[k_2\, C_{Bo}^{p}\, C_{co}^{q} - k_3\, C_{Eo}^{p'}\, C_{Fo}^{q'} \right] 1\; z_B \qquad [2.19]$$

In Equation [2.19] the mass flux of component B at the end of the film is equated to the quantity consumed by reaction in the bulk. The linearised form of Equation [2.9] is then solved through boundary condition [2.19] to give the enhancement for component B:

$$\phi_B = M' \frac{D_A\, z_B}{D_B} \frac{C_A^*}{C_B^*} \left[\frac{C_{Bo}}{C_B^*} e^{\phi_A} E_4[\phi_A] + \left(1 - \frac{C_{Bo}}{C_B^*}\right) e^{[\phi_A + \phi_B]} E_4[\phi_A + \phi_B] \right] + 2\left(1 - \frac{C_{Bo}}{C_B^*}\right) \phi_B\, e^{\phi_B} E_1[\phi_B] \qquad [2.20]$$

The values of the enhancement factors ϕ_A and ϕ_B can be calculated from Equations [2.15] and [2.18] by a trial and error method.

In deriving Equation [2.18] for the enhancement factor for component A, it has been assumed that the interfacial concentration of the liquid phase reactants is constant, viz. $w_E = w_{Ei}$. This assumption can be relaxed under certain circumstances. Thus for an arbitrary case when the order with respect to each component involved is unity, the dimensionless Equation [2.8] becomes

$$\frac{d^2\, w_A}{d\, x^2} = M_1\, w_A\, w_B + M_4\, w_A\, w_E \qquad [2.21]$$

Substituting for the concentration of the species E in terms of the concentrations of A and B from Equation [2.14], and solving the resulting equation subject to boundary conditions [2.11] and [2.12] leads to

$$\phi_A = \frac{M_4}{q_E} e^{2\phi_A} E_4 [2\phi_A] + \left(M_1 - \frac{M_4 q_B}{q_E}\right)\Big[w_{Bo} e^{\phi_A} E_4 [\phi_A] +$$

$$[1 - w_{Bo}] e^{[\phi_A + \phi_B]} E_4 [\phi_A + \phi_B]\Big] - e^{\phi_A}\Big[\frac{M_4 q_B}{q_E}[1 - w_{Bo}] +$$

$$M_4 [w_{E1} - 1] - \frac{M_4}{q_E}\Big]\Big(E_4 [\phi_A] - E_5 [\phi_A]\Big) + 2\phi_A e^{\phi_A} E_1 [\phi_A] \qquad [2.22]$$

Similarly, Equation [2.9] can be solved to give the following equation for ϕ_B:

$$\phi_B = M_1 \Big[w_{Bo} e^{\phi_A} E_4 [\phi_A] + [1 - w_{Bo}] e^{[\phi_A + \phi_B]} [E_4 [\phi_A + \phi_B]\Big] +$$

$$2 [1 - w_{Bo}] \phi_B e^{\phi_B} E_1 [\phi_B] \qquad [2.23]$$

Equations [2.22] and [2.23] take into account the effect of variation of the concentration of the species E in the film for a first order system, and can be solved with the basic Equation [2.15] to give ϕ_A and ϕ_B.

A comparatively simple solution to Equations [2.8] - [2.10] can also be obtained by neglecting the higher order terms obtained in the expansion of the terms under the exponent. The resulting approximate expressions for ϕ_A and ϕ_B obtained by Chaudhary [21] are:

$$\phi_A = M_1' \left[\left\{ \frac{2\, w_{Bo}}{[n+1]\, \phi_A} + \frac{2}{[n+1]} \frac{[1 - w_{Bo}]}{[\phi_A + \phi_B]} \right\} + \frac{m+1}{u+1} \frac{K_1\, C_{Ei}^{v}}{C_B^{*n}\, \phi_A} \right]$$

[2.24]

and

$$\phi_B = M_1' \left(\frac{\nu_B\, C_A^*}{r_B\, C_B^*} \right) \left[\frac{2}{[n+1]} \left\{ \frac{w_{Bo}}{\phi_B} + \frac{[1 - w_{Bo}]}{[\phi_A + \phi_B]} \right\} + \frac{[m+1]}{[p+1]} K_2 \frac{C_B^{*\,p-n}}{C_A^*} C_{co}^{q} \right.$$

$$\left(\frac{[1 - w_{Bo}]}{\phi_B} + w_{Bo} \right) + \frac{[m+1]}{[p'+1]} K_3 \frac{C_{Ei}^{p'-1}\, C_{Fo}^{q'}}{C_B^{*\,n-1}} C_A^{*\,2-p'-q'-n}$$

$$\left. \left\{ \frac{\nu_B\, C_A^*}{r_E\, C_B^*} \left(1 - \frac{1}{\phi_A} - \frac{\phi_A}{2} \right) + \frac{\nu_{EB}}{\nu_{BE}} \left[(1 - w_{Bo}) \left(\frac{1}{\phi_B} - 1 \right) + \frac{\phi_B}{2} \right] - \frac{C_{Ei}}{C_B^*} \right\} \right]$$

[2.25]

where K_1, K_2, K_3 are dimensionless ratios of rate constants and are defined in the nomenclature.

Trigonometric profiles for the concentrations of the species A and B, viz

$$w_A = \frac{\sinh m_a\, [1 - x]}{\sinh m_a} \qquad [2.26]$$

$$w_B = w_{Bo} + \frac{[1 - w_{Bo}] \sinh m_b [1 - x]}{\sinh m_b} \qquad [2.27]$$

can be used to solve Equations [2.8] - [2.10]. With these profiles, the enhancement factors ϕ_A and ϕ_B can be obtained from Equations [2.26] and [2.27] by simple differentiation:

$$\phi_A = \frac{m_a}{\tanh m_a} \qquad [2.28]$$

$$\phi_B = \frac{m_b [1 - w_{Bo}]}{\tanh m_b} \qquad [2.29]$$

It is apparent from the above equations that a knowledge of m_a, m_b and w_{Bo} is necessary for the calculation of ϕ_A and ϕ_B. They can be obtained as follows.

Equations [2.8] and [2.9], after substituting for the concentration profiles for w_A, w_B and w_e, and on integration and rearrangement, give

$$\frac{q_B\, m_b}{M_1} \left(M_1 - \frac{M_4\, q_B}{q_E} \right) \left(\frac{1}{\tanh m_b} - \frac{1}{\sinh m_b} \right)$$

$$= m_a \left(\frac{1}{\tanh m_a} - \frac{1}{\sinh m_a} \right) + \frac{1}{m_a^2} \Bigl(\frac{M_4\, q_B}{q_E} (1 - w_{Bo}) +$$

$$M_4 [w_{Ei} - 1] - \frac{M_4}{q_E} \Bigr) - \frac{1}{m_a \tanh m_a} \left(\frac{M_4\, q_B}{q_E} + M_4\, w_{Ei} - \frac{M_4}{2\, q_E} \right) +$$

$$\frac{M_4}{m_a \sinh m_a} \left(1 + \frac{q_B}{q_E} w_{Bo} \right) \qquad [2.30]$$

and

$$q_B\, m_b \left(\frac{1}{\tanh m_b} - \frac{1}{\sinh m_b} \right) = \frac{M_1}{m_a}\, \frac{w_{Bo}}{[1 - w_{Bo}]} \left(\frac{1}{\tanh m_a} - \frac{1}{\sinh m_a} \right)$$

$$+ \frac{M_1}{m_a^2 - m_b^2} \left(\frac{m_a}{\tanh m_a} - \frac{m_b}{\tanh m_b} \right) \qquad [2.31]$$

The dimensionless concentrations w_{Ei} and w_{Bo} appearing in the above equations may be obtained from Equations [2.14] and [2.19] by simple mathematical manipulations:

$$w_{Ei} = 1 + \frac{1}{q_E} - \frac{m_a}{q_E \tanh m_a} + \frac{q_B}{q_E}\, \frac{m_b\,[1 - w_{Bo}]}{\tanh m_b} - \frac{q_B}{q_E}\,[1 - w_{Bo}] \qquad [2.32]$$

$$w_{Bo} = \frac{1 - \dfrac{r_2 \sinh m_b}{m_b} + \sqrt{\left(1 - \dfrac{r_2 \sinh m_b}{m_b}\right) + \dfrac{4\, r_3 \sinh m_b}{m_b}}}{2} \qquad [2.33]$$

Equations [2.30] - [2.33] can now be solved simultaneously to obtain the values of m_a, m_b and w_{Bo}.

For the special case of C_{Bo} and C_{Eo} equal to zero, Equations [2.30], [2.32] and [2.33] can be simplified to give

$$q_B m_b \tanh\left(\frac{m_b}{2}\right) = m_a \tanh\left(\frac{m_a}{2}\right) = \frac{M_1}{m_a^2 - m_b^2} \left(\frac{m_a}{\tanh m_a} - \frac{m_b}{\tanh m_b} \right) \qquad [2.34]$$

Equation [2.34] can be solved by a trial and error method to give m_a and m_b. The values of ϕ_A and ϕ_B can then be calculated from Equations [2.28] and [2.29].

2.3 RESULTS AND DISCUSSION

A comparatively simple solution to Equations [2.8] - [2.10] has been obtained by neglecting the higher order terms in the expansion of the terms under the exponent by Chaudhary [21]. Juvekar [22] proposed a trigonometric profile for the gaseous component A and B and obtained the expressions for the enhancement factors ϕ_A and ϕ_B. In comparing the results of the approximate analytical solutions with the numerical solutions, Chaudhari and Doraiswamy [19] as well as Juvekar [22] earlier used the numerical solutions of Roper *et al* [23] based on the penetration theory. Since, however, the approximations are based on the film theory, it would be more reasonable to compare their predictions with the numerical solution obtained from the film theory. Accordingly, in the present work, the following approximations were compared with the numerical film theory solutions at several values of $\sqrt{M}$ in the range 1 to 3:

[i] exponential profile with all the terms retained [present work];

[ii] exponential profile with higher order terms neglected; and

[iii] trigonometric profile.

The parameter values chosen are:

$$C_{Bo} = C_{Eo} = 0,\ C_B^*/C_A^* = 3,\ \frac{D_A}{D_B} = z_B = 1,\ m = n = 1$$

The results of the comparison are presented in Table 2.1. It can be seen that approximation [i] is the most accurate in the entire range of $\sqrt{M}$ studied, with an average error of less than 5%. Approximation [ii] is, understandably, the least acceptable, while the trigonometric approximation [iii] is only slightly inferior to approximation [i]. It is a reasonable conclusion from these observations that an exponential profile approximates the actual situation remarkably well both for simple and complex gas-liquid reactions.

2.3.1 Some salient observations

Having established the applicability of the proposed profiles, particularly the exponential profile with higher order terms retained, it would be interesting to examine the effects of different parameters on the behaviour of the complex scheme considered. The variables involved are:

reaction orders [m, n, p, q, p', q', u and v];

diffusivity ratios [r_B, r_E];

stoichiometric coefficients [ν_B, ν_E];

solubility ratio [C_B^*/C_A^*]; and

dimensionless rate groups [K_1, K_2, K_3].

Solutions were generated by varying the value of any one parameter with all other parameters fixed and computing ϕ_A and ϕ_B. The results of the computations for several situations considered are summarised in Table 2.2. The effects of each of the parameters varied on ϕ_A and ϕ_B are shown in column 4 and 5, respectively.

2.3.2 Special cases

Several special cases can be obtained from the general solution by imposing different constraints. Thus the solubility of B can be considerably higher than that of A, both A and B may react in the liquid bulk, and different steps of the reaction may occur in different regimes. Several such cases are summarised in Table 2.3 in which the simplified solutions for each case as well as the conditions to be fulfilled are given, along with some remarks pertaining to each case. The chlorohydrination of ethylene, an industrially important system, probably corresponds to special case [6] considered here. In view of the industrial importance of this system it is discussed in greater detail in Chapter 5 along with experimental data.

2.4 SUMMARY AND CONCLUSIONS

The simultaneous absorption of two gases accompanied by a complex reaction of the type shown in [i], [ii] and [iii] provides the basic framework from which various special cases, many of them corresponding to industrial reactions, can be analysed. In this chapter equations are developed for an analysis of such a complex scheme based on certain logical assumptions. Equations have been developed for the enhancement of two gaseous reactants A and B and numerical solutions are provided to gain a quantitative insight into the behaviour of the system at different values of the absorption and reaction parameters involved. In certain range of these values the complex system degenerates into certain single systems that have already been considered earlier by several investigators, viz. reaction of two gases between themselves, absorption accompanied by a single first order irreversible reaction with the liquid phase reactant. The numerical solutions also show that the stoichiometric coefficients as well as the solubilities of the gases can have a profound influence on the enhancement. Thus a ten-fold variation in the solubility ratio $\frac{C^*_B}{C^*_A}$ results in an eight-fold increase in the enhancement of B. Similarly the effect of the stoichiometric coefficient of B $[\nu_B]$ on the enhancement of B is also quite significant. It has also been observed that the diffusivity ratio r_E influences the enhancement of A significantly. On the other hand, the ratio r_B influences ϕ_B but has practically no effect on ϕ_A, a rather unusual effect which has also been observed by other investigators.

The general solution discussed above is based on the assumption that all the reactions are complete in the film. This assumption can be relaxed in several ways by postulating that the three reactions involved occur in one or more regimes simultaneously. Six such special cases have been considered. In the majority of cases the general solution is likely to reduce to any of the special cases mentioned, and this can be easily verified by certain selected preliminary runs. The analysis then not only becomes simpler but more realistic.

Table 2.1

Comparison of the approximate solutions with the numerical solutions

M	Numerical solution		Exponential profile [higher order terms retained]		Exponential profile [higher order terms neglected]		Trigonometric profile	
	film theory	pen. theory						
	ϕ_A	ϕ_A	ϕ_A	ϕ_B	ϕ_A	ϕ_B	ϕ_A	ϕ_B
2	1.85	1.70	1.90	1.30	1.50	1.16	1.74	1.25
2.5	2.25	2.10	2.20	1.40	1.93	1.31	2.08	1.34
3.0	2.66	2.55	2.60	1.50	2.40	1.46	2.61	1.45
5.98	-	-	4.90	2.50	6.00	3.00	5.00	2.16
11.62	-	-	9.70	3.90	10.50	4.00	10.00	3.55

Table 2.2

Some salient observations

Parameter	Parameters fixed	Parameter varied	Effect on ϕ_A	Effect on ϕ_B
1	2	3	4	5
Effect of selectivity group K_4	i. reaction orders = 1 ii. $r_B = r_E = \nu_E = \nu_B = 1$ iii. $K_2 = K_3 = 1$ iv. $C_B^*/C_A^* = 3$	K_4 [0,0.1,0.5,1.0, 2.0] i. at low values	The effect on ϕ_A is significant. The absorption of A reduces to absorption accompanied by a single chemical reaction and the equation for the simultaneous absorption and [1,1]-st order irreversible chemical reaction of two gases in a liquid [19] can be used.	The effect on ϕ_B is very small.
		ii. at high values	The absorption of A reduces to gas absorption accompanied by a single [1,1]-st order irreversible chemical reaction with the liquid phase reactant. The solution tends to an asymptote at higher values of $\sqrt{M}$ as observed by Van Krevelen and Hoftizer [20].	-

1	2	3	4	5
Effect of selectivity group K_2	i. m,n,p,q,p',q', u and v = 1 ii. $r_B = r_E = \nu_E = \nu_B = 1$ iii. $K_1 = K_3 = 1$ iv. $C_B^*/C_A^* = 3$	K_2 i. at low values	ϕ_A increases as K_2 increases. At lower values of K_2, the rate of second reaction step is negligible and there is no intermediate species available for the third reaction; as such the rate of the third step [which depends on second] also becomes negligible. In this situation, the problem reduces to the simultaneous absorption of two gases which react among themselves in a liquid medium.	ϕ_B increases as K_2 increases.
		ii. at higher values	The concentration of intermediate species increases resulting in the higher ϕ_A values.	ϕ_B also increases.
Effect of selectivity group K_3	i. reaction orders = 1 ii. $r_B = r_E = \nu_E = \nu_B = 1$ iii. $K_2 = K_1 = 1$ iv. $C_B^*/C_A^* = 3$	K_3 [effect of reversibility] = [5,2,1,0.5, 0.3,0.1,0.0]	When $K_3 = 0$ the second reaction step becomes irreversible, and most of the intermediate formed is available for the third step; as such ϕ_A and ϕ_B both increase as K_3 decreases. As K_3 increases the reversible step becomes significant which depresses both ϕ_A and ϕ_B. At very high values of K_3, the approximate solution becomes identical with the approximate solution for the simultaneous absorption of two gases which react between themselves.	ϕ_B decreases as K_3 increases.

1	2	3	4	5
Effect of diffusivity ratio $r_B = D_B/D_A$	i. reaction orders = 1 ii. $K_1 = K_2 = K_3 = 1$ iii. $r_E = \nu_E = \nu_B = 1$ iv. $C_B^*/C_A^* = 3$	$r_B = [5,2,1,0.5,0.1]$ $= D_B/D_A$	ϕ_A does not change appreciably with r_B.	Significant variation in ϕ_B as compared to ϕ_A. This kind of unusual effect of diffusivity ratio on ϕ_A and ϕ_B has also been reported by Shah and Kenney [18].
Effect of diffusivity ratio $r_E = D_E/D_A$	i. reaction orders = 1 ii. $K_1 = K_2 = K_3 = 1$ iii. $r_B = \nu_E = \nu_B = 1$ iv. $C_B^*/C_A^* = 3$	r_E	ϕ_A changes more sharply with r_E as compared to ϕ_B.	ϕ_B does not change appreciably with r_E.
Effect of stoichiometric ratio $\nu_B = Z_B/Z_A$	i. reaction orders = 1 ii. $K_1 = K_2 = K_3 = 1$ iii. $r_B = r_E = \nu_E = 1$ iv. $C_B^*/C_A^* = 3$	ν_B	The effect of ν_B on ϕ_A is negligible. The effect of ν_E on ϕ_A is negligible at lower values of M, but at higher values of M the effect is quite marked.	The effect on ϕ_B is significant. The effect of ν_E is negligible at lower values of M, but at higher values of M the effect is quite marked.
Effect of solubility ratio C_B^*/C_A^*	i. reaction orders = 1 ii. $K_1 = K_2 = K_3 = 1$ iii. $r_B = r_E = \nu_E = \nu_B = 1$	$C_B^*/C_A^* = [0.3, 0.5, 1.0, 2.0, 3.0]$	The effect on ϕ_A is marginal; a ten-fold variation of C_B^*/C_A^* enhanced ϕ_A by only 50%.	The effect on ϕ_B is significant; a ten-fold variation of C_B^*/C_A^* causes an eight-fold increase in ϕ_B.

Table 2.3

Some special cases

Case considered	Conditions to be fulfilled	Rate of absorption, R_A of enhancement factor, ϕ_A	Remarks
1	2	3	4
Solubility of B is much greater than of A	$C_B^* >> C_A^*$	$R_A = \dfrac{D_A C_A^* \sqrt{M_1}}{\tanh \sqrt{M_1}\ \delta}$ $R_B = k_L [C_B^* - C_{Bo}]$	There can be a significant resistance in the gas phase to the absorption of the more soluble gas. It is also likely that the absorption of the less soluble gas would be followed by a pseudo-order reaction.
When A and B both react in the liquid bulk	$[1 k_1 C_{Bo} + 1 k_4 C_{Eo}] \simeq k_L a$	$R_A' = \dfrac{\left[1 k_1 C_B^* - \dfrac{1 k_1 R_A'}{k_L a} - 1 k_4 C_{Eo}\right] C_A^*}{1 + \dfrac{\left[1 k_1 C_B^* - \dfrac{1 k_1 R_B'}{k_L a} + 1 k_4 C_{Eo}\right]}{k_L a}}$	R_A' and R_B' can be calculated by a trial-and-error method.

1	2	3 4	5
	$\left[1 k_1 C_{Ao} + 1 k_2 C_{co} - 1 k_3 \frac{C_{Eo} C_{Fo}}{C_B^*}\right] = k_L a$	$R_B' = \dfrac{\left[1 k_2 C_B^* C_{co} + 1 k_1 C_A^* C_B^* - \dfrac{1 k_1 C_B^* R_A'}{k_L a} - 1 k_3 C_{Eo} C_{Fo}\right]}{1 + \dfrac{\left[1 k_2 C_{co} + 1 k_1 C_A^* - \dfrac{1 k_1 R_A'}{k_L a}\right]}{k_L a}}$	
The first two steps occur in the bulk and the third step in the film	$\frac{\sqrt{D_A k_1 C_B^*}}{k_{LA}} << 1$ $\frac{\sqrt{D_B k_2 C_{co}}}{k_{LB}} << 1$ $1 < \frac{\sqrt{D_A k_4 C_{Eo}}}{k_L} < 1 + \frac{z_A C_{Eo}}{z_B A^*}$	$R_A' = \dfrac{a A^* \sqrt{D_A k_4 C_{Eo}}}{\tanh \dfrac{\sqrt{D_A k_4 C_{Eo}}}{k_L}}$ $R_A' = \dfrac{a A^* \sqrt{D_A k_4 C_{Eo}}}{\tanh \dfrac{\sqrt{D_A k_4 C_{Eo}}}{k_L}}$ $R_B' = \dfrac{\left[1 k_2 C_B^* C_{co} - 1 k_3 C_{Eo} C_{Fo}\right]}{1 + \left(\dfrac{1 k_2 C_{co}}{k_L a}\right)}$	The additional condition to be satisfied is $\left[1 k_2 C_{co} - 1 k_3 \frac{C_{Eo} C_{Fo}}{C_B^*}\right] = k_L a$

1	2	3	4
The first and the third steps occur in the bulk and the second step in the film	$\frac{\sqrt{D_A\ k_1\ C_B^*}}{k_{LA}} << 1$ $1 < \frac{\sqrt{D_B\ k_2\ C_{co}}}{k_{LB}} < 1 + \frac{z_B\ C_{co}}{z_C\ C_B^*}$ $\frac{\sqrt{D_A\ k_4\ C_{Eo}}}{k_{LA}} << 1$ $1\ k_4\ C_{Eo} \quad k_L\ a$	$R_A' = \frac{1\ k_4\ A^*\ C_{Eo}}{1 + \frac{1\ k_4\ C_{Eo}}{k_L\ a}}$ $R_B = a\ [C_B^* - C_{Bo}]\ \sqrt{D_A\ k_2\ C_{co}}$	Equation for R_B is valid only when the concentration of E and F at the interface are almost euqa equal to their bulk concentrations.
Reaction of B with C is instantaneous and reactions of A are in the fast reaction regime	$1 < \frac{\sqrt{D_A\ k_4\ C_{Eo}}}{k_{LA}} < 1 + \frac{z_A\ C_{Eo}}{z_E\ C_A^*}$	$R_A = \frac{A^*\ \sqrt{D_A\ k_4\ C_{Eo}}}{\tanh \frac{\sqrt{D_A\ k_4\ C_{Eo}}}{k_L}}$	Selectivity for Y can be very high.

1	2	3	4
Reaction of A and E is instantaneous and those of B are in the fast reaction regime	$\frac{k_{GB}\ P_G}{k_{LB}\ C_{co}} << 1$ $\frac{\sqrt{D_A\ k_1\ C_B^*}}{k_{LA}} > 1$ $1 < \frac{\sqrt{D_A\ k_2\ C_{co}}}{k_{LB}} < 1 + \frac{Z_B\ C_{co}}{Z_c\ C_B^*}$ $k_{GA}\ P_G << k_L\ C_{Eo}$ $\frac{\sqrt{D_A\ k_1\ C_B^*}}{k_{LA}} > 1$ $\frac{\sqrt{D_A\ k_4\ C_{Eo}}}{k_L} >> 1 + \frac{Z_A\ C_{Eo}}{Z_E\ C_A^*}$	$R_B = k_{GB}\ P_G$ $R_A = k_{GA}\ P_{GA}$ $R_B = C_B^* \sqrt{D_B\ k_2\ C_{co}}$	Equation for R_B is valid provided the reaction is pseudo-first-order and there is no depletion in the concentration of the liquid phase reactants at the interface.

NOTATION

A	gaseous species A or concentration of A at any point in the liquid film, g mole/cm^3
a	effective gas-liquid interfacial area, cm^2/cm^3
B	gaseous species B or concentration of B at any point in the liquid film, g mole/cm^3
b	dimensionless concentration of B defined as B/B^*
C,E,F	liquid phase reactants or products or concentrations of C, E or F at any point in liquid film, g mole/cm^3
D_i	diffusivity of the i^{th} species
e,f	dimensionless concentrations of E and F, defined as E/E_o and F/F_o
H	Henry's law solubility coefficient, g mole/cm^3 atm
I_1	$\frac{M_4}{q_E}$
I_2	$\frac{q_B}{M_1}\left(M_1 - \frac{M_4 q_B}{q_E}\right)$
I_3	$\frac{M_4 q_B}{q_E}[1 - b_o] + M_4 [e_1 - 1] - \frac{M_4}{q_E}$
I_4	$\frac{M_4}{q_E} - \frac{M_4 q_B}{q_E} - M_4 e_1$
K_1	$\frac{k_4}{k_1} A^{*u+v-m-n}$

K_1'	$\dfrac{k_4}{k_1'} A^{*u+v-m}$
K_2	$\dfrac{k_2}{k_1} A^{*p+q-m-n}$
K_3	$\dfrac{k_3}{k_1} A^{*p'+q'-m-n}$
$k_1, k_2,$ k_3, k_4	general order reaction rate constants
k_1'	pseudo m^{th} order rate constant
k_G	gas-side mass transfer coefficient, g mole/cm^2 sec atm
k_L	liquid side mass transfer coefficient in absence of chemical reaction, cm/sec
$\underline{l}$	fractional hold up of liquid phase
$m, n, p,$ $a, p', q',$ u, v	orders of reaction with respect to various species
M_1	$\dfrac{Z_A \delta^2 k_1 B^*}{D_A}$
M_2	$\dfrac{k_2 Z_A \delta^2 B^* C_o}{D_A A^*}$

M_3	$\dfrac{k_3\ Z_A\ \delta^2\ E_o\ F_o}{A^*\ D_A}$
M_4	$\dfrac{Z_A\ \delta^2\ k_4\ E_o}{D_A}$
M'	$\dfrac{4\ Z_A\ k_1\ A^{*m-1}\ B^{*n}\ \delta^2}{[m+1]\ [n+1]\ D_A}$
M''	$\dfrac{2\ Z_A\ k_4\ A^{*u}\ E_i^v\ \delta^2}{[u+1]\ D_A}$
M'_1	$\dfrac{2}{m+1}\ \dfrac{Z_A\ k_1\ A^{*m-1}\ B^{*n}\ \delta^2}{D_A}$
p	partial pressure of the soluble gas, atm
q_B	$\dfrac{D_B\ Z_A\ B^*}{D_A\ Z_B\ A^*}$
q_C	$\dfrac{D_C\ Z_A\ C_o}{Z_C\ D_A\ A^*}$

q_E	$\frac{D_E Z_A E_o}{D_A Z_E A^*}$
q_F	$\frac{D_F Z_A F_o}{D_A Z_F A^*}$
R	rate of absorption of the gaseous component at the interface, g mole/cm^2 sec
R'	rate of absorption of the gaseous component per unit volume of the liquid, g mole/cm^3 sec
r_2	$\frac{\underline{1} Z_B \delta k_2 C_o}{\underline{a} D_B B^*}$
r_3	$\frac{\underline{1} Z_B \delta k_3 E_o F_o}{\underline{a} D_B B^*}$
$r_B, r_C,$ r_E, r_F	defined by D_B/D_A, D_C/D_A, D_E/D_A, D_F/D_A
X,Y	product species
x	dimensionless distance defined as y/δ
y	distance in the direction of diffusion, cm
Z	stoichiometric coefficient, subscript indicating the species

Greek symbols

δ	film thickness, cms
ν_B, ν_C ν_E, ν_F	defined by Z_B/Z_A, Z_C/Z_A, Z_E/Z_A, Z_F/Z_A
ϕ	enhancement factor, subscript indicating the species

Subscripts

*	denotes the value of the concentration of a species when the solution attains equilibrium with the gas
i	gas-liquid interface
o	liquid bulk
G	gas phase

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CHAPTER 3

DETERMINATION OF OPTIMUM BULK PHASE COMPOSITION

The simultaneous absorption of two gases in a liquid with or without chemical reaction is involved in many industrially important processes and a sizeable amount of information is available in the literature on different aspects of absorption of two gases. Ramachandran and Sharma [1] have reviewed the pertinent literature. Guidelines for the selection of the best composition of gases to get the maximum yield of the desired product are however lacking and it is the purpose of this chapter to set guidelines for the absorption of two gases which react between themselves. This is an industrially important problem. For instance ammonia and carbon dioxide are absorbed in water in the manufacture of urea.

Selection of optimum parameters so as to get the best results is not a new problem in the field of chemical engineering and there are many articles in the literature referring to optimal determination [2 - 7]. Calculus of variation or dynamic programming methods are usually employed in seeking solutions to this class of problems. Since maximizing the yield of a desired product by suitably changing the composition of the gaseous feed falls under the category of natural variational problems [8] the method of variational calculus can be employed in solving the present problem. Bailey [9] has used this approach in the case of gas-solid reactions.

The optimum linearisation method explained in Chapter 1 and the approximate profile derived on the basis of a linear reaction rate are used here to obtain the solution.

A reaction of the type

$$A\,[g] \;+\; z\,B\,[g] \;\rightarrow\; \text{Products}$$

is considered. The gases A and B are assumed to react between themselves in the presence of a liquid. Depending on the solubilities and diffusivities of the components A and B a certain concentration profile is developed in the film. Two distinct cases are considered, viz. [1] solubility of A is far greater than that of B but their diffusivities comparable, and [2] solubilities of A and B are comparable but the diffusivity of A is far greater than that of B. Gas film resistance is expected to be present for the transfer of the species A and B since the gases are present as a mixture. In the general case it may so happen that the concentration fluxes of A and B at the end of the film are not in stoichiometric proportion. This represents an accumulation of one of the components in the bulk and suggests that the components are not fully utilised for the purpose of reaction. The necessary condition for the maximum amount of reaction between the reactants would thus be that the flux of one component at the end of the film is in stoichiometric proportion with that of the other component. This constraint has been used in the basic formulation of the problem presented in the next section.

3.1 BASIC FORMULATION

Let C_{Ag} and C_{Bg} be the concentrations of species A and B in the gas phase corresponding to their partial pressures p_A and p_B respectively. The mass balance equations for the species can be written as

$$D_A \frac{d^2 C_A}{d y^2} = k_1 C_A C_B \qquad [3.1]$$

$$D_B \frac{d^2 C_B}{d y^2} = z k_1 C_A C_B \qquad [3.2]$$

with the boundary conditions

$$C_A = C_{Ai}, \quad y = \delta \qquad [3.3]$$

$$y=0 \;; \quad D_A \frac{d C_A}{d y} = \frac{k_1 C_{Ao} C_{Bo}}{a} = z D_B \frac{d C_B}{d y} \qquad [3.4]$$

where the boundary condition [3.4] has been dictated from the consideration of maximum reaction.

Let θ be the mole fraction of A in the bulk gas phase, i.e.

$$C_{Ag} = \theta C \qquad [3.5]$$

$$C_{Bg} = [1 - \theta] C \qquad [3.6]$$

where C represents the total concentration of the gas phase. Equations [3.1] - [3.4] can be transformed into dimensionless form as

$$\frac{d^2 w_A}{d x^2} = m^2 w_A w_B \tag{3.7}$$

$$r \frac{d^2 w_B}{d x^2} = m^2 w_A w_B \tag{3.8}$$

with

$$\left.\begin{aligned} w_A[1] &= \theta - \frac{1}{Sh_A} \left.\frac{d w_A}{d x}\right|_{x=1} \\ w_B[1] &= 1 - \theta - \frac{1}{Sh_B} \left.\frac{d w_B}{d x}\right|_{x=1} \end{aligned}\right\} \text{at } x = 1 \tag{3.9}$$

$$\frac{d w_A}{d x} = r z \frac{d w_B}{d x} = m^2 \beta\, w_{Ao} w_{Bo} \quad \text{at } x = 0 \tag{3.10}$$

Equations [3.7] and [3.8] can be represented in terms of a single independent variable v defined by

$$w_A = \theta - \frac{1}{Sh_A} \left.\frac{d w_A}{d x}\right|_{x=1} - m^2 v \tag{3.11}$$

$$w_B = 1 - \theta - \frac{1}{Sh_B} \left.\frac{d w_B}{d x}\right|_{x=1} - \frac{m^2 v}{r} \tag{3.12}$$

so that they can be transformed into

$$-\frac{d^2 v}{d x^2} = \left(\theta - \frac{1}{Sh_A} \left.\frac{d w_A}{d x}\right|_{x = 1} - m^2 v\right)\left(1 - \theta - \frac{1}{Sh_B} \left.\frac{d w_B}{d x}\right|_{x = 1} - \frac{m^2 v}{r}\right) \qquad [3.13]$$

with the transformed boundary conditions

$$v\,[1] = 0 \qquad [3.14]$$

$$\frac{d v\,[0]}{d x} = -\beta\, w_{Ao}\, w_{Bo} \qquad [3.15]$$

The overall rate of reaction is equal to the rate of consumption of species A, and is maximum when

$$R = -\left.\frac{d v}{d x}\right|_{x = 1} \qquad [3.16]$$

is maximum with respect to θ. The optimum value of θ for a set of values of other parameters [m, β, r, Sh_A and Sh_B] can be determined using the methods developed in the following section.

3.2 PARAMETRIC ANALYSIS

There are two methods available for obtaining the optimum value of θ. In one method the basic Equation [3.13] is directly integrated to obtain the concentration profile and flux. In view of the nonlinear equation involved, however, an analytic solution is not possible here and suitable approximation has to be made. In another approach [9] an adjoint variable λ is introduced in the basic equation and variation in rate is computed for a small change in θ.

3.2.1 Variational approach

Introducing the adjoint variable λ, the basic Equation [3.13] can be recast as

$$R = -\left.\frac{d\,v}{d\,x}\right|_{x=1} + \int_0^1 \lambda\,[x] \left[\frac{d^2\,v}{d\,x^2} + \left(\theta - \frac{1}{Sh_A}\,\frac{d\,w_A}{d\,x} - m^2\,v\right)\right.$$

$$\left.\left(1 - \theta - \frac{1}{Sh_B}\,\frac{d\,w_B}{d\,x} - \frac{m^2\,v}{r}\right)\right] d\,x \qquad [3.17]$$

A small change in θ induces a correspondingly small change in R and v and can be obtained from Equation [3.17] thus:

$$\delta\,R = -\frac{d\,\delta\,v[x]}{d\,x} + \int_0^1 \lambda[x] \left[\frac{d^2\,\delta\,v[x]}{d\,x^2} + \frac{\partial\,\mathcal{R}\,[v,\theta]}{\theta}\,\delta\,\theta - \right.$$

$$\left.\frac{\partial\mathcal{R}\,[v,\,\theta]}{\partial\,v}\,\delta\,v\right] d\,x \qquad [3.18]$$

where

$$\mathcal{R} = \left(\theta - \frac{1}{Sh_A} \left. \frac{d\, w_A}{d\, x} \right|_{x=1} - m^2\, v \right) \left(1 - \theta - \frac{1}{Sh_B} \left. \frac{d\, w_B}{d\, x} \right|_{x=1} - \frac{m^2\, v}{r} \right)$$

[3.19]

The first term under the integral sign in Equation [3.18] can be integrated and the result rearranged to give

$$\delta\, R = \frac{d\, \delta\, v[1]}{d\, x} \left(\lambda[1] - 1 \right) - \lambda[0] \frac{d\, \delta\, V[0]}{d\, x} - \frac{d\, \lambda[1]}{d\, x}\, \delta\, v[1]$$

$$\underbrace{+ \frac{d\, \lambda[0]}{d\, x}\, \delta\, v[0]}_{\neq 0} + \int_0^1 \left[\frac{d^2\, \lambda[x]}{d\, x^2} + \lambda[x] \frac{\partial \mathcal{R}\, [v,\theta]}{\partial\, v}\, \delta\, v \right] d\, x$$

$$+ \int_0^1 \lambda[x] \frac{\partial \mathcal{R}\, [v,\theta]}{\partial\, \theta}\, \delta\, \theta\, d\, x \qquad [3.20]$$

If the adjoint vector λ is chosen to satisfy the equation

$$\frac{d^2\, \lambda[x]}{d\, x^2} + \lambda[x] \frac{\partial \mathcal{R}\, [v,\theta]}{\partial\, v} = 0 \qquad [3.21]$$

with the boundary conditions $\lambda[1] = 1$ and $\lambda[0] = 0$, then Equation [3.$\overset{20}{19}$] can be written as

$$\frac{\delta R}{\delta \theta} = \int_0^1 \lambda[x] \frac{\partial \mathcal{R}[v,\theta]}{\partial \theta} \, d\,x \qquad [3.22]$$

Equations [3.21] and [3.22] can be evaluated numerically to obtain the derivative of R and hence the optimum value of θ.

3.2.2 Optimum linearisation method

In obtaining an approximate solution to the problem it is assumed that the concentration of component B in the film can be represented by a certain optimum value $\bar{w}_B$. Thus Equation [3.13]

$$-\frac{d^2\,v}{d\,x^2} = \left(\theta - \frac{1}{Sh_A}\frac{d\,w_A}{d\,x}\bigg|_{x=1} - m^2\,v\right)\left(1 - \theta - \frac{1}{Sh_B}\frac{d\,w_B}{d\,x}\bigg|_{x=1} - \frac{m^2\,v}{r}\right)$$

[3.13]

becomes

$$-\frac{d^2\,v}{d\,x^2} = \left(\theta - \frac{1}{Sh_A}\,\frac{d\,w_1}{d\,x}\bigg|_1 - m^2\,v\right)\bar{w}_B \qquad [3.23]$$

and the error generated is given by

$$\varepsilon = \left(\theta - \frac{1}{Sh_A}\,\frac{d\,w_A}{d\,x}\bigg|_1 - m^2\,v\right)\left(1 - \theta - \frac{1}{Sh_B}\frac{d\,w_B}{d\,x}\bigg|_1 - \frac{m^2\,v}{r} - \bar{w}_B\right)$$

[3.24]

This error is then made minimum

$$I = \int_0^1 \xi^2 \, d\,x \qquad [3.25]$$

$$= \int_0^1 \left(\theta - \frac{1}{Sh_A} \left.\frac{d\,w_A}{d\,x}\right|_1 - m^2\,v\right)^2 \left[\left(1 - \theta - \frac{1}{Sh_B} \left.\frac{d\,w_B}{d\,x}\right|_1 - \frac{m^2\,v}{r}\right)^2 + \bar{w}_B^2 - 2\,\bar{w}_B \left(1 - \theta - \frac{1}{Sh_B} \left.\frac{d\,w_B}{d\,x}\right|_1 - \frac{m^2\,v}{r}\right)\right] d\,x \qquad [3.26]$$

Equation [3.26] has the form

$$I = A\,\bar{w}_B^2 + B\,\bar{w}_B + C \qquad [3.27]$$

where

$$A = \int_0^1 \left(\theta - \frac{1}{Sh_A} \left.\frac{d\,w_A}{d\,x}\right|_1 - m^2\,v\right) d\,x$$

$$B = \int_0^1 2\left(\theta - \frac{1}{Sh_A} \left.\frac{d\,w_A}{d\,x}\right|_1 - m^2\,v\right)\left(1 - \theta - \frac{1}{Sh_B} \left.\frac{d\,w_B}{d\,x}\right|_1 - \frac{m^2\,v}{r}\right) d\,x$$

and

$$C = \int_0^1 \left(\theta - \frac{1}{Sh_A} \left.\frac{d\,w_A}{d\,x}\right|_1 - m^2\,v\right)\left(1 - \theta - \frac{1}{Sh_B} \left.\frac{d\,w_B}{d\,x}\right|_1 - \frac{m^2\,v}{r}\right) d\,x$$

[3.28]

differentiating Equation [3.27] gives

$$\frac{d\,I}{d\,\bar{w}_B} = 0 = 2\,A\,\bar{w}_B + B = 0$$

or

$$\bar{w}_B = -\frac{B}{2\,A} \qquad [3.29]$$

$$\bar{w}_B = \frac{\displaystyle\int_0^1 2\left(\theta - \frac{1}{Sh_1}\frac{d\,w_A}{d\,x}\bigg|_{x=1} - m^2 v\right)\left(1 - \theta - \frac{1}{Sh_1}\frac{d\,w_B}{d\,x}\bigg|_{x=1} - \frac{m^2 v}{\phi}\right) dx}{\displaystyle\int_0^1 2\left(\theta - \frac{1}{Sh_1}\frac{d\,w_A}{d\,x}_{x=1} - m^2 v\right) d\,x}$$

$$[3.30]$$

Equation [3.30] represents the optimum value of the concentration of B in the film which when replaced for w_B will lead to a minimum error. Using this optimum value of w_B, Equation [3.13] can now be simplified and rearranged as

$$\frac{d^2\,v}{d\,x^2} - m_1^2\,v = -\left[\theta - \frac{1}{Sh_1}\frac{d\,w_A}{d\,x}\bigg|_{x=1}\right]\bar{w}_B \qquad [3.31]$$

where

$$m_1 = m\,\sqrt{\bar{w}_B}$$

$\left.\begin{matrix}\frac{\partial c_A}{\partial x} = 0 \\ c = 0\end{matrix}\right\}$ y_1 bc.

The solution to this subject to boundary condition [3.14] and [3.15] is

$$v = \left[\frac{\beta\, w_{Ao}\, w_{Bo}}{m_1}\, e^{m_1} - \frac{\left[\theta - \frac{1}{Sh_1}\left.\frac{d\, w_A}{d\, x}\right|_{x=1}\right]\bar{\bar{w}}_B}{m_1^2}\right]\frac{\cosh m_1 x}{\cosh m_1}$$

$$- \frac{\beta\, w_{Ao}\, w_{Bo}}{m_1}\, e^{m_1 x} + \frac{\left[\theta - \frac{1}{Sh_1}\left.\frac{d\, w_A}{d\, x}\right|_{x=1}\right]\bar{\bar{w}}_B}{m_1^2} \qquad [3.32]$$

The flux can now be readily obtained as

$$\left.\frac{d\, v}{d\, x}\right|_{x=1} = \frac{\left(\theta - \frac{1}{Sh_1}\frac{d\, w_A}{d\, x}\right)\sqrt{\bar{\bar{w}}_B}}{m}\tanh\, m\sqrt{\bar{\bar{w}}_B}$$

$$+ \beta\, w_{Ao}\, w_{Bo}\, e^{m\sqrt{\bar{\bar{w}}_B}}\left[1 - \tanh m\sqrt{\bar{\bar{w}}_B}\right] \qquad [3.33]$$

Thus for $\frac{d\, R}{d\, \theta} = 0$, we get the optimum value of θ as

$$\frac{d\, R}{d\, \theta} = \frac{d}{d\, \theta}\left[\frac{\left(\theta - \frac{1}{Sh_1}\left.\frac{d\, w_A}{d\, x}\right|_{x=1}\right)\sqrt{\bar{\bar{w}}_B}}{m}\tanh\, m\sqrt{\bar{\bar{w}}_B}\right.$$

$$\left.+ \beta\, w_{Ao}\, w_{Bo}\, e^{m\sqrt{\bar{\bar{w}}_B}}\left[1 - \tanh\, m\sqrt{\bar{\bar{w}}_B}\right]\right] \qquad [3.34]$$

For the simple case $r \rightarrow \infty$, Equation [3.30] simplifies to

$$\overline{w}_B = 1 - \theta - \frac{1}{Sh_B} \left. \frac{d\, w_B}{d\, x} \right|_{x=1} \qquad [3.35]$$

Substituting this equation in [3.34] and differentiating with respect to θ gives, for $\beta = 0$

$$\theta - \frac{1}{Sh_A} \left. \frac{d\, w_A}{d\, x} \right|_{x=1} = + \frac{\text{Sinh } 2\, m \sqrt{1 - \theta - \frac{1}{Sh_B} \left. \frac{d\, w_B}{d\, x} \right|_{x=1}}}{2\, m \sqrt{1 - \theta \frac{1}{Sh_B} \left. \frac{d\, w_B}{d\, x} \right|_{x=1}}} \times$$

$$\left(2 + \frac{1}{Sh_A} \left. \frac{d\, w_A}{d\, x} \right|_{x=1} - \frac{2}{Sh_B} \left. \frac{d\, w_B}{d\, x} \right|_{x=1} - 3\, \theta \right) \qquad [3.36]$$

For $\beta = 0$, $m = 3$, and $Sh_A = Sh_B = \infty$, Equation [3.36] can be solved to give θ_{opt} as 0.632. This asymptotic value has been obtained by Bailey [9] and is rederived here using the approximate solution thus confirming its validity. θ_{opt} obtained as a function of Thiele modulus is plotted in Figure 3.1. The asymptotic values lie between 0.50 and 0.65. For finite values of the gas-liquid parameter β and Sherwood numbers, Equation [3.34] can be differentiated to give the optimum value of θ.

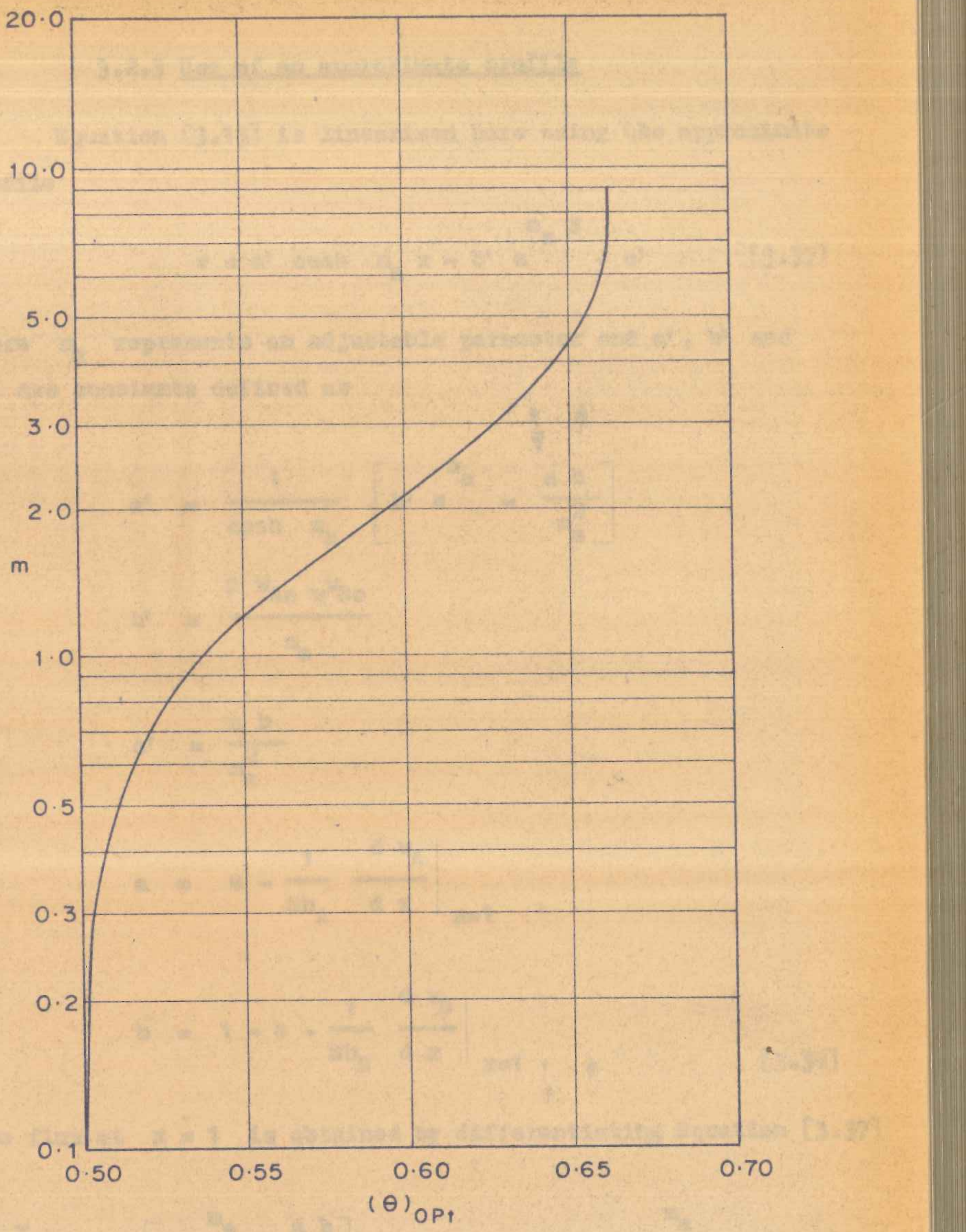

FIGURE 3·1: VARIATION OF OPTIMUM BULK PHASE COMPOSITION AS A FUNCTION OF THIELE MODULUS FOR $r \longrightarrow \infty$

3.2.3 Use of an approximate profile

Equation [3.13] is linearised here using the approximate profile

$$v = a' \cosh m_a x - b' e^{m_a x} + c' \qquad [3.37]$$

where m_a represents an adjustable parameter and a' , b' and c' are constants defined as

$$a' = \frac{1}{\cosh m_a} \left[b' e^{m_a} - \frac{a\, b}{m_a^2} \right]$$

$$b' = \frac{\beta\, w_{Ao}\, w_{Bo}}{m_a}$$

$$c' = \frac{a\, b}{m_a^2}$$

$$a = \theta - \frac{1}{Sh_A} \left. \frac{d\, w_A}{d\, x} \right|_{x=1}$$

$$b = 1 - \theta - \frac{1}{Sh_B} \left. \frac{d\, w_B}{d\, x} \right|_{x=1} \qquad [3.38]$$

The flux at x = 1 is obtained by differentiating Equation [3.37]

$$\left. \frac{d\, v}{d\, x} \right|_{x=1} = \left[b' e^{m_a} - \frac{a\, b}{m_a^2} \right] m_a \tanh m_a - m_a\, b' e^{m_a} \qquad [3.39]$$

or

$$\left.\frac{d\,v}{d\,x}\right|_{x=1} = \beta\; w_{Ao}\; w_{Bo}\; e^{m_a}\,[\tanh m_a - 1] - \frac{a\;b\;\tanh m_a}{m_a} \qquad [3.40]$$

For the simple case of $\beta = 0$, this reduces to

$$-\left.\frac{d\,v}{d\,x}\right|_{x=1} = \frac{\left(\theta - \frac{1}{Sh_A}\left.\frac{d\,w_A}{d\,x}\right|_{x=1}\right)\left(1 - \theta - \frac{1}{Sh_B}\left.\frac{d\,w_B}{d\,x}\right|_{x=1}\right)\tanh m_a}{m_a} \qquad [3.41]$$

The parameter m_a in Equations [3.38] - [3.41] can be obtained by substituting the concentration profile [3.37] in Equation [3.13] and integrating twice to give

$$\begin{aligned}[v]_{x=0} = {} & - \frac{a\;b}{2} - m^2\left(b + \frac{a}{r}\right)\left[\frac{a'}{m_a^2} - \frac{b'}{m_a^2} + C_2 + \frac{a'\;\cosh m_a}{m_a^2}\right. \\ & \left. + \frac{b'\;e^{m_a}}{m_a^2} - \frac{c'}{2} - C_2 + \frac{b'}{m_a}\right] + \frac{m^4}{r}\left[\left(\frac{b'^{\,2}}{4\;m_a^2} - \frac{2\;b'\;c'}{m_a^2}\right.\right. \\ & \left. + \frac{2\;a'\;c'}{m_a^2} - \frac{a'\;b'}{4\;m_a^2}\right) - \left(a'\left\{\frac{\sinh^2 m_a}{4\;m_a^2} + \frac{1}{4}\right\}\frac{c'^{\,2}}{2} + \frac{b'^{\,2}\;e^{2m_a}}{4\;m_a^2}\right. \\ & \left. - \frac{2\;b'\;c'\;e^{m_a}}{m_a^2} + \frac{2\;a'\;c'\;\cosh m_a}{m_a^2} - \frac{a'\;b'\;e^{2m_a}}{4\;m_a^2} + \frac{a'\;b'}{2}\right) \\ & \left. - \left(\frac{b'^{\,2}}{2\;m_a} - \frac{2\;b'\;c'}{m_a} - \frac{a'\;b'}{2\;m_a}\right)\right] \qquad [3.42]\end{aligned}$$

For the simple case of $\beta = 0$, this reduces to

$$[v]_{x=0} = -\frac{a\ b}{2} - m^2\left(b + \frac{a}{r}\right)\left[\frac{a'}{m_a^2}\ (1 - \cosh m_a) - \frac{c'}{2}\right] + \frac{m^4}{r}$$

$$\left[\frac{2\ a'c'}{m_a^2} - \left\{a'\left(\frac{\sin\ m_a}{4\ m_a^2} + \frac{1}{4}\right) + \frac{c'^2}{2} + \frac{2\ a'c'\ \cosh m_a}{m_a^2}\right\}\right] \qquad [3.43]$$

w_{Ao} and w_{Bo} appearing in the term b' in Equation [3.42] can be obtained from Equations [3.11], [3.12] and [3.37] at $x = 0$ as

$$w_{Ao} = a - m^2\,[a' - b' + c'] \qquad [3.44]$$

$$w_{Bo} = b - \frac{m^2}{r}\,[a' - b' + c'] \qquad [3.45]$$

Equations [3.44] and [3.45] can be solved simultaneously to get explicit expressions for w_{Ao} and w_{Bo} as

$$w_{Ao} = \frac{a - m^2\,[a' + c']}{1 - \dfrac{m^2\ \beta\ w_{Bo}}{m_a}} \qquad [3.46]$$

$$w_{Bo}^2 + \left[\frac{1}{r}\ \ [a - m^2\ (a' + c')] - \ \ [b - \frac{m^2}{r}\,[(a' + c')] - \frac{m_a}{m^2\beta}\right]\ w_{Ao}$$

$$+ \frac{m_a}{m^2\ \beta}\left[b - \frac{m^2}{r}\ (a' + c')\right] = 0 \qquad [3.47]$$

For a given value of the Thiele modulus, diffusivity ratio and the gas-liquid parameter, w_{Ao} and w_{Bo} are evaluated using Equations [3.46] and [3.47]. For known values of gas film resistances [in terms of the respective Sherwood numbers], the parameter m_a can be evaluated from Equation [3.42]. The mass flux is then calculated using Equation [3.39].

For the simple case when $\beta = 0$ and no gas film resistance [$Sh_A = Sh_B = \infty$] the governing equations can be simplified considerably. Figure 3.2 shows a plot of the rate R as a function of composition in the gas phase for $m = 3$, $\beta = 0$, $Sh_A = Sh_B = \infty$, $r = 0.1$. The rate is calculated using Equation [3.41]:

$$R = \frac{a\ b \tanh m_a}{m_a} = \frac{\theta\ [1 - \theta] \tanh m_a}{m_a} \qquad [3.48]$$

A close inspection of Equation [3.41] indicates that the rate becomes zero both for $\theta = 0$ and $\theta = 1$. This can be easily understood since no reaction can occur in absence of either one of the components. For a certain value of θ [$0 < \theta < 1$] the rate goes through a maximum and this optimum θ depends on the value of the parameter m_a. For the case when diffusivity of one of the components, say A, is far greater than B, the physical situation corresponds to a case where A is diffusing much faster and thus has a larger concentration in the bulk than component B. Not Having the reactants in stoichiometric amounts will thus entail improper utilisation of the reactants. On the other hand if the concentration of B is increased in the gas phase, a higher concentration gradient is provided

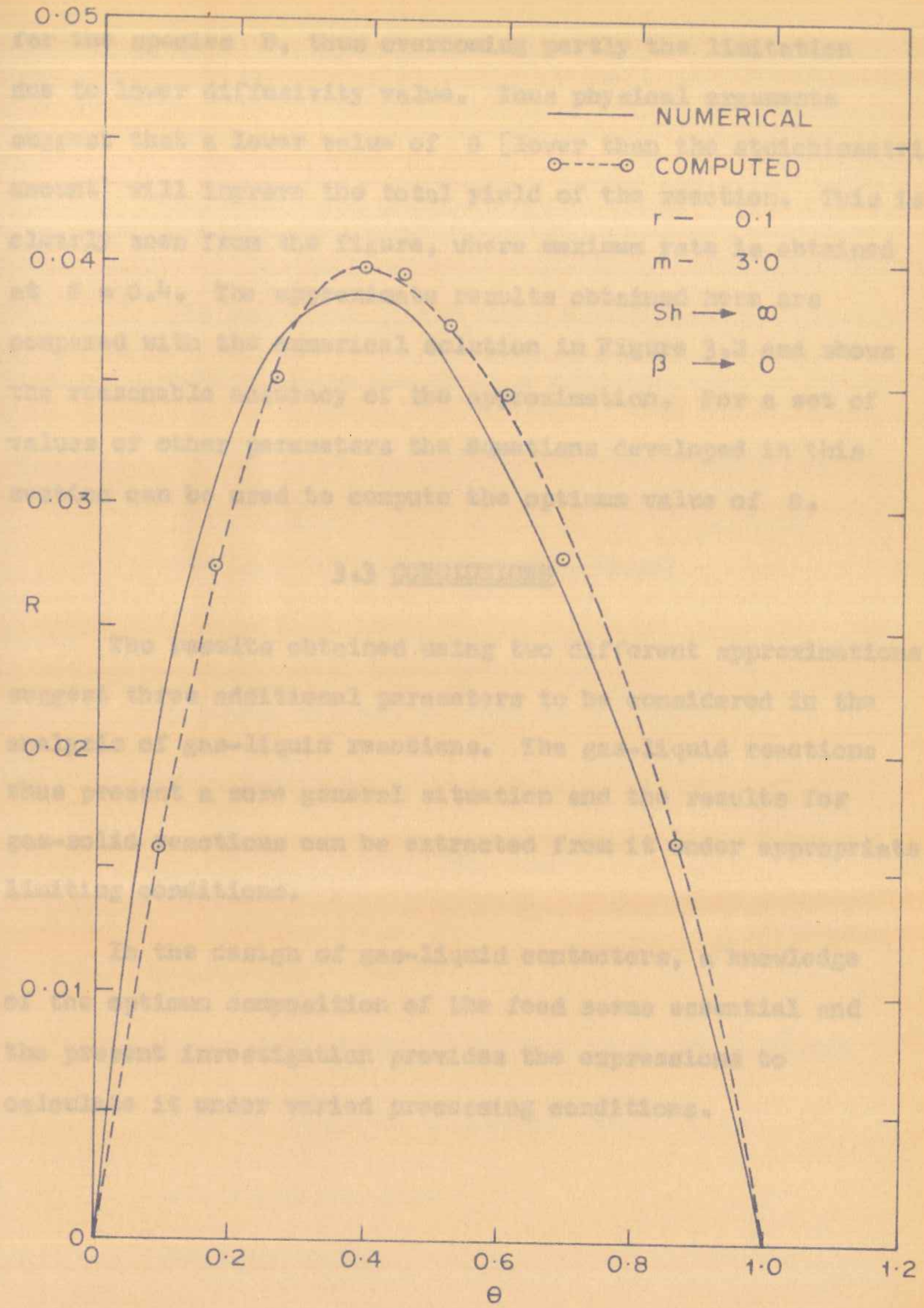

FIGURE 3·2: DEPENDENCE OF REACTION RATE ON COMPOSITION IN THE BULK FLUID PHASE for the species B, thus overcoming partly the limitation due to lower diffusivity value. Thus physical arguments suggest that a lower value of θ [lower than the stoichiometric amount] will improve the total yield of the reaction. This is clearly seen from the figure, where maximum rate is obtained at $\theta = 0.4$. The approximate results obtained here are compared with the numerical solution in Figure 3.2 and shows the reasonable accuracy of the approximation. For a set of values of other parameters the equations developed in this section can be used to compute the optimum value of θ.

3.3 CONCLUSIONS

The results obtained using two different approximations suggest three additional parameters to be considered in the analysis of gas-liquid reactions. The gas-liquid reactions thus present a more general situation and the results for gas-solid reactions can be extracted from it under appropriate limiting conditions.

In the design of gas-liquid contactors, a knowledge of the optimum composition of the feed seems essential and the present investigation provides the expressions to calculate it under varied processing conditions.

NOTATION

a	interfacial area, cm^2/cm^3
a, b, a', b', c'	constants defined by Equation [3.38]
A, B	gas phase reactants; constants defined by Equation [3.28]
C_A, C_B	concentration of A, B, g mole/cm^3
C_{Ag}, C_{Bg}	concentration of gases in the bulk, g mole/cm^3
C	total concentration of gas phase, g mole/cm^3; constant defined by Equation [3.28]
D_A, D_B	diffusivity of species A and B in liquid, cm^2/sec
I	integral defined by Equation [3.25]
k_1	rate constant, cm^3/g mole sec
m	Thiele modulus $\delta \sqrt{\frac{k_1}{D_A} C_A^{*\,n-1}}$
m_1	$m \sqrt{\bar{w}_B}$
m_a	adjustable parameter defined by Equation [3.37]
R	rate of reaction, g mole/cm^3 sec
$\mathcal{R}$	defined by Equation [3.19]
Sh	Sherwood number
v	concentration variable defined by Equation [3.11]
w_A, w_B	dimensionless concentration of A and B species

$\bar{w}_B$	optimum dimensionless concentration of B
x	dimensionless distance
y	distance parameter, cm
z	stoichiometric coefficient

Greek symbols

β	dimensionless parameter defined as $\frac{1}{a\delta}$
δ	film thickness; difference operator
θ	mole fraction of A in the bulk gas
ϕ	diffusivity ratio
λ	adjoint variable
ϵ	error

Subscripts

i	conditions at the interface
o	condition in the bulk
A,B	for the species A or B

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CHAPTER 4

EFFECTIVENESS FACTORS IN GAS-LIQUID REACTIONS

4.1 INTRODUCTION

In the analysis of chemical reactions occurring in fluid-fluid and fluid-solid systems, two entirely different approaches have been employed. In the case of fluid-fluid reactions, particularly gas-liquid reactions, it is customary to regard chemical reaction as an accelerator of the absorption process and to define an enhancement factor which is the ratio of the absorption rate with chemical reaction to that under conditions of no reaction. On the other hand, for fluid-solid reactions, particularly solid catalysed gas phase reactions, chemical reaction is regarded as the main process with diffusion acting as a retarding influence; thus an effectiveness factor is defined which is the ratio of chemical reaction in the presence of diffusion to that in the absence of any diffusional effect.

As long as one is designing an equipment with the object of carrying out a chemical reaction in it, it is logical to regard chemical reaction as the principal process. Thus, irrespective of the type of system employed [viz. gas-liquid, gas-solid catalytic, gas-solid noncatalytic, liquid-liquid, etc.], it seems reasonable to use a single concept of the effectiveness factor as a common means of accounting for diffusion. This concept has been widely employed for gas-solid catalytic and gas-solid noncatalytic systems, but there are very few reported attempts to extend it to other systems. Rony [1] applied it to a simple gas-liquid catalysed system and Shah and Kenney [2] to another simple reaction scheme. A general analysis similar to that for gas-solid systems is still lacking, and it is the purpose of this chapter to present an analysis of gas-liquid systems in terms of the effectiveness factor and to propose methods of delineating the controlling regimes based on this concept.

Based on the film theory four distinct regimes can be identified in gas-liquid reaction: [1] very slow reaction where the reaction occurs entirely in the bulk; [2] slow reaction where there is a diffusional resistance in the film but the reaction still occurs only in the bulk; [3] the reaction is complete in the film, and [4] the reaction is so fast that the active species from the liquid diffuses partly into the film and the reaction occurs on a plane within the film. In the first case the reaction is completely kinetically controlled, in the second diffusion controlled, in the third controlled both by diffusion and chemical reaction, and in the fourth instantaneous.

In Section 4.1 of this chapter, the concept of the effectiveness factor is applied to the analysis of a simple first order irreversible isothermal reaction. Two cases, viz. [1] reaction confined to the bulk with film diffusion controlling, and [2] reaction occurring both in the film and the bulk, are considered. Case [1] corresponds to regime [2] and case [2] to the regime between [2] and [3]. The treatment is then extended to complex reaction schemes. The analysis of consecutive and parallel reaction schemes is presented in Section 4.2, and the case of a general order reaction and of nonisothermal gas-absorption is considered in Sections 4.3 and 4.4 respectively. As with the simple reaction, in the analysis of these complex reactions the object is to show that the gas-liquid system provides a general framework within which the gas-solid catalytic reaction fits under certain conditions.

Although the application of this concept to gas-liquid reactions has been hinted in the book by Astarita [3], the present investigation provides perhaps the first comprehensive analysis of the effectiveness factor concept as applied to gas-liquid reactions. In view of the work being done in this laboratory on gas-solid catalytic and noncatalytic reactions as well as on gas-liquid reactions, the use of a generalised approach based on a single concept - the effectiveness factor - arose as a distinct possibility.

Two dimensionless parameters β and θ are defined in this work to generalise the concept of effectiveness factor to gas-solid as well as gas-liquid reactions. The parameter β defined as the ratio of the area per unit volume in the film $[1/\delta]$ to that in the bulk $[a]$ is a measure of the participation of bulk in the overall process. For simple isothermal reactions this parameter is adequate to generalise the concept of effectiveness factor to gas-solid and gas-liquid reactions. The dimensionless parameter θ defined as a surface reaction modulus is a measure of the contribution to the total reaction at the interface and together with parameter β, generalises the concept of the effectiveness factor to nonisothermal gas-solid and gas-liquid system as well.

The chief objective of an analysis of this kind is to enable the determination of the true kinetic parameters of a reaction as well as to predict the performance of industrial contactors under specific conditions of operation.

4.2 EFFECTIVENESS FACTOR FOR A SIMPLE FIRST ORDER REACTION

4.2.1 Reaction complete in the bulk

This regime is characterised by a pure diffusional resistance in the film, with reaction confined exclusively to the bulk. The reaction is not so fast as to occur in the film simultaneously with diffusion, but is fast enough to offer less resistance than pure diffusion in the film. The concentration gradients for this regime are shown in Figure 4.1a.

Considering the reaction

$$A \rightarrow \text{Products}$$

the following mass balance equation can be written for A:

$$-D_A \left. \frac{d\,C_A}{d\,y} \right|_{y\,=\,\delta} = k_L \left[C_A^* - C_{Ao} \right] \qquad [4.1]$$

or, in dimensionless form,

$$- \left. \frac{d\,w_A}{d\,x} \right|_{x\,=\,1} = 1 - w_{Ao} \qquad [4.2]$$

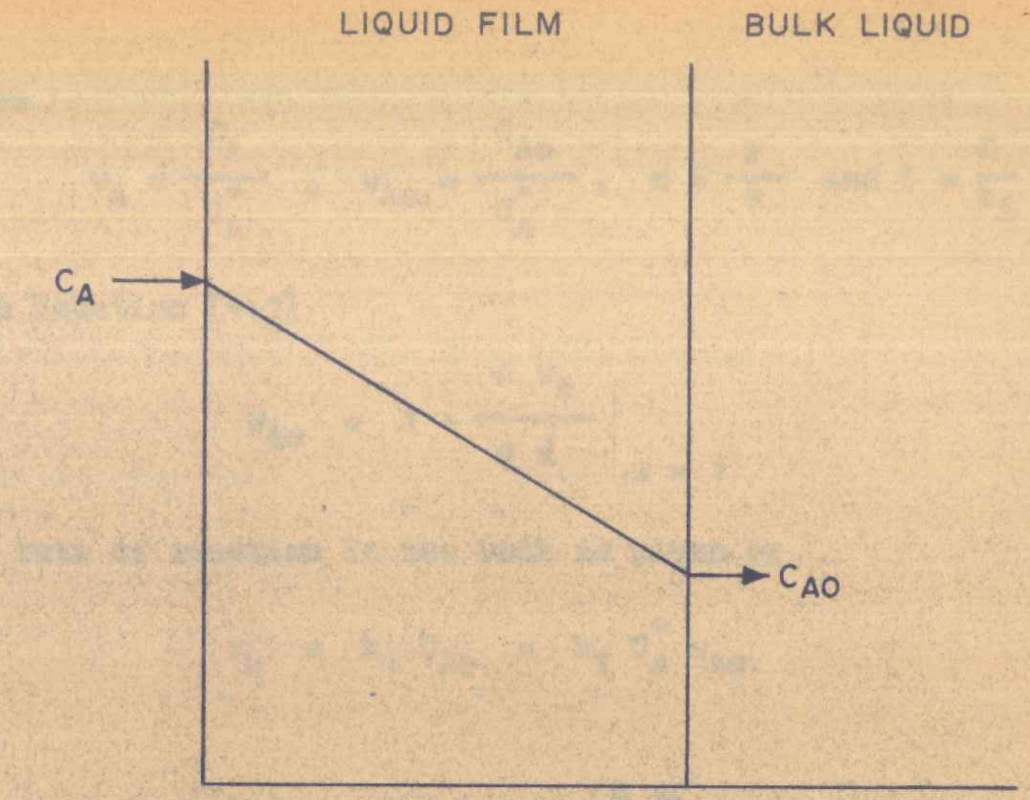


FIGURE 4·1a. CONCENTRATION PROFILES IN THE FILM: DIFFUSIONAL RESISTANCE

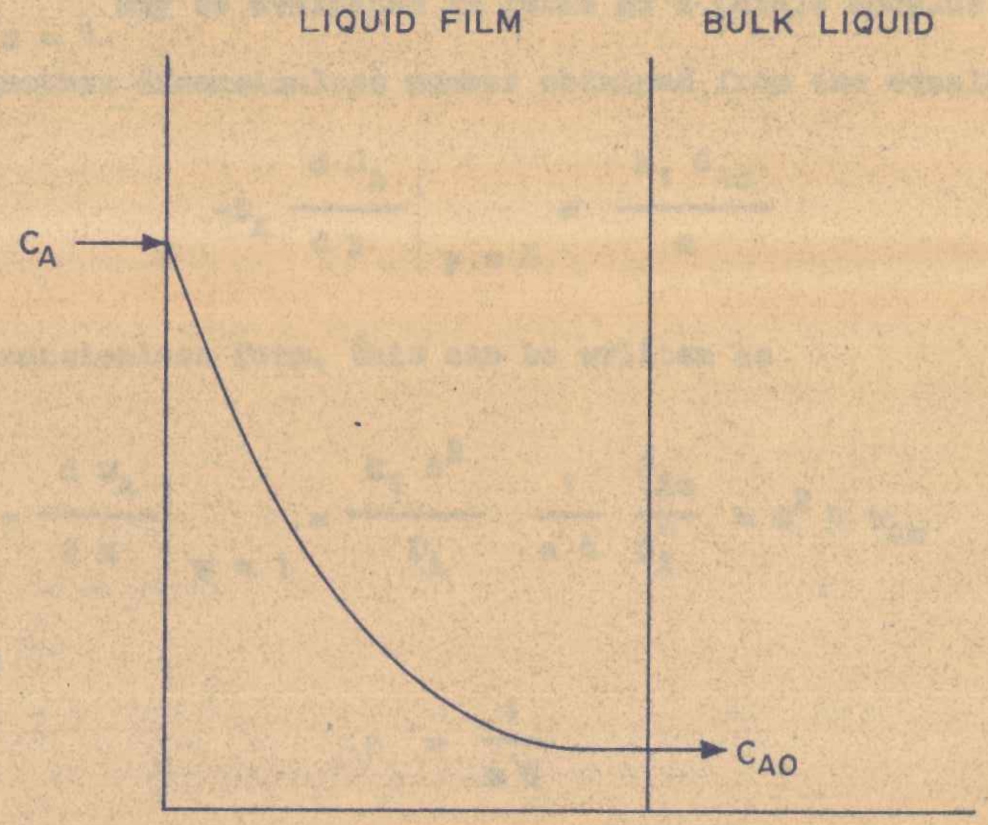


FIGURE 4·1b: CONCENTRATION PROFILES IN THE FILM: PART OF REACTION IN FILM AND REST IN BULK

where

$$w_A = \frac{C_A}{C_A^*}\ , \quad w_{Ao} = \frac{C_{Ao}}{C_A^*}\ , \quad x = \frac{y}{\delta} \quad \text{and} \quad \delta = \frac{D}{k_L} \tag{4.3}$$

From Equation [4.1]

$$w_{Ao} = 1 + \left.\frac{d\,w_A}{d\,x}\right|_{x = 1} \tag{4.4}$$

The rate of reaction in the bulk is given by

$$r_B = k_1\,C_{Ao} = k_1\,C_A^*\,w_{Ao} \tag{4.5}$$

or

$$r_B = k_1\,C_A^* \left[1 + \left.\frac{d\,w_A}{d\,x}\right|_{x = 1} \right] \tag{4.6}$$

$\left.\frac{d\,w}{d\,x}\right|_{x = 1}$ may be evaluated in terms of a Thiele modulus m and another dimensionless number obtained from the equality

$$-D_A \left.\frac{d\,C_A}{d\,y}\right|_{y = \delta} = \frac{k_1\,C_{Ao}}{a} \tag{4.7}$$

In dimensionless form, this can be written as

$$- \left.\frac{d\,w_A}{d\,x}\right|_{x = 1} = \frac{k_1\,\delta^2}{D_A}\;\frac{1}{a\,\delta}\;\frac{C_{Ao}}{C_A^*} = m^2\,\beta\,w_{Ao} \tag{4.8}$$

where

$$\beta = \frac{1}{a\,\delta} \tag{4.9}$$

and represents the ratio of the volume per unit area of the bulk [1/a] to the volume per unit area of the film [δ].

Substitution of Equation [4.8] in [4.6] leads to

$$r_B = k_1 C_A^* [1 + -m^2 \ \beta \ w_{Ao}]$$

$$= k_1 C_A^* - r_B m^2 \beta \qquad [4.10]$$

or

$$r_B = \frac{k_1 C_A^*}{1 + m^2 \beta} \qquad [4.11]$$

The rate of reaction in the absence of any diffusional resistance will be given by $k_1 C_A^*$; hence the following expression for the effectiveness factor can be written:

$$\eta = \frac{k_1 C_A^*}{k_1 C_A^* [1 + m^2 \beta]} = \frac{1}{1 + m^2 \beta} \qquad [4.12]$$

From Equation [4.12] it can be seen that the effectiveness factor is not only a function of the modulus m but also of the dimensionless ratio β. Since this analysis is restricted to control by pure diffusion in the film and it is assumed that chemical reaction is reasonably fast, the effectiveness factor should necessarily be less than one. This can happen only when β has a finite value. For a value of β close to zero [viz. the interfacial area $a \to \infty$], the physical situation would be that no liquid bulk exists. This situation is clearly impossible, which also upholds the absurdity of η becoming equal to unity in the diffusion regime. Thus Equation [4.12] is strictly valid only up to a certain finite value of β. If, as in the case of catalytic reactions, it is stipulated that the reaction can be assumed to be diffusion influenced if η is $\overline{<}$ 0.95, the following condition can be written for the applicability of Equation [4.12]:

$$\frac{1}{1 + m^2 \beta} \; \overline{<} \; 0.95$$

or

$$m^2 \beta \; \overline{<} \; 0.05 \qquad [4.13]$$

η is plotted as a function of the modulus m for various values of β in Figure 4.2. For β equal to zero, i.e. when the interfacial area a tends to infinity, practically no liquid bulk exists, and hence for a system under diffusion control no reaction can occur.

4.2.2 Reaction both in the film and bulk

Let us now consider the more general case where a part of the reaction occurs in the film and the rest in the bulk. The concentration profile for this situation will be as shown in Figure 4.1b. This should be distinguished from regime 3 in which the reaction is complete in the film. The situation considered is thus a more general one which reduces to regime 3 when there is no reaction in the bulk. In the present analysis a simple irreversible first-order reaction will first be considered and the treatment then extended to a complex

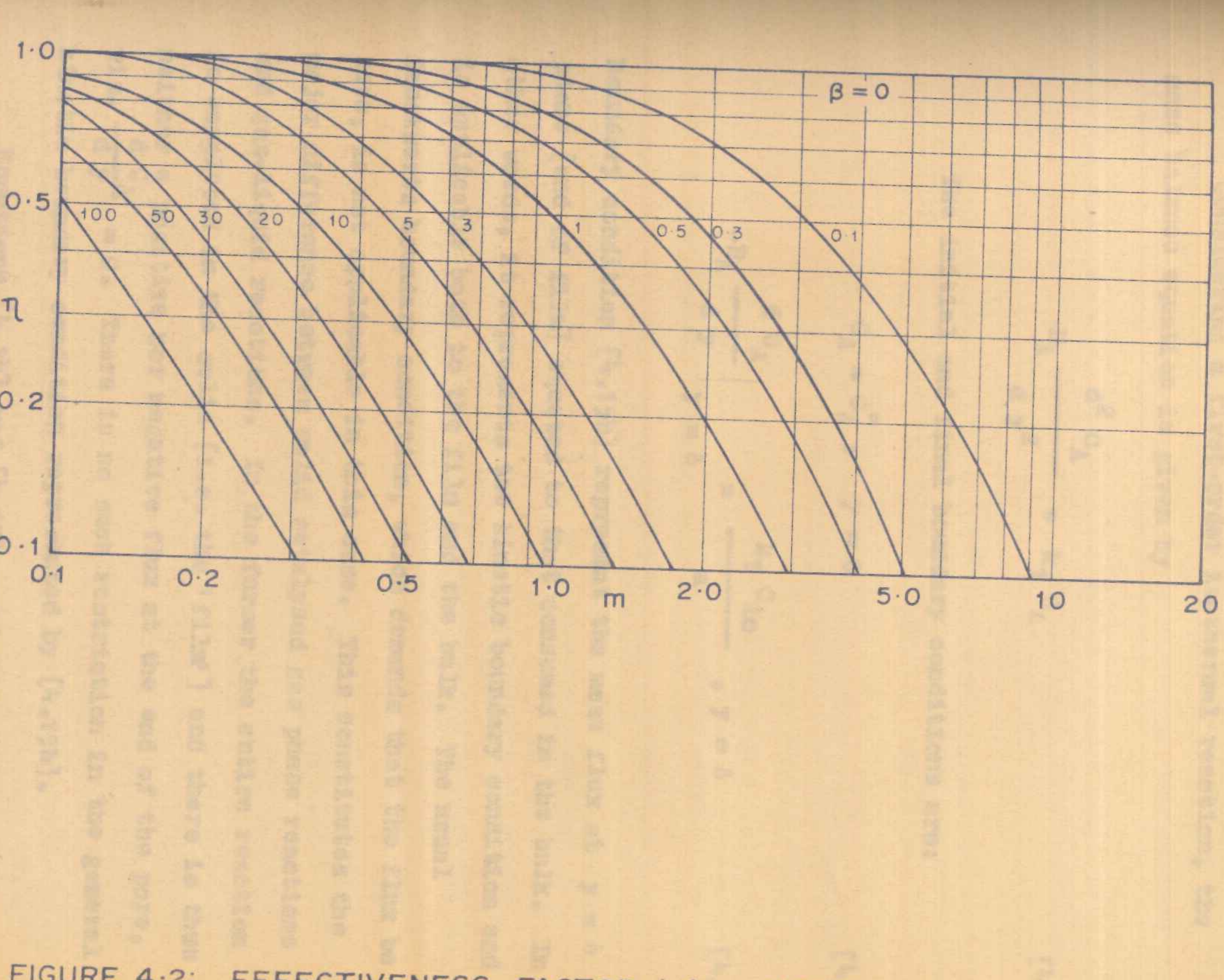


FIGURE 4·2: EFFECTIVENESS FACTOR (η) vs MODULUS (m) FOR VARIOUS VALUES OF β IN THE DIFFUSION REGIME (CASE 1) reaction in Section 4.3.

Considering a first-order isothermal reaction, the mass balance equation is given by

$$D_A \frac{d^2 C_A}{d y^2} = k_1 C_A \qquad [4.14]$$

The initial and final boundary conditions are:

$$C_A = C_A^* , \quad y = 0 \qquad [4.15a]$$

$$-D_A \left. \frac{d C_A}{d y} \right|_{y = \delta} = \frac{k_1 C_{Ao}}{a} , \quad y = \delta \qquad [4.15b]$$

Boundary condition [4.15b] represent the mass flux at $y = \delta$ plane [end of film] equated to that consumed in the bulk. In other words, it represents the kinetic boundary condition and is applicable both to the film and the bulk. The usual Danckwerts boundary condition, which demands that the flux be zero, is not applicable in this case. This constitutes the major difference between solid catalysed gas phase reactions and gas-liquid reactions. In the former the entire reaction is completed in the solid [i.e. the 'film'] and there is thus neither a positive nor negative flux at the end of the pore, viz. $\frac{d C_A}{d y} = 0$. There is no such restriction in the general kinetic boundary condition represented by [4.15b].

Equations [4.14] and [4.15] can be written in dimensionless form as

$$\frac{d^2\,w_A}{d\,x^2} = m^2\,w_A \qquad [4.16]$$

and

$$w_A = 1,\; x = 0 \qquad [4.17a]$$

$$-\left.\frac{d\,w_A}{d\,x}\right|_{x\,=\,1} = m^2\,\beta\,w_{Ao} \qquad [4.17b]$$

Equation [4.15] may be solved through boundary condition [4.17] to give the following equation for the concentration profile:

$$w_A = \frac{-\,m\,\beta\,w_{Ao}\,[\sinh mx] + \cosh m\,[1 - x]}{\cosh m} \qquad [4.18]$$

The total mass flux at $x = 0$ is then calculated as

$$-D_A\left.\frac{d\,C_A}{d\,x}\right|_{x\,=\,0} = \frac{D_A\,C_A^*}{\delta}\left[\frac{m^2\,\beta\,w_{Ao}}{\cosh m} + m\tanh m\right] \qquad [4.19]$$

Equation [4.19] represents the total mass flux consumed by reaction in the film plus that in the bulk. The total reaction flux under ideal conditions [i.e. with no diffusional influence] will be given by reaction occurring in the film [usually a very small quantity] plus the reaction occurring in the bulk:

$$\begin{aligned} r_A &= k_1\,C_A^*\,\delta + \frac{k_1\,C_A^*}{a} \\ &= k_1\,C_A^*\left[\frac{1 + a\,\delta}{a}\right] \end{aligned} \qquad [4.20]$$

In writing Equation [4.20], the assumption has been made that at the film-bulk interface the conditions existing in the bulk and the film are both operative. Actually in the kinetic regime the only difference between the two is in respect of the area available for the reaction, the concentration of A in both being equal to C_A^* [as there is no diffusional resistance]. In reality, in a situation of this kind, the film can be ignored. But in order to maintain similarity with the developments that follow, the total intrinsic reaction is hypothetically divided into film and bulk contributions.

The effectiveness factor for the system is given by

$$\eta = \frac{D_A\, C_A^*\, a}{\delta\, k_1\, C_A^*\, [a\, \delta + 1]} \left[\frac{m^2\, \beta\, w_{Ao}}{\cosh m} + m \tanh m \right] \qquad [4.21]$$

$$\eta = \frac{1}{1 + \beta} \left[\frac{\beta\, w_{Ao}}{\cosh m} + \frac{\tanh m}{m} \right] \qquad [4.22]$$

w_{Ao}, the dimensionless concentration in the bulk, may be expressed in terms of the modulus m using Equation [4.18] with the condition that at $x = 1$, $w_A = w_{Ao}$, Thus:

$$w_{Ao} = \frac{1}{\cosh m} \left[\frac{1}{1 + m\, \beta\, \tanh m} \right] \qquad [4.23]$$

Substituting Equation [4.23] in Equation [4.22]

$$\eta = \frac{1}{1 + \beta} \left[\frac{\beta}{[\cosh m]^2\, [1 + m\, \beta\, \tanh m]} + \frac{\tanh m}{m} \right] \qquad [4.24]$$

This equation is plotted in Figure 4.3, and the main features of the plot are discussed in the section on Controlling Regimes.

4.2.3 Controlling regimes

An examination of Figure 4.4 brings out some interesting features, based on which certain generalised conclusions can be drawn with respect to regimes 1, 2 and 3.

In preparing this plot for gas-liquid reactions, the effectiveness factor η is plotted against the modulus m for various values of the parameter β with the curve for $\beta = 0$ representing the upper bound. Three separate regions A, B and C representing the fast reaction regime [regime 3], regime between 2 and 3, and the diffusion regime [regime 2] can be identified. The upper and lower bounds for a diffusion controlled reaction to occur in the bulk [regime 2] can be fixed from the following considerations.

Let us take the curves for, say, $\beta = 1$. The upper curve represents the case where a part or whole of the reaction occurs in the film [regimes 2 and 3], while the lower curve represents the case where there is a pure diffusional resistance and the reaction is confined to the bulk [regime 2]. P represents the point of separation between these curves, and the locus of all such points at various values of β will give the upper bound above which the reaction is in the diffusional regime, and below which a part of the reaction occurs in the film also. For fixing the lower bound for reaction to occur in the bulk,

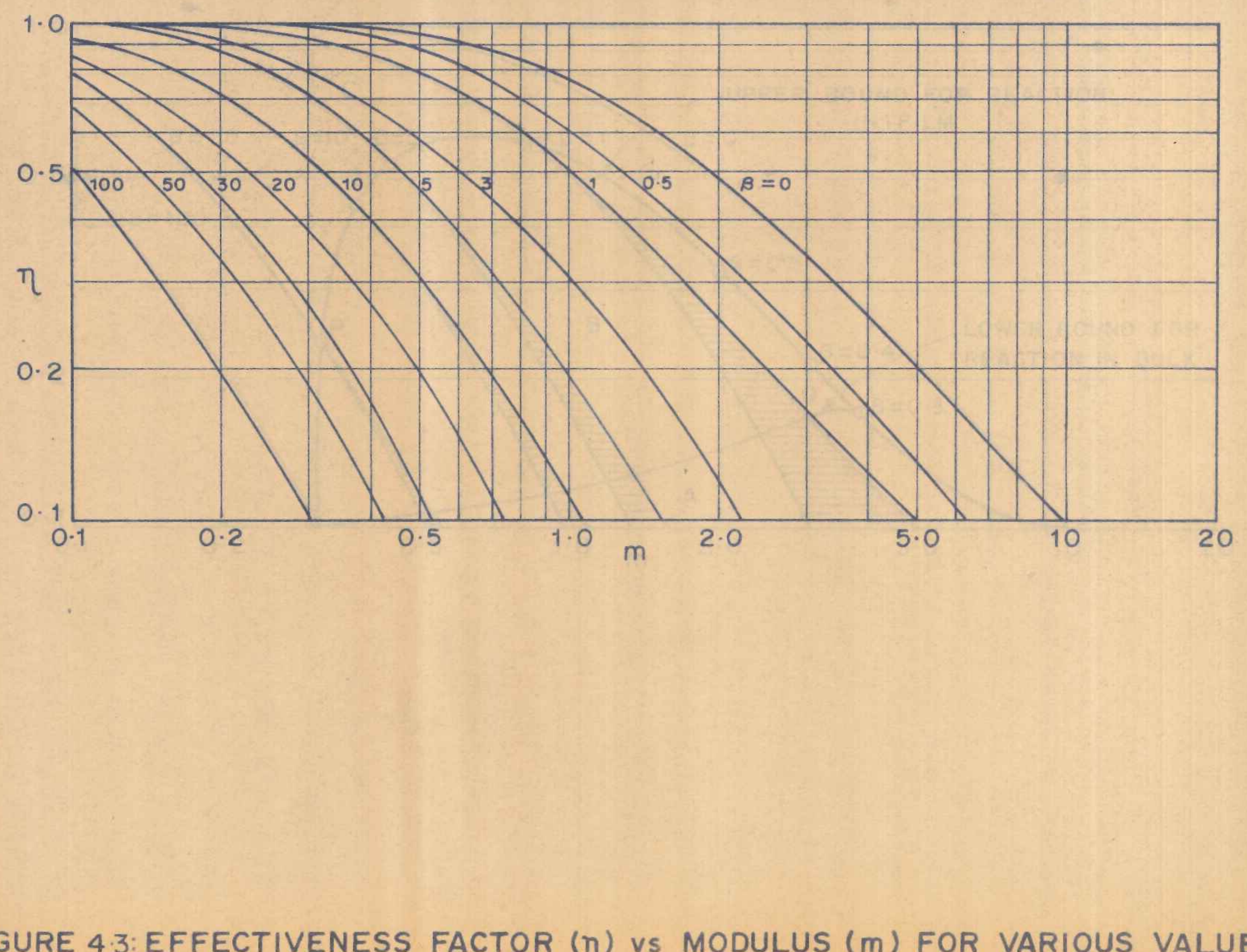


FIGURE 4·3: EFFECTIVENESS FACTOR (η) vs MODULUS (m) FOR VARIOUS VALUES OF β FOR PART OF REACTION IN THE FILM AND REST IN THE BULK (CASE II)

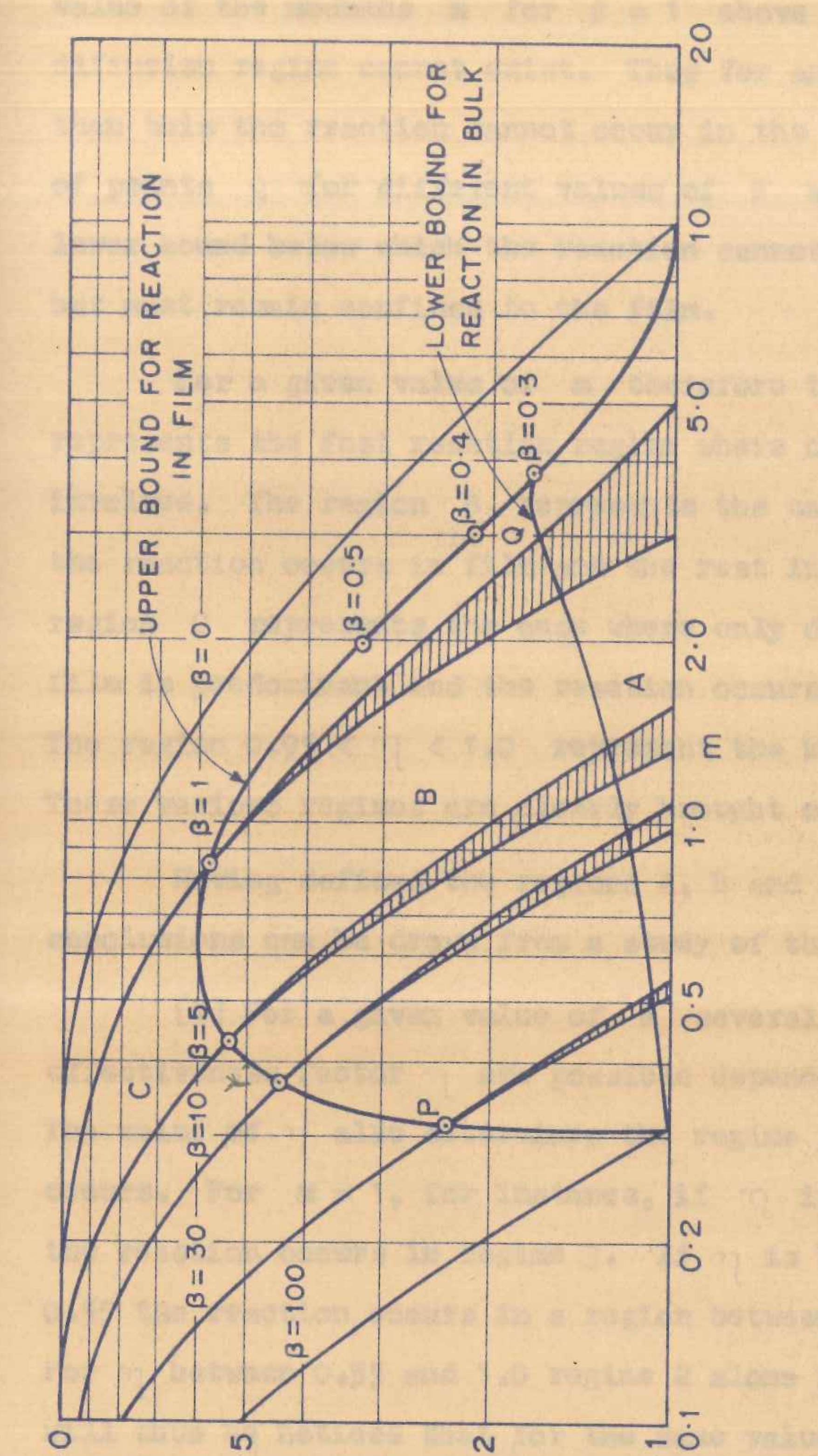


FIGURE 4·4: DETERMINATION OF THE LOWER AND UPPER BOUNDS FOR REACTION IN THE BULK let us consider the point Q which represents the highest value of the modulus m for $\beta = 1$ above which the pure diffusion regime cannot exist. Thus for any value of m greater than this the reaction cannot occur in the bulk, and the locus of points Q for different values of β will represent the lower bound below which the reaction cannot occur in the bulk but must remain confined to the film.

For a given value of m therefore the region A represents the fast reaction regime where only the film is involved. The region B represents the case where a part of the reaction occurs in the film and the rest in the bulk. The region C represents the case where only diffusion in the film is predominant and the reaction occurs wholly in the bulk. The region $0.95 < \eta < 1.0$ represent the kinetic regime. These various regimes are clearly brought out in Figure 4.5.

Having defined the regions A, B and C, some interesting conclusions can be drawn from a study of these regions.

[1] For a given value of m several values of the effectiveness factor η are possible depending on the value of β. The value of η also determines the regime in which the reaction occurs. For $m = 1$, for instance, if η is less than 0.12 the reaction occurs in regime 3. If η is between 0.12 and 0.55 the reaction occurs in a region between regimes 2 and 3. For η between 0.55 and 1.0 regime 2 alone is involved. It will thus be noticed that for the same value of m several regimes of control are possible. This is distinctly different from solid catalysed reactions where a unique value of η exists

for a given value of m. If an analogy is to be drawn between gas-liquid and gas-solid catalytic reactions, it can be stated that any diffusional limitation in the latter will always place it in regime 3. This is so since there is nothing like a "bulk" in catalytic reactions and the reaction must be confined to the catalyst which may be regarded as equivalent to the 'film' in gas-liquid reactions. It is interesting to note that for the case where the reaction is complete in the film [a situation analogous to that for catalytic reactions] the effectiveness factor for a gas-liquid reaction is very much lower than for a catalytic reaction, being represented by a point in region A.

[2] If experiments are carried out in an equipment for which the interfacial area of contact a is known, then β can be estimated and the rate constant of the reaction determined as follows. The effectiveness factor is first determined by carrying out the reaction under a given set of conditions and then under conditions where the diffusional resistance has been eliminated, so that

$$\eta = \frac{[\text{reaction under actual experimental conditions}]}{[\text{reaction under conditions of no diffusional resistance}]}$$

From this value of η and the known value of β the regime of control is determined from Figure 4.4, and the value of m also obtained, from which the rate constant k can be extracted.

[3] In view of the fact that the upper bound for regime 3

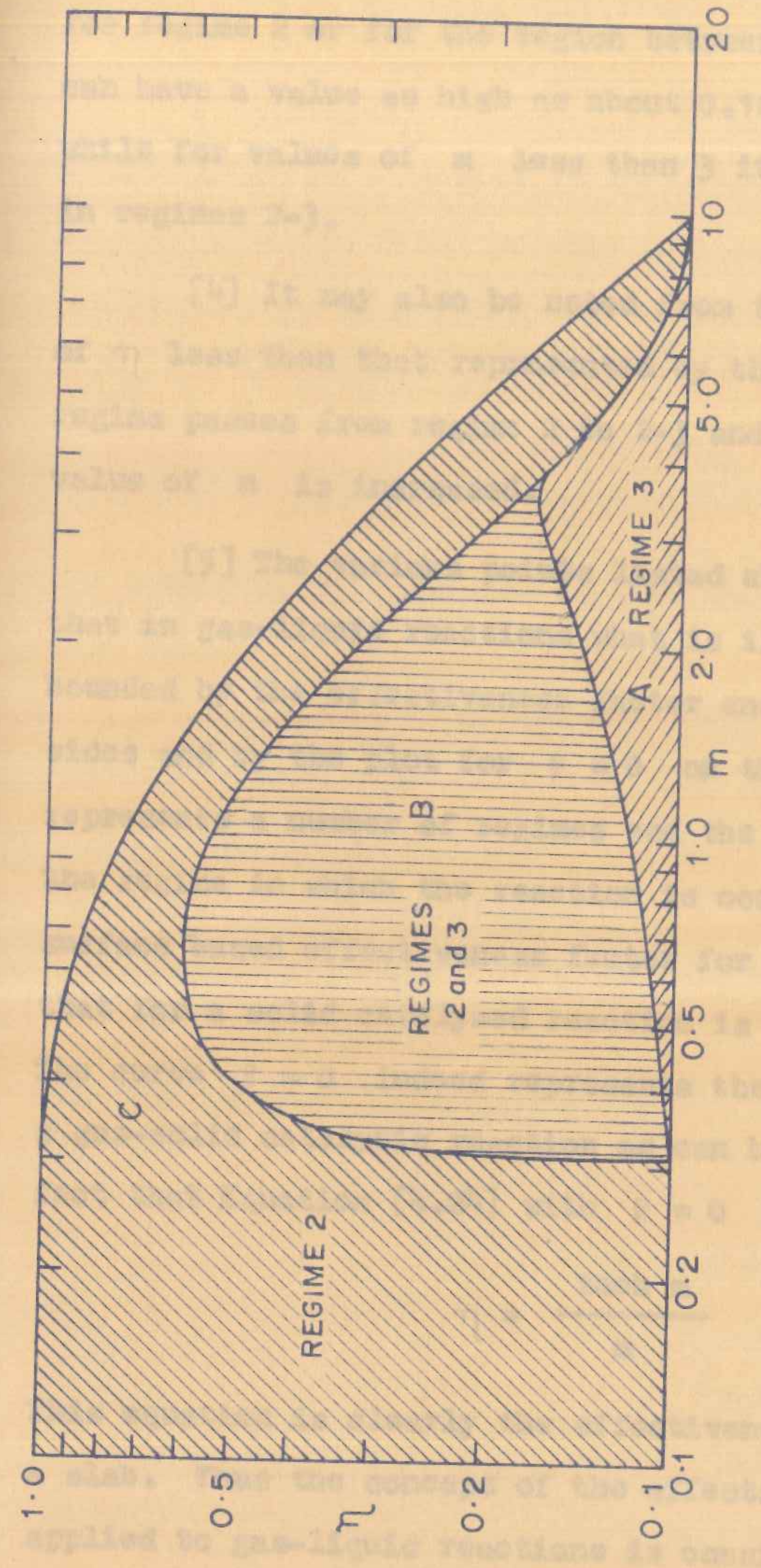


FIGURE 4·5: DEPICTION OF CONTROLLING REGIMES AS DISTINCT REGIONS ON AN EFFECTIVENESS FACTOR PLOT is much lower than for regime 2, it might appear that the effectiveness factor for regime 3 should always be less than for regime 2 or for the region between regimes 2 and 3. Thus can have a value as high as about 0.16 for $m = 3$ in regime 3; while for values of m less than 3 it will be lower than 0.16 in regimes 2-3.

[4] It may also be noted from the figure that for a value of η less than that represented by the point Y, the controlling regime passes from regime 2 to 2-3 and back to regime 2 as the value of m is increased.

[5] The various points listed above bring out the fact that in gas-liquid reactions what is involved is the region bounded by the effectiveness factor and modulus axes on two sides and by the plot for $\beta = 0$ on the third. This region represents a number of regimes and the value of η depends on the regime in which the reaction is occurring. As against this surface based effectiveness factor for gas-liquid reactions, that for a solid catalysed reaction is determined by a line. The curve $\beta = 0$ indeed represents the effectiveness factor for a gas-solid catalytic reaction as can be verified from the fact that Equation [4.24] with $\beta = 0$ reduces to

$$\eta = \frac{\tanh m}{m} \qquad [4.25]$$

This equation is clearly the effectiveness factor equation for a slab. Thus the concept of the effectiveness factor as applied to gas-liquid reactions is considerably more complicated and is expressed in terms of a region instead of a line.

4.3 EFFECTIVENESS FACTORS IN COMPLEX REACTIONS

4.3.1 Consecutive reactions

A first-order consecutive chemical reaction of the dissolved gaseous species A in a liquid B is considered here in order to bring out the applicability of the effectiveness factor concept to gas absorption followed by a complex reaction. Thus, for the scheme

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

the following differential mass balance can be written for each species:

$$D_A \frac{d^2 C_A}{d y^2} = k_1 C_A \qquad [4.26]$$

$$D_B \frac{d^2 C_B}{d y^2} = -k_1 C_A + k_2 C_B \qquad [4.27]$$

with the boundary conditions:

$$\left.\begin{aligned} C_A &= C_A^* \\ C_B &= C_B^* \end{aligned}\right\} \text{ at } y = 0 \text{, and} \qquad [4.28]$$

$$\left.\begin{aligned} -D_A \left.\frac{d C_A}{d y}\right|_{y=\delta} &= \frac{k_1 C_{Ao}}{a} \\ -D_B \left.\frac{d C_B}{d y}\right|_{y=\delta} &= \frac{k_2 C_{Bo}}{a} - \frac{k_1 C_{Ao}}{a} \end{aligned}\right\} \qquad [4.29]$$

These equations can be arranged in dimensionless form using the transformation

$$w_i = \frac{D_i\ C_i}{\Sigma D_i\ C_i^*}\ ,\quad i \text{ species } A,\ B \qquad [4.30]$$

which reduces to $w_A = \frac{C_A}{C_A^*}$ where only A is involved.

Thus

$$\frac{d^2\ w_A}{d\ x^2} = m_1^2\ w_A \qquad [4.31]$$

and

$$\frac{d^2\ w_B}{d\ x^2} = -m_1^2\ w_A + m_2^2\ w_B \qquad [4.32]$$

with the boundary conditions as

$$w_A = \frac{D_A\ C_A^*}{\Sigma D_i\ C_i^*}\ ,\ w_B = \frac{D_B\ C_B^*}{\Sigma D_i\ C_i^*}\ ,\text{ at } x = 0 \qquad [4.33]$$

$$-\left.\frac{d\ w_A}{d\ x}\right|_{x=1} = m_1^2\ \beta\ w_{Ao},\ -\left.\frac{d\ w_B}{d\ x}\right|_{x=1} = [m_2^2\ w_{Bo} - m_1^2\ w_{Ao}]\beta \qquad [4.34]$$

where in writing Equations[4.29] and [4.34] the kinetic boundary condition explained earlier in Section 4.2.2 has been used.

Equation [4.31] under boundary conditions [4.33] and

[4.34] can be solved to get the concentration profile for A as

$$w_A = \frac{D_A C_A^*}{\Sigma D_i C_i^*} \left[\frac{\cosh m_1 [1 - x]}{\cosh m_1} - \frac{m_1 \beta w_{Ao} \sinh m_1 x}{\cosh m_1} \right] \qquad [4.35]$$

With this concentration profile, Equation [4.32] becomes

$$\frac{d^2 w_B}{d x^2} = -m_1^2 \left[\frac{D_A C_A^*}{\Sigma D_i C_i^*} \frac{\cosh m_1 [1 - x]}{\cosh m_1} \frac{m_1 \beta w_{Ao} \sinh m_1 x}{\cosh m_1} \right] + m^2 w_B$$

$$[4.36]$$

This is a second-order differential equation, which can be solved to get the concentration profile for the species B:

$$w_B = c_1 e^{m_2 x} + c_2 e^{-m_2 x} + \frac{m_1^3 \beta w_{Ao}}{m_1^2 - m_1^2} \frac{\sinh m_1 x}{\cosh m_1} -$$

$$\frac{m_1^2}{m_1^2 - m_2^2} \frac{D_A C_A^*}{\Sigma D_i C_i^*} \frac{\cosh m_1 [1 - x]}{\cosh m_1}$$

or

$$w_B = c_1 e^{m_2 x} + c_2 e^{-m_2 x} - \frac{m_1^2}{m_1^2 - m_2^2} w_A \qquad [4.37]$$

The constants c_1 and c_2 can be determined using the boundary conditions [4.33] and [4.34] to give

$$w_B = \left(w_B^* + \frac{\Delta^2}{\Delta^2 - 1}\, w_A^*\right) \frac{\cosh m_2\,[1 - x]}{\cosh m_2} + m_2\left[\left(w_{Bo} - \Delta^2 w_{Ao}\right) - \frac{\Delta^2}{\Delta^2 - 1}\,\frac{m_1^2\,\beta\, w_{Ao}}{m_2}\right]\frac{\sinh m_2 x}{\cosh m_2} - \frac{\Delta^2}{\Delta^2 - 1}\, w_A \qquad [4.38]$$

where

$$\Delta = \frac{m_1}{m_2} \qquad [4.39]$$

From Equations [4.35] and [4.38], the ratio of the rates of production of B and reaction of A can be obtained as

$$\frac{\left.\dfrac{d\,w_B}{d\,x}\right|_{x=0}}{\left.\dfrac{d\,w_A}{d\,x}\right|_{x=0}} = \frac{\text{rate of production of } B}{\text{rate of consumption of } A} = \gamma' \qquad [4.40]$$

Hence

$$\gamma' = \frac{m_2 \tanh m_2 \left(w_B^* + \dfrac{\Delta^2}{\Delta^2-1}\, w_A^*\right) + \left[m_2^2\left(w_{Bo} - \Delta^2 w_{Ao}\right) - \dfrac{\Delta^2}{\Delta^2-1}\, m_1^2 \beta\, w_{Ao}\right]\dfrac{1}{\cosh m_2}}{m_1 \tanh m_1\, w_A^* + \dfrac{m_1^2\,\beta\, w_{Ao}}{\cosh m_1}}$$

$$+ \frac{\Delta^2}{\Delta^2 - 1} \qquad [4.41]$$

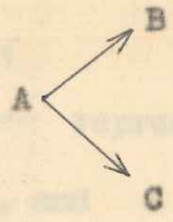
For the case where the reaction of both B and A is complete in the film, w_{Bo} and w_{Ao} are zero. Further m_1 and m_2 being high [for a fast reaction] tanh m_1 and tanh m_2 approach unity. Thus

$$\gamma' = \frac{\Delta}{\Delta + 1} - \frac{w_B^*}{\Delta w_A^*} \qquad [4.42]$$

Equation [4.42] is the well known equation for a first-order consecutive reaction scheme in an isothermal catalyst where the reaction is considered to be complete in the 'film'. Thus Equation [4.41] represents the most general solution for a first-order consecutive chemical reaction under isothermal conditions.

4.3.2 Parallel reactions

The effectiveness factor concept can also be used to define the selectivity of a product in a parallel reaction scheme in gas-liquid reactions. Let us consider a general p^{th} q^{th} order reaction



The mass balance equation for this scheme may be written as

$$D_A \frac{d^2 C_A}{d y^2} = k_1 C_A^p + k_2 C_A^q \qquad [4.43]$$

with the initial and final boundary conditions

$$y = 0, \quad C_A = C_A^* \qquad [4.44a]$$

$$y = L, \quad -D_A \frac{d\,C_A}{d\,y} = \left[k_1\,C_{Ao}^{\,p} + k_2\,C_{Ao}^{\,q}\right]\frac{1}{a} \qquad [4.44b]$$

Equation [4.44b] represents the kinetic boundary condition explained earlier.

Equation [4.43] can be integrated once to give

$$\frac{d\,C_A}{d\,y} = \left\{\frac{2}{D_A}\left[\frac{k_1}{p+1}\left(C_A^{\,p+1} - C_{Ao}^{\,p+1}\right) + \frac{k_2}{q+1}\left(C_A^{\,q+1} - C_{Ao}^{\,q+1}\right)\right] - \left(\frac{1}{a\,D_A}\right)^2\left[k_1\,C_{Ao}^{\,p} + k_2\,C_{Ao}^{\,q}\right]^2\right\}^{1/2} \qquad [4.45]$$

which, in dimensionless form, becomes

$$\frac{d\,w_A}{d\,x} = \sqrt{2}\,m\left\{\frac{\left(w_A^{\,p+1} - w_{Ao}^{\,p+1}\right)}{p+1} + \frac{M^*\left(w_A^{\,q+1} - w_{Ao}^{\,q+1}\right)}{q+1} - \frac{\left[m\,\beta\,w_{Ao}^{\,p}\,(1+M^o)\right]^2}{2}\right\}^{1/2} \qquad [4.46]$$

where $m = \delta\sqrt{\dfrac{k_1\,C_A^{*\,p-1}}{D_A}}$ represents the usual Thiele modulus for p^{th} order reaction, and

M^* = ratio of the true rates of reaction $\dfrac{k_2\,C_A^{*\,q+1}}{k_1\,C_A^{*\,p+1}}$

M^o = ratio of the rates of reaction in the bulk $\dfrac{k_2\,C_{Ao}^{\,q+1}}{k_1\,C_A^{\,p+1}}$

The effectiveness factor is given by

$$\eta = \frac{-D_A \left.\frac{d\,C_A}{d\,y}\right|_{y=0}}{\left[k_1\,C_A^{*p} + k_2\,C_A^{*q}\right]\left(\frac{1}{a} + \delta\right)} \qquad [4.47]$$

or, in dimensionless form, by

$$\eta = \frac{\left.\frac{d\,w_A}{d\,x}\right|_{x=0}}{m^2\,[1+\beta]\,[1+M^*]} \qquad [4.48]$$

where

$$\left.\frac{d\,w_A}{d\,x}\right|_{x=0} = \sqrt{2}\,m\left\{\frac{\left(1 - w_{Ao}^{p+1}\right)}{p+1} + \frac{M^*\left[1 - w_{Ao}^{q+1}\right]}{q+1} - \frac{\left(m\,\beta\,w_{Ao}^{p}[1+M^o]\right)^2}{2}\right\}^{1/2}$$

The selectivity for the component B can then be obtained as the ratio of the rate of formation of B to the actual rate of consumption of A:

$$\gamma' = \frac{\int_0^1 k_1\,C_A^{p}\,d\,x + \frac{k_1\,C_{Ao}}{a}}{\left[k_1\,C_A^{*p} + k_1\,C_A^{*q}\right]\left(\frac{1}{a} + \delta\right)} \qquad [4.50]$$

or in dimensionless form

$$\gamma' = \frac{\int_0^1 w_A^{p}\,d\,x + \beta\,w_{Ao}^{p}}{[1+M^*]\,[\beta+1]} \qquad [4.51]$$

For the specific case when $\beta = 0$ Equation [4.51] reduces to

$$\gamma' = \frac{\int_0^1 w_A^p \, d\,x}{[1 + M^*]} \qquad [4.52]$$

which is the equation for a gas-solid catalytic reaction derived recently by Roberts [4]. Thus Equation [4.51] is of the correct form and represents the situation for the more general case where β has finite positive values.

For specific orders [p, q] Equation [4.45] can be cast into standard forms of integration and evaluated to obtain the concentration profile. Equations [4.48] and [4.51] can then be used to calculate the effectiveness factor and selectivity of the reaction. The procedure is similar to that followed in the case of gas-solid reactions [4] and is not repeated here. The important point to stress here is that by changing the usual Danckwerts boundary condition at the end of the film by the kinetic boundary condition [Equation 4.44b] it is possible to derive an expression for gas-liquid reactions of which gas-solid reactions [flat plate geometry] constitute a special case [$\beta = 0$]. Thus it seems reasonable to use the single concept of effectiveness factor irrespective of the type of system involved to represent the selectivity in the case of parallel reactions also. Onda <u>et al</u> [5] analysed this system in terms of the enhancement factor usually employed for gas-liquid reactions.

4.4 EFFECTIVENESS FACTOR FOR A GENERAL n^{th} ORDER REACTION

The concept of the effectiveness factor, commonly used in gas-solid catalytic and noncatalytic reactions to account for the effect of diffusion, was extended in earlier sections to include gas-liquid reactions with first order kinetics. In the present analysis a general n^{th} order reaction is considered using the same parameter β defined earlier to represent the relative contributions to the reaction from the bulk and the film. The effectiveness factor expression for an n^{th} order isothermal gas-solid catalytic reaction obtained by Mehta and Aris [6] is shown to be a special case of this more general analysis by letting β tend to zero, which represents the condition where the bulk may be regarded as nonexistent. This case is analogous to gas-solid catalytic reactions where the reaction is essentially complete within the catalyst [regarded as 'film' in gas-liquid reactions].

4.4.1 Equations for the reactant concentration profile

Let us consider a system in which gas A is absorbed in a liquid and is consumed according to a general n^{th} order reaction. The mass balance equation for A can then be written as

$$D_A \frac{d^2 C_A}{d y^2} = k_1 C_A^n \qquad [4.53]$$

with the boundary conditions

$$C_A = C_A^* , \quad y = 0 \qquad [4.54a]$$

$$-D_A \frac{d\, C_A}{d\, y} = \frac{k_1\, C_{Ao}^{n}}{a} \quad \text{at} \quad y = \delta \qquad [4.54b]$$

Equation [4.54b] represents the kinetic boundary condition explained earlier.

Equations [4.53] and [4.54] can be rendered dimensionless to give

$$\frac{d^2\, w_A}{d\, x^2} = m^2\, w_A^{n} \qquad [4.55]$$

$$w_A = 1, \quad x = 0 \qquad [4.56a]$$

$$-\frac{d\, w_A}{d\, x} = m^2\, \beta\, w_{Ao}^{n} , \quad x = 1 \qquad [4.56b]$$

where m is the usual Thiele modulus $\delta \sqrt{\frac{k_1}{D_A}\, C_A^{*n-1}}$, and β is the ratio of the area per unit volume in the film to that in the liquid bulk and is given by

$$\beta = \frac{1}{a\, \delta} \qquad [4.9]$$

This parameter provides the bridge between gas-solid catalytic and gas-liquid reactions as explained earlier. It may be noted that the definitiono of β is based on unit volume of the bulk exclusive of the film volume. This has been done primarily in the interest of mathematical simplicity, but it is also possible to base the definition of β on the total volume of the bulk and the film. The two definitions are related by the expression:

$$\beta' = \frac{1}{1 + \beta} \qquad [4.57]$$

where β' is now based on the total volume.

Since a pure gas A is considered for analysis the gas phase resistance to the transfer of the species has been assumed to be negligible in writing the conservation equation.

Equation [4.55] can be integrated once with the boundary conditions [4.56] to give

$$\frac{d\,w_A}{d\,x} = \left(\frac{2}{n + 1}\right)^{1/2} m \left[w_A^{n+1} - w_{Ao}^{n+1} + \frac{n + 1}{2} \left(m\,\beta\,w_{Ao}^{n}\right)^2 \right]^{1/2} \qquad [4.58]$$

Further integration of Equation [4.58] leads to

$$m = \left(\frac{2}{n + 1}\right)^{1/2} \int_{w_{Ao}}^{1} \left[w_A^{n+1} - w_{Ao}^{n+1} + \frac{n + 1}{2} \left(m\,\beta\,w_{Ao}^{n}\right)^2 \right]^{1/2} d w_A \qquad [4.59]$$

Defining now a new concentration variable

$$\psi = 1 - \left(\frac{w_{Ao}}{w_A}\right)^{n+1} + \frac{n + 1}{2} \left[\frac{m^2\,\beta\,w_{Ao}^{2n}}{w_A^{n+1}} \right] \qquad [4.60]$$

Equation [4.59] may be transformed to

$$m = \left(\frac{2}{n+1}\right)^{1/2} \frac{1}{n+1} \left(w_{Ao}^{n+1} - \frac{n+1}{2} m^2 \beta^2 w_{Ao}^{2n} \right)^{\frac{1-n}{2[n+1]}}$$

$$\left[\int_0^{\psi_1} \psi^{-1/2} (1-\psi)^{-\frac{n+3}{2[n+1]}} d\psi - \int_0^{\psi_o} \psi^{-1/2} (1-\psi)^{-\frac{n+3}{2[n+1]}} d\psi \right] \qquad [4.61]$$

The integrals on the R.H.S. of Equation [4.61] are incomplete β functions which can be expanded in terms of the hypergeometric series and rearranged to give

$$w_A = \left[\frac{\left(\frac{2}{n+1}\right)^{-1/2} m \, (1-\psi)^{-\frac{1-n}{2[n+1]}}}{\psi_1^{1/2} F_1\left[\frac{1}{2}, \frac{1}{2} + \frac{1}{n+1}; \frac{3}{2}; \psi_1\right] - \psi_o^{1/2} F_1\left[\frac{1}{2}, \frac{1}{2} + \frac{1}{n+1}; \frac{3}{2}, \psi_o\right]} \right]^{\frac{2}{1-n}}$$

Equation [4.62] represents the concentration in terms of the defined variable ψ.

For the specific case when β is equal to zero, ψ_o also becomes zero and Equation [4.61] reduces to

$$w_A = \left[\frac{\left(\frac{2}{n+1}\right)^{-1/2} m \, (1-\psi)^{-\frac{1-n}{2[n+1]}}}{F_1\left[\frac{1}{2}, \frac{1}{2} + \frac{1}{n+1}; \frac{3}{2}, \psi_1\right]} \right]^{\frac{2}{1-n}} \qquad [4.63]$$

This expression has been obtained by Mehta and Aris [6] for the case of an n^{th} order gas-solid catalytic reaction and is clearly a special case of the more general equation for gas-liquid systems considered in the present section.

4.4.2 Generalized effectiveness factors

The effectiveness factor η can now be defined as

$$\frac{-D_A \left.\frac{d\,C_A}{d\,y}\right|_{y=0}}{k_1\, C_A^*\left(\frac{1}{a}+\delta\right)} = \frac{1}{m^2\,[\beta+1]}\left.\frac{d\,w_A}{d\,x}\right|_{x=0} \qquad [4.64]$$

where the reaction flux in the absence of diffusion is hypothetically divided into contributions from the film and the bulk. When combined with Equation [4.58] this becomes

$$w_{Ao}^{n+1} - \frac{n+1}{2}\left(m\,\beta\, w_{Ao}^{n}\right)^2 = 1 - \eta^2\, m^2\,[1+\beta]^2\,\frac{n+1}{2} \qquad [4.65]$$

An expression for η can now be derived by comparing the above equation with Equation [4.62] written for the surface concentration $[w_A = 1]$, i.e.

$$w_{Ao}^{n+1} - \frac{n+1}{2}\left(m\,\beta\, w_{Ao}^{n}\right)^2 = \left[\psi_1^{1/2}\, F_1\left(\frac{1}{2}, \frac{1}{2}+\frac{1}{n+1}\,;\,\frac{3}{2}, \psi_1\right) - \psi_o^{1/2}\, F_1\left(\frac{1}{2}, \frac{1}{2}+\frac{1}{n+1}\,;\,\frac{3}{2}, \psi_o\right)\right]^{\frac{1-n}{2[n+1]}} m^{\frac{2[n+1]}{1-n}} \left(\frac{2}{n+1}\right)^{-\frac{-n+1}{1-n}} = C_1 \qquad [4.66]$$

Thus:

$$C_1 = 1 - \eta^2\, m^2\,[1+\beta]^2\,\frac{n+1}{2} \qquad [4.67]$$

The term C_1 in this equation [defined by Equation [4.66] contains the quantities ψ_1 and ψ_o. These can be expressed in terms of the modulus m using Equation [4.60]:

$$1 - \psi_1 = w_{Ao}^{n+1} - \frac{n+1}{2} m^2 \beta^2 w_{Ao}^{2n} \text{ , and}$$

$$\psi_o = \frac{n+1}{2} m^2 \beta^2 w_{Ao}^{n-1} \qquad [4.68]$$

where w_{Ao} can be obtained from Equation [4.62] at $x = 1$.

For known values of ψ_1 and ψ_o, Equation [4.67] can be written as

$$\eta = \left[\frac{2\,[1 - C_1]}{m^2\,[\beta + 1]^2\,[n + 1]}\right]^{1/2} \qquad [4.69]$$

This equation represents a complete generalisation of the case considered in an earlier section. The value of the effectiveness factor can be obtained for a reaction of any order n from Equation [4.69] for a given value of the gas-liquid parameter β by first estimating the concentration variables ψ_1 and ψ_o from Equation [4.68] and calculating C_1 from Equation [4.66].

Figure 4.6 shows a graphical representation of Equation [4.69] as plots of η vs m for four specific values of β, viz. 0, 2, 5 and 10, and for three reaction orders, zero, first and second. It will be noticed that the curves for all the three orders tend to be displaced towards the right with decreasing β. For $\beta = 0$ the curves for the three orders coincide completely with those for reaction in a catalyst slab. Thus, as already pointed out in Section 4.2, at $\beta = 0$ there is

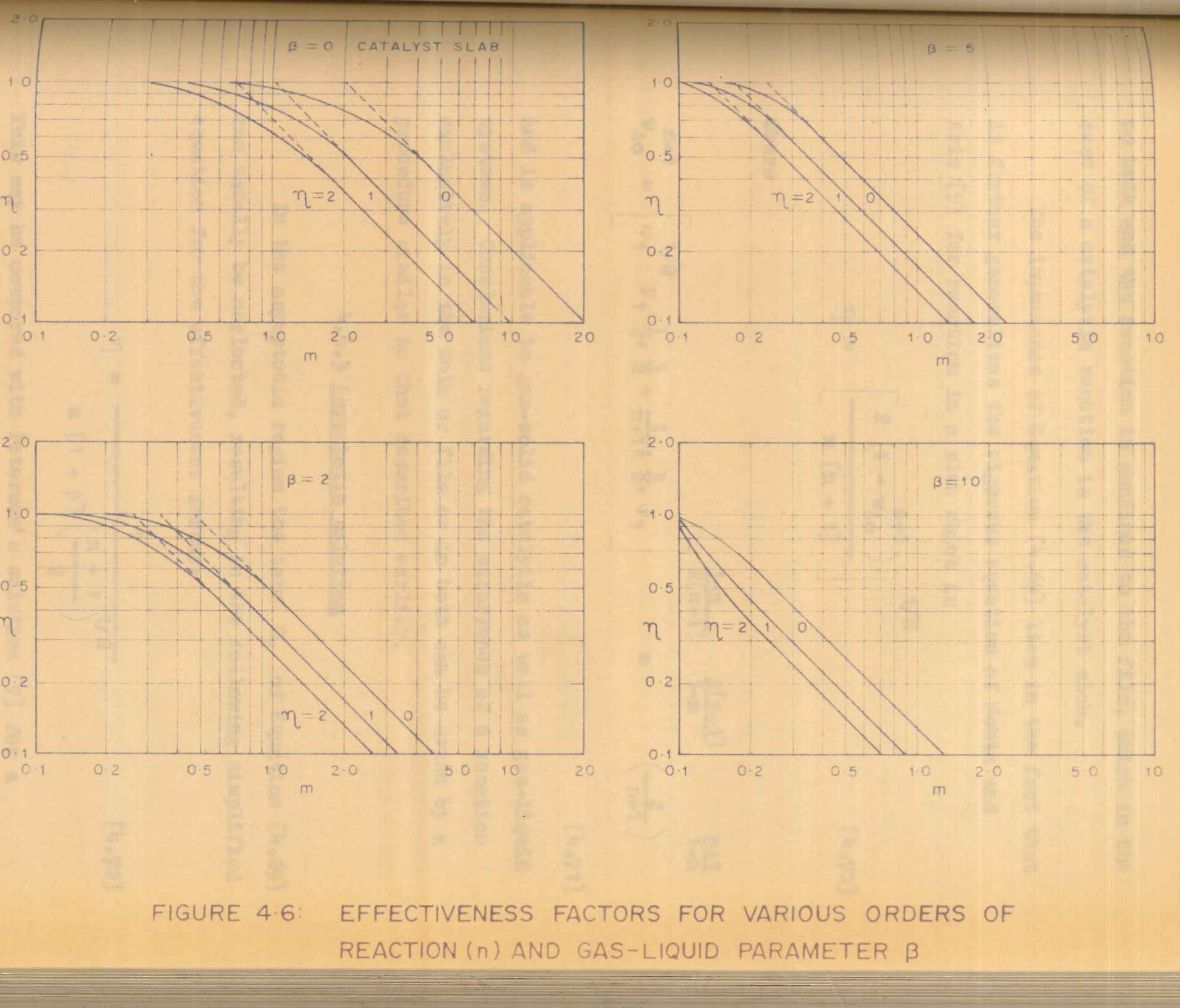


FIGURE 4·6: EFFECTIVENESS FACTORS FOR VARIOUS ORDERS OF REACTION (n) AND GAS-LIQUID PARAMETER β no bulk and the reaction is confined to the film, which in the case of a catalytic reaction is the catalyst slab.

The importance of Equation [4.69] lies in the fact that it further generalises the rigorous equation of Mehta and Aris [5] for reaction in a slab which is

$$\eta = \left[\frac{2\left(1 - w_{Ao}^{n+1}\right)}{m\,[h + 1]} \right]^{1/2} \qquad [4.70]$$

where

$$w_{Ao}^{n+1} = \left[\psi_1^{1/2}\; F_1\, \frac{1}{2}, \frac{1}{2} + \frac{1}{n+1}; \frac{3}{2}, \psi_1 \right]^{\frac{1-n}{2[n+1]}} m^{\frac{2[n+1]}{1-n}} \left(\frac{2}{n+1}\right)^{\frac{n+1}{1-n}} \qquad [4.71]$$

and is applicable to gas-solid catalytic as well as gas-liquid systems. Conclusions regarding the occurrence of a reaction exclusively in the bulk or film or in both can be drawn by a procedure similar to that described earlier.

4.4.3 Asymptotic solution

In the asymptotic region the term C_1 of Equation [4.69] can usually be neglected, resulting in the following simplified equation for the effectiveness factor:

$$\eta = \frac{1}{m\,[1 + \beta]\left(\frac{n + 1}{2}\right)^{1/2}} \qquad [4.72]$$

This may be compared with Petersen's solution [7] for a reaction of general order in a slab:

$$\eta = \frac{\sqrt{A}}{m} \qquad [4.73]$$

where $A = 2$, 1 and 2/3 for a zero, first and second order reaction. It may be noticed that the effectiveness factor equation for the gas-liquid reaction reduces to that for the slab when $\beta = 0$.

For first order kinetics the equation for the gas-liquid reaction is: $\eta = 1/m\,[\beta + 1]$. This was derived in earlier section specifically for a simplified gas-liquid system involving first order kinetics, which reduces to the well known equation, $\eta = 1/m$, for a catalyst slab.

4.4.4 Extension to packed or bubble columns

In many industrial packed or bubble column reactors the residence time of the liquid phase in the reactor is finite, so that the boundary condition [4.54b] should be corrected for the material leaving in the effluent stream. If Q represents the liquid holdup, then Equation [4.54b] becomes

$$-D_A \left.\frac{d\,C_A}{d\,y}\right|_{y = \delta} = \frac{k_1\,C_{Ao}^{\,n}}{a} + \frac{Q\,C_{Ao}}{[a + \frac{1}{\delta}]} \qquad [4.74]$$

A similar boundary condition has been employed by Hoffman et al [8]. Boundary condition [4.74] can be recast in dimensionless form as

$$\left.\frac{d\,w_A}{d\,x}\right|_{x=1} = m^2\,\beta\,w_{Ao}^{n} + \frac{\beta}{1+\beta}\,\theta\,w_{Ao} \qquad [4.75]$$

Using boundary condition [4.75] in place of [4.54b] to calculate the effectiveness factor, the following expression results:*

$$\eta = \frac{1}{m[\beta+1]\left(\frac{n+1}{2}\right)^{1/2}}\left[1 - w_{A8}^{n+1} + \frac{n+1}{2}\left(m\,\beta\,w_{Ao}^{n} + \frac{\beta}{1+\beta}\,\theta\,\frac{w_{Ao}}{m}\right)^{2}\right]^{1/2} \qquad [4.76]$$

which can be rearranged to the form of Equation [4.69] with the following modified expressions for the concentration variables:

$$1 - \psi_1 = w_{Ao}^{n+1} - \frac{n+1}{2}\left(m\,\beta\,w_{Ao}^{n} + \frac{\beta}{1+\beta}\,\theta\,\frac{w_{Ao}}{m}\right)^{2} \qquad [4.77]$$

$$\psi_o = \frac{n+1}{2}\left(m\,\beta\,w_{Ao}^{n} + \frac{\beta}{1+\beta}\,\theta\,\frac{w_{Ao}}{m}\right)^{2} \Big/ \frac{1}{w_{Ao}^{n+1}} \qquad [4.78]$$

Equation [4.76] represents the general solution for the effectiveness factor in a packed or bubble column reactor involving a gas-liquid reacting system. Since the very nature of these columns demands a finite residence time, C_1 cannot be zero and asymptotic solution is not possible. Thus the

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* Convective terms have not been included here for the sake of simplicity and also because our object is primarily to show the effect of finite residence time.

effectiveness factor will now be a function not only of the gas-liquid parameter β but also of the time θ and the concentration in the bulk. In view of the large number of parameters involved, graphical representation of this equation is not justified. Values of the effectiveness factor can be readily computed for specific values of a system. Equation [4.76] assumes the asymptotic form of Equation [4.72] for large residence times of the liquid.

4.5 EFFECTIVENESS FACTORS UNDER NONISOTHERMAL CONDITIONS

In the present section the analysis is extended to a general nonisothermal reaction with the object of presenting further generalisations in the treatment of gas-solid [catalytic] and gas-liquid reactions. The case of nonisothermal absorption of a gas in a liquid has been analysed by various workers [10-12]. Danckwerts [12] first obtained a quantitative measure of the interface temperature rise. The increase in temperature could be as high as 20°C as is evident from the analysis of Chiang and Toor [11]. This increase in temperature alters the interphase mass transport through its effect on the physical properties [like concentration, mass transfer coefficient, etc.] and hence should be precisely evaluated. The conditions under which the nonisothermal nature of the system becomes important, and the analogy in general between gas-solid [catalytic] and gas-liquid reactions, have however not been analysed so far, and form the subject matter of the present work.

4.5.1 Unifying concept: the generalized boundary condition at the interface

In all treatments of gas-solid [catalytic] reactions the boundary condition at the interface is expressed as

$$\frac{d\,C_B}{d\,y} = 0 \qquad [4.79]$$

In these cases the reaction is always expressed in terms of the catalyst surface, so that the happenings on the external boundary of the catalyst are no different from those on the internal surface. This concept was extended to gas-liquid reactions in earlier sections. While for all practical purposes this extension is valid for isothermal situations, for the nonisothermal case it may not be valid. In fact, conceptually, a completely different boundary condition has to be defined for gas-liquid reactions in general, whether isothermal or nonisothermal, which reduces to the gas-solid [catalytic] case as a limiting solution.

In the case of gas-liquid reactions, while the entire reaction occurs in the bulk and/or film of the liquid, in which case a volume based rate constant k_v is involved, a small portion of the reaction also occurs at the surface wherein a surface based rate constant is involved. In all analyses of gas-liquid reactions which have appeared so far, the reaction at the surface is ignored and it is assumed that the mass flux of the liquid phase component B at the surface is zero, leading to boundary condition [4.79]. This boundary condition is restrictive and should be replaced by a more general condition which accounts for reaction at the gas-liquid interface as well. Such a boundary condition can be expressed by

$$D_B \frac{d\, C_B}{d\, y} = k_s\, C_{As}\, C_{Bi} \qquad [4.80]$$

where k_s represents the surface rate constant and C_{As}, C_{Bi} the interface concentrations.

The application of this boundary condition is illustrated in Appendix 4.1 for the problem considered by DeCoursey [9]. The modified enhancement factor obtained is

$$E = \left\{ 1 + \frac{M}{1 + r\,\theta\, \exp[-Sh]} \left[1 - \frac{z\, A_o}{B_o} \left(1 - \frac{E}{z} \exp[-Sh] \right) + \frac{1}{E_a - 1} \left(1 - \frac{E}{z} \exp[-Sh] \right) \right] \right\}^{1/2} \qquad [4.81]$$

where θ represents a surface reaction parameter defined by

$$\theta = \left(\frac{k_s\, \delta}{D_A} \right)^{1/2} \qquad [4.82]$$

and r denotes the diffusivity ratio $[D_A/D_B]$. If in this equation the Sherwood number Sh is assumed to be infinity, the situation would correspond to the kinetic regime in which the entire reaction occurs in the bulk of the liquid. Thus the amount of reaction occurring on the surface can be neglected, leading to the usual boundary condition [4.79]. For $Sh = \infty$ Equation [4.81] therefore reduces to

$$E = 1 + M \left(\frac{E_a - E}{E_a - 1} \right)^{1/2} \qquad [4.83]$$

which is identical with the expression developed by DeCoursey [9] assuming the usual boundary condition.

On the other hand, for finite values of Sh, the surface reaction parameter θ enters into the expression and its effect should be taken into account. For a nonisothermal feaction there is a tendency for the interface temperature to rise, leading to an enhanced value of k_s which, in turn, leads to more reaction at the surface. In this situation the normal boundary condition does not hold and the condition given by Equation [4.80] should be used.

Using the general boundary condition proposed above an attempt will now be made to present solutions which provide a qualitative understanding of the behaviour of gas-liquid reactions in relation to that of gas-solid catalytic reactions, both under nonisothermal conditions. Quantitative approximate solutions will also be given which reduce to isothermal gas-liquid or gas-solid [catalytic] reactions under appropriate limiting conditions.

4.5.2 System criteria

Let us consider a reaction between gas A absorbing in a liquid with an active component B and reacting with it. The following nondimensional continuity and conservation equations can be written:

$$\frac{d^2 w_A}{d x^2} = m^2 w_A w_B x^{-4}$$

$$\frac{d^2 w_B}{d x^2} = r m^2 w_A w_B x^{-4} \qquad [4.84]$$

$$\frac{d^2 t}{d x^2} = \gamma m^2 w_A w_B x^{-4}$$

Let $m^2 w_A w_B = C_1 x^n$, where C_1 and n are arbitrary constants; then Equations [4.84] become

$$\frac{d^2 w_A}{d x^2} = C_1 x^{n-4}$$

$$\frac{d^2 w_B}{d x^2} = [C_1 r] x^{n-4} \qquad [4.85]$$

$$\frac{d^2 t}{d x^2} = [\gamma C_1] x^{n-4}$$

The asymptotic solutions to these equations subject to boundary condition [4.80] recast in dimensionless form as

$$\left.\frac{d w_B}{d x}\right|_x = \theta^2 w_{Bi} \qquad [4.86]$$

are:

$$w_A = C_1 \left[a_1 x + a_2 + \left[1 + 0\ (1)\right] \frac{x^{n-2}}{[n+3]\ [n+2]} \right] \qquad [4.87]$$

$$w_B = C_1 r \left[a_3 x + a_4 + \left[1 + 0\ (1)\right] \frac{x^{n-2}}{[n+3]\ [n+2]} \right] \qquad [4.88]$$

$$t = C_1 \left[a_5 x + a_6 + \left[1 + 0\ (1)\right] \frac{x^{n-2}}{[n+3]\ [n+2]} \right] \qquad [4.89]$$

where a_1 = mass flux at the interface; $a_2 = 1$

$a_3 = -\theta^2 w_{Bi}$; $a_4 = w_{Bi}$ [4.90]

a_5 = heat flux at the interface; $a_6 = t_i$

The dimensionless reaction term $m^2 w_A w_B$ appearing in Equations [4.85] are then given by

$$m^2 w_A w_B = m^2 w_A \left\{ r C_1 \left[a_3 x + a_4 + \left[1 + 0\ (1)\right] \frac{x^{n-2}}{[n-3][n-2]} \right] \right\}$$

[4.91]

In the above equations the constants a_1-a_6 are defined by expressions which are listed in Table 4.1. It will be noted that a_2 alone has a simple value [of unity], while the others are relatively complex equations involving the gas-liquid parameter β defined earlier

$$\beta = \frac{1}{a\ \delta} \qquad [4.9]$$

Table 4.1

Expressions for the constants a_1-a_6

Constants	Expression
a_1	$\frac{1}{r}\left(\frac{d\,w_B}{d\,x} - \left.\frac{d\,w_B}{d\,x}\right\vert_{x=1}\right) + m^2\,\beta\,w_{Ap}\,w_{Bo}$
a_2	1
a_3	$-\,\theta^2\,w_{Bi}$
a_4	w_{Bi}
a_5	$\frac{1}{r}\left(\frac{d\,t}{d\,r} - \left.\frac{d\,t}{d\,x}\right\vert_{x=1}\right) + m^2\,\beta\,w_{Ao}\,w_{Bo}$
a_6	t_1

This parameter expresses the ratio of the volume per unit area in the bulk to that in the film and is therefore a measure of the relative amounts of reaction occurring in the film and the bulk.

For the case where the usual boundary condition [4.79] is valid, we have for $x \to \infty$ the following solutions:

$$w_A = \text{Equation [4.87]}$$

$$w_B = a_4 + [1 + 0\ (1)] \frac{x^{n-2}}{[n-3][n-2]} \qquad [4.92]$$

$$t = \text{Equation [4.89]}$$

The reaction term now becomes

$$m^2\ w_A\ w_B = m^2\ w_A \left[a_4 + [1 + 0\ (1)] \frac{x^{n-2}}{[n-3]\ [n-2]} \right] \qquad [4.93]$$

Equations [4.91] and [4.93] provide values of the nondimensional term $m^2\ w_A\ w_B$ under two different conditions, viz. using boundary condition [4.80] and boundary condition [4.79] respectively. By incorporating these expressions in Equations [4.90] and [4.92], it can be seen that the use of the modified boundary condition [4.80] results in a lower value of the concentration of B in the film. In other words, there is a lowering of the mass flux and hence of the effectiveness factor. Neglecting the existence of a finite flux of B at the interface can therefore lead to wrong predictions of the effectiveness factor.

Let us now analyse the entire sequence of situations as we proceed from the most general nonisothermal gas-liquid reaction to the simple gas-solid catalytic reaction. This will provide a clear understanding of the concept presented and the influence of the parameters β and θ in defining the system and the regimes.

[1] A nonisothermal gas-liquid reaction is characterised by finite values of β as already pointed out in the earlier section. Let us now examine the further generality introduced by the incorporation of the new boundary condition. The role of this boundary condition may be expressed quantitatively in terms of the surface reaction parameter θ defined by Equation [4.82]. In the case of a gas-liquid reaction, the modified boundary condition demands a finite reaction at the gas-liquid interface. While strictly this is true both for isothermal and nonisothermal situations, under practical conditions the contribution of the surface reaction at the interface for an isothermal reaction [in which the surface temperature is the same as that in the film or the bulk] is usually negligible. On the other hand, for a nonisothermal exothermic reaction, the surface temperature can be higher leading to a contribution of the surface reaction which cannot be neglected. We thus come to the second condition for a general nonisothermal gas-liquid reaction, viz. $\theta > 0$. It may therefore be stated that while $\beta > 0$ is a necessary condition, the necessary and sufficient conditions are

$$\begin{aligned} \beta &> 0 \\ \theta &> 0 \end{aligned} \qquad [4.94]$$

[2] In the case of isothermal gas-liquid reactions, as already stated under [1] above, for all practical purposes the necessary and sufficient condition is

$$\beta \geq 0 \qquad [4.95]$$

[3] For gas-solid catalytic reactions, whether isothermal or nonisothermal, the necessary and sufficient condition is

$$\beta = 0 \qquad [4.96]$$

The surface reaction parameter θ does not come into the picture here, since a separate surface rate constant is not involved. The same rate constant is used for reaction within the catalyst matrix as well as on its external surface.

The various conditions outlined above are summarised in Table 4.2. It will be noticed that gas-liquid and gas-solid catalytic systems have now been treated on a common basis using the parameters β and θ. The Thiele modulus m appears in both the cases and is not a distinguishing quantity.

4.5.3 Approximate solutions

The continuity and conservation equations are given in nondimensional form as

$$\frac{d^2 w_A}{d y^2} = m^2 w_A w_B$$

$$\frac{d^2 w_B}{d y^2} = r m^2 w_A w_B$$

Table 4.2

Systems criterian for gas-liquid and gas-solid reactions

System		β	θ
Gas-liquid			
	Isothermal	> 0	0
	Nonisothermal	> 0*	> 0
Gas-solid catalytic			
	Isothermal	0	0
	Nonisothermal	0	0

* β = 0 corresponds to reaction restricted to the film.

$$\frac{d^2 t}{d y^2} = \gamma m^2 w_A w_B \qquad [4.97]$$

where γ is the thermicity factor defined as $\gamma = \frac{[-\Delta H] D_A C_A^*}{k_e T_i}$.
The boundary conditions are:

$$y = 0, \quad w_A = 1, \quad w_B = w_{Bi}, \quad \frac{d t}{d y} = \gamma_s \left. \frac{d w_A}{d y} \right|_{y=0}$$

$$y = 1, \quad - \frac{d w_A}{d y} = m^2 \beta w_{Ao} w_{Bo}, \quad w_B = w_{Bo}, \quad t = t_o \qquad [4.98]$$

The temperature boundary condition $\frac{dtt}{d y} = \gamma_s \left. \frac{d w_A}{d y} \right|_{y=0}$, where γ_s is a dimensionless parameter involving the heat of solution $[\Delta H_s]$, is the same as that proposed by Shah [13].

Equations [4.97] can be integrated twice to obtain the relationship between the concentration and temperature profiles as

$$w_A = \frac{w_B}{r} + \left(w_{Ao} - 1 - \frac{w_{Bo}}{r} + \frac{w_{Bi}}{r} \right) y - \frac{w_{Bi}}{r} + 1, \text{ and}$$

$$w_A = \frac{t}{\gamma} + \left(w_{Ao} - 1 - \frac{t_o}{\gamma} + \frac{t_i}{\gamma} \right) y - \frac{t_i}{\gamma} + 1 \qquad [4.99]$$

If now the transformation

$$z = \int_0^y [m^2 w_B]^{1/2} \, d y + [m_o^2 w_{Bo}]^{1/2} y \qquad [4.100]$$

is used, Equations [4.97] can be recast as

$$\frac{d^2\, w_A}{d\, z^2} + p\,[z]\, \frac{d\, w_A}{d\, z} = w_A$$

$$\frac{d^2\, w_B}{d\, z^2} + p\,[z]\, \frac{d\, w_B}{d\, z} = r\, w_A$$

$$\frac{d^2\, t}{d\, z^2} + p\,[z]\, \frac{d\, t}{d\, z} = \gamma\, w_A \qquad [4.101]$$

with the transformed boundary conditions

$$z = 0, \;\; w_A = 1, \;\; w_B = w_{Bo}, \;\; \frac{d\, t}{d\, z} = \gamma_s \left(\frac{d\, w_A}{d\, y}\, \frac{d\, y}{d\, z} \right)_{z\, =\, 0}$$

$$z = z_1 = [m_o^2\, w_{Bo}]^{1/2} + \int_0^1 [m^2\, w_B]^{1/2}\, d\, y, \;\; -\frac{d\, w_A}{d\, z} = \frac{m^2\, \beta\, w_{Ao}\, w_{Bo}}{d\, z\, /\, d\, y},$$

$$w_B = w_{Bo}, \;\; t = t_o \qquad [4.102]$$

Using Equation [4.99], Equation [4.101] can be rewritten as

$$\frac{d^2\, w_A}{d\, z^2} + p\,[z]\, \frac{d\, w_A}{d\, z} = w_A$$

$$\frac{d^2\, w_B}{d\, z^2} + p\,[z]\, \frac{d\, w_B}{d\, z} = w_B + f_1\,[z] \qquad [4.103]$$

$$\frac{d^2\, t}{d\, z^2} + p\,[z]\, \frac{d\, t}{d\, z} = t + f_2\,[z]$$

where

$$p\,[z] = \frac{d^2\ z/d\ y^2}{[d\ z/d\ y]^2}$$

$$f_1\,[z] = r\,Q_B = \left(w_{Ao} - 1 - \frac{w_{Bo}}{r} + \frac{w_{Bi}}{r}\right)y - \frac{w_{Bi}}{r} + 1$$

$$f_2\,[z] = \gamma\,Q_t = \left(w_{Ao} - 1 - \frac{t_o}{\gamma} + \frac{t_i}{\gamma}\right)y - \frac{t_i}{\gamma} + 1 \qquad [4.104]$$

Implicit solutions

Equations [4.103] can be solved subject to the boundary conditions [4.102] to obtain the implicit concentration and temperature profiles, which can be further solved by a trial and error method.

The first in the set of Equations [4.103] is taken as an example and three different approximate solutions are obtained. The solutions for the other two equations can be obtained in a similar manner. These are also linear equations of the second order and the complete primitive of the original equations can always be found if any solution whatever of the original equation with the right hand side equated to zero can be found. Although the solutions obtained are in the implicit form, certain properties of these equations as regards their boundedness, asymptotic behaviour, etc. should be precisely understood, in view of their common occurrence in describing various physical phenomenon. These approximate solutions along with their properties are summarieed in Tables 4.3 and 4.4.

TABLE - 4.3

Implicit solutions using various approximations

EQUATION CONSIDERED	TRANSFORMATION USED	TRANSFORMED EQUATION	APPROXIMATE SOLUTION	REMARKS
$\frac{d^2 w_A}{dz^2} + P(z)\frac{d w_A}{dz} = Q_A W_A$	$dl = Q_A e^{\int P dz} dz$	$\frac{d}{dl}\left(\frac{1}{U_A}\frac{dw_A}{dl}\right) = w_A$ $\frac{1}{U_A} = Q_A e^{2\int P dz}$ $= m^2 w_B$	$W_{Aj} = \int \frac{1}{m^2 w_B}\left[C - \int w_{Aj-1}\, dl\right] dl$ Where $j = 1, 2$ ------- and w_{Aj} is some trial solution	1) The method used is the method of succesive approxim. 2) Lord Kelvin (1876) has indicated the mechanical means of approximating the equation 3) When j tends to a large number, W_{Aj} dose not sensibly differ from W_{Aj-1} hence each is sensibly the solution of the problem or $W_A = \int \frac{1}{m^2 W_B}\left[C - \int W_A\, dl\right] dl$ 4) $m^2 W_B$ can be expressed in terms of W_A from eqation (18')
$\frac{d^2 w_A}{dz^2} + P(z)\frac{d w_A}{dz} = Q_A w_A$	$w_A = u \exp\left[-\frac{1}{2}\int P(z)\, dz\right]$	$\frac{d^2 u}{dz^2} - Iu = 0$ $I = -Q_A + \frac{1}{2}\frac{dP}{dz} + \frac{1}{4}P^2$	$w_A = \exp\left[-\frac{1}{2}\int P dz\right] \exp\left[\int^x \left(I^{1/4} - \frac{I'}{4I}\right) dz\right]$	1) This is commonly known as the WKB approximation 2) The conditions for the validity of this approximation are given as i) $I'/I \ll 1$, ii) $I''/I < 1$ } Northover (1969) I' and I'' are 1st and 2nd derivatives of I
$\frac{d^2 u}{dz^2} - Iu = 0$	$z_1/z_1 - z = l$ $u = v \exp\left[-\frac{1}{2}\int P_l(l)\, dl\right]$	$\frac{d^2 v}{dl^2} - G(l) v = 0$		1) Asymptotic solution
$\frac{d^2 v}{dl^2} - G(l) v = 0$	$S = \int_0^1 [G(l)]^{1/2} dl$ $\epsilon = v [G(l)]^{1/2} dl$	$\frac{d^2 \epsilon}{ds^2} - [1 + \psi(s)]\epsilon = 0,$ $\psi(s) \to 0, \; s \to \infty$	$\epsilon = C_1 e^s + C_2 e^{-s}$	2) All solutions are bounded provided $\int \psi'(s)\, ds < \infty$, $\psi(s) \to 0$ as $s \to \infty$ (ψ' is the 1st derivative of ψ)

TABLE - 4·4

Lower and upper bounds for the solution

1	EQUATION CONSIDERED	$\dfrac{d^2 w_A}{dz^2} + P(z)\dfrac{dw_A}{dz} + Q_A W_A = 0$
2	TRANSFORMATION USED	$w_A \doteq e^{\int u\,dz}$
3	TRANSFORMED EQUATION	$\dfrac{du}{dz} = a(z)\,u^2(z) + P(z)\,u(z) + Q(z)$ $a(z) = 1$ $Q(z) = -1$
4	LOWER BOUND BELLMAN (1955)	$u(z) = \min\limits_{v}\Big[u_o \exp\Big(-\int_0^Z [P(z') + 2a(z')\,v(z')]\,dz'\Big)$ $+ \int_0^Z [a(z')\,v^2(z') - Q(z')]\,dz'$ $\times \exp\Big(-\int_0^Z [P(z'') + 2a(z'')\,v(z'')]\,dz''\Big)\Big]$ Conditions: $a(z)$ should be positive semidefinite and $u(z)$ should be continuous, actual minimum at $v(z) = u(z)$
5	UPPER BOUND	$u(z) = \max\limits_{w}\Big[u_o \exp\Big(\int_0^Z [P(z') + 2Q(z')\,w(z')]\,dz\Big)$ $+ \int_0^Z [a(z') - Q(z')\,w(z')]\,dz$ $\times \exp\Big(\int_{z'}^Z [P(z'') + 2C(z'')\,w(z'')]\,dz''\Big)\Big]^{-1}$ Conditions: $Q(z)$ should be negative semidefinite $u(z)$ should never vanish actual maximum occurs at $w(z) = \dfrac{1}{u(z)}$

In obtaining implicit solutions Equations [4.103] can be transformed into an equation of the form

$$\frac{d}{d\,l}\left(\frac{1}{u_n}\,\frac{d\,w_n}{d\,l}\right) = w_A \qquad [4.105]$$

using the transformation

$$d\,l = Q_n\, e^{\int p\, d\, z}\, d\, z \qquad [4.106]$$

where $\frac{1}{u_n} = Q_n\, e^{2/\sqrt{m\, w_B}}$ and n stands for the species A, B or temperature t. Lord Kelvin [14] has indicated the mechanical means of approximating Equation [4.105]. The solution using the method of successive approximations

$$w_{Az} = \int_0^1 e^{-2/m\sqrt{w_B}} \left[C - \int_0^1 w_{A1}\, d\, l \right] d\, l \qquad [4.107]$$

$$\vdots$$

$$w_{Aj} = \int_0^1 e^{2/m\sqrt{w_B}} \left[C - \int_0^1 w_{A\ j-1}\, d\, l \right] d\, l \qquad [4.107]$$

is shown to converge to one of the solutions of Equation [4.105] as j increases and where w_{A1} is some trial solution. When w_{Aj} does not sensibly differ from $w_{A\ j-1}$, then each is sensibly the solution of this equation, or

$$w_{Aj} = \int_0^1 e^{-2/m\sqrt{w_B}} \left[C - \int_0^1 w_{Aj}\, d\,l \right] d\,l \qquad [4.108]$$

m and w_B can be expressed in terms of the concentration w_A using the Equations [4.99]. Thus Equation [4.108] is an implicit equation in w_A and can be solved by a trial-and-error method to get the concentration profile.

Alternatively, changing the dependent variable w_A in Equation [4.10$\overset{3+}{4}$] using the transformation

$$w_A = v \exp\left[-\frac{1}{2} \int p\,[z]\, d\,z \right] \qquad [4.109]$$

gives

$$\frac{d^2 v}{d\,z^2} - I\,v = 0 \qquad [4.110]$$

where

$$I = -Q_A + \frac{1}{2}\frac{d\,p}{d\,z} + \frac{1}{4}p^2 \qquad [4.111]$$

The approximate solution to Equation [4.110], when I is assumed to be a slowly varying function of $[z]$, can be obtained as

$$w_A = \exp\left[-\frac{1}{2} \int p\,[z]\, d\,z \right] \exp\left[\int^x \left(I^{1/4} - \frac{I'}{4\,I} \right) d\,z \right] \qquad [4.112]$$

Equation [4.112] is again implicit in w_A and a numerical evaluation is necessary to get the concentration profiles.

This approximation which is commonly known as the WBK approximation is shown to be valid by Northover [16] when the following conditions are satisfied

$$[i] \quad I'/I \ll 1; \quad [ii] \quad I''/I < 1 \qquad [4.113]$$

Although Equation [4.104] or its various transformations give an implicit solution for the concentration and temperature profiles in the film, it would be instructive to examine certain properties of these equations [which, as already mentioned, have been summarised in Tables 4.3 and 4.4].

Thus Equation [4.110] can be transformed to the equation

$$\frac{d^2 u}{d l^2} - G u = 0 \qquad [4.114]$$

using the transformations for independent and dependent variables defined as

$$\frac{z_1}{z_1 - z} = l \qquad [4.115]$$

and

$$v = u \exp \left[-\frac{1}{2} \int p_1 [l] \, d l \right] \qquad [4.116]$$

where

$$p_1 = \frac{d^2 l/d z^2}{[d l/d z]^2} \quad \text{and} \quad G = -\frac{I}{[d l/d z]^2} + \frac{1}{2} \frac{d p_1}{d l} + \frac{1}{4} p_1^2 \qquad [4.117]$$

Using Liouville transformations

$$s = \int_0^l [G]^{1/2} \, d l \qquad [4.118]$$

$$G = u \left[G [l] \right]^{1/2} \qquad [4.119]$$

Equation [4.114] can thus be transformed into a standard form

$$\frac{d^2\epsilon}{d\,l^2} - [1 + \psi[s] \quad = 0 \qquad [4.120]$$

where $\psi[s] \rightarrow 0$ as $s \rightarrow \infty$ [i.e. $z \rightarrow z_1$]

$$\psi[s] = \frac{1}{2}\frac{d}{d\,s}\left(\frac{[G'[l]]^{1/2}}{G[l]}\right) + \frac{1}{4}\left(\frac{[G'[l]]^{1/2}}{G[l]}\right) \qquad [4.121]$$

boundedness:

The solutions of Equation [4.120] are bounded provided

$$\psi'[s]\,d\,s < \infty \quad , \quad \psi[s] \rightarrow 0 \text{ as } s \rightarrow \infty \qquad [4.122]$$

This can be easily verified by multiplying Equation [4.120] by ϵ' and integrating between 0 to s.

asymptotic solution:

For the case when $\psi[s] \rightarrow 0$ as $s \rightarrow \infty$, the existence of two solutions ϵ_1 and ϵ_2 is known, for which

$$\frac{\epsilon_1'}{\epsilon_1} \rightarrow 1, \qquad \frac{\epsilon_2'}{\epsilon_2} \rightarrow -1 \qquad [4.123]$$

Also for the case $\int^{\infty}|\psi[s]|\;d\,s < \infty$, the following solutions can be asserted

$$\epsilon_1 \sim e^{s}$$

$$\epsilon_2 \sim e^{-s} \qquad [4.124]$$

The general solution is then obtained as

$$\epsilon = C_1 e^{s} + C_2 e^{-s} \qquad [4.125]$$

lower and upper bounds:

Equation [4.103] can be transformed to the Riccati equation using the transformation

$$w_A = e^{\int^{z} u \, d z} \qquad [4.126]$$

as

$$\frac{d u}{d z} = a [z] u^2 [z] + p [z] u [z] + Q [z] = 0, \; a [z] = 1$$

$$Q [z] = -1 \qquad [4.127]$$

The lower and upper bounds for the solution of this Riccati equation can be established under certain circumstances. Bellman [14] has given a solution $u [z]$ of this problem which appears as a minimum of the known functional, as

$$u [z] = \min_{v} \left[u_o \exp \left(- \int_0^z \left[p [z'] + 2 a [z'] v [z'] \right] d z' \right) + \int_0^z \left[Q [z'] u^2 [z'] - Q [z'] \right] d z' \; x \; \exp \left(- \int_{z'}^{z} \left[p [z''] + 2 a [z''] v [z''] \right] d z'' \right) \right] \qquad [4.128]$$

The necessary condition for the validity of Equation [4.128] being $a [z]$ should be positive semidefinite and $u [z]$ continuous.

Following Bellman [14] the solution $u [z]$ can be obtained as a maximum of another known functional as

$$u[z] = \max \left[u_o \exp\left(\int_0^z \left[p[z'] + 2\,Q[z']\,w[z'] \right] d\,z' \right) \right.$$

$$\int_0^z \left[a[z'] - Q[z']\,w^2[z'] \right] d\,z' \; x$$

$$\left. \exp\left(\int_{z'}^{z} \left[p[z''] + 2\,c[z'']\,w[z''] \right] d\,z'' \right) \right] \qquad [4.129]$$

The necessary condition for the validity of Equation [4.129] being $Q[z]$ should be negative semidefinite and $u[z]$ never vanishes.

The maximum and minimum actually occurs at $w[z] = \frac{1}{u[z]}$ and $v[z] = u[z]$.

Explicit solution

Most of the gas-liquid reactions are not highly exothermic, i.e. $\frac{d\,m}{d\,x}$ is usually a very weak function of x. Also, if the initial concentration of the liquid reactant $[w_B]$ is high compared with that of A in the film, then $\frac{d\,w_B}{d\,x}$ is also small and Equation [4.97] simplifies to

$$\frac{d^2\,w_A}{d\,z^2} = w_A$$

$$\frac{d^2\,w_B}{d\,z^2} = r\,w_A$$

$$\frac{d^2\,t}{d\,z^2} = \gamma\,w_A \qquad [4.130]$$

These equations may be solved subject to the boundary conditions [4.102] to give the following concentration and temperature profiles in the film:

$$w_A = C_1\,e^{z} + C_2\,e^{-z}$$

$$w_B = r\left[C_1\,e^{z} + C_2\,e^{-z}\right] + C_3\,z + C_4$$

$$t = \gamma\left[C_1\,e^{z} + C_2\,e^{-z}\right] + C_5\,z + C_6 \qquad [4.131]$$

where

$$C_1 = \frac{1}{2\cosh z_1}\left[\frac{m_o^2\,\beta\,w_{Ao}\,w_{Bo}}{{m_o^2\,w_{Bo}}^{1/2}} + e^{-z_1}\right]$$

$$C_2 = \left[\frac{m_o^2\,\beta\,w_{Ao}\,w_{Bo}}{{m_o^2\,w_{Bo}}^{1/2}} - e^{-z_1}\right]\frac{1}{2\cosh z_1}$$

$$C_3 = \frac{e^2\,w_{Bi}}{\left(m_1^2\,w_{Bi}\right)^{1/2}} - r\,[C_1 - C_2]$$

$$C_4 = w_{Bo} - r\left[C_1\,e^{z_1} + C_2\,e^{-z_1}\right] - C_3\,z_1$$

$$C_5 = \frac{1}{{m_1^2\,w_{Bi}}^{1/2}}\left.\frac{d\,t}{d\,z}\right|_{z=0} - \gamma[C_1 - C_2], \text{ and}$$

$$C_6 = t_o - \gamma\left[C_1\,e^{z_1} + C_2\,e^{-z_1}\right] - C_5\,z_1 \qquad [4.132]$$

The effectiveness factor for this system can be defined as

$$\eta = \frac{\text{actual reaction occurring}}{\text{reaction at the interface conditions with no diffusion}} \qquad [4.133]$$

$$\eta = \frac{-D_A\left.\dfrac{d\,C_A}{d\,x}\right|_{x=0} + k_s\,C_{Ai}\,C_{Bi}}{\delta\,k_v\,C_{Ai}\,C_{Bo} + k_s\,C_{Ai}\,C_{Bo}} \qquad [4.134]$$

This can be written in dimensionless form as

$$\eta = \frac{-\left.\dfrac{d\,w_A}{d\,y}\right|_{y=0} + \theta^2\, w_{Bi}}{m_i^2\left(w_{Bo} + \dfrac{\theta^2}{m_i^2}\, w_{Bo}\right)} \qquad [4.135]$$

This can be rearranged to the form

$$\frac{\eta_{\text{non}}}{\eta_{\text{iso}}} = \exp\left\{-\frac{E}{2\,R}\,\frac{\Delta T}{T_1\,T_o}\right\}\left[\frac{\sqrt{w_{Bi}}}{w_{Bo}}\,\frac{1}{\left(1+\dfrac{\theta^2}{m_i^2}\right)} + \frac{m_o\,w_{Bi}}{w_{Bo}\left(1+\dfrac{m_i^2}{\theta^2}\right)}\right] \qquad [4.136]$$

where

$$w_{Bi} = \left\{w_{Bo} - z_1\left[\frac{\theta^2\,w_{Bi}}{\left(m_i^2\,w_{Bi}\right)^{1/2}} - r\left(\frac{2\,m^2\,w_{Ao}\,w_{Bo}}{\left(m_o^2\,w_{Bo}\right)^{1/2}} - 2\sinh z_1\right)\right]\right\} \qquad [4.137]$$

For the simple case of β = 0, this reduces to the form

$$w_{Bi} = \frac{1}{2}\left\{-\frac{\theta^2\,z_1}{m_i} \pm \left[\left(\frac{\theta^2\,z_1}{m_i}\right)^2 - 4\left(2\,r\,z_1\sinh z_1 - w_{Bo}\right)\right]^{1/2}\right\} \qquad [4.138]$$

Equation [4.136] can be simplified for certain cases, thus for a pseudo first order reaction

$$\frac{\eta_{non}}{\eta_{iso}} = \exp\left[-\frac{E}{2R}\frac{\Delta T}{T_1 T_o}\right]\frac{1}{\left(1+\frac{\theta^2}{m_1^2}\right)} + \frac{m_o w_{Bi}}{w_{Bo}\left(1+\frac{m_1^2}{\theta^2}\right)} \qquad [4.139]$$

For the case when $m_1^2 >> \theta$, i.e. the surface reaction is negligible in comparison with the reaction occurring in the volume of the liquid, this simplifies to

$$\frac{\eta_{non}}{\eta_{iso}} = \exp\left[-\frac{E}{2R}\frac{\Delta T}{T_1 T_o}\right] \qquad [4.140]$$

For the case when activation energy is high, say greater than 20 kcal/gm mole, the reaction is mostly kinetically controlled and occurs almost entirely in the liquid bulk. Because of the high turbulence in the liquid, hardly any temperature difference can be noticed across the film. Thus the effectiveness factor ratio almost tends to unity. This is in agreement with Carberry's analysis [15] which shows that the effectiveness factor ratio tends to unity in many gas-liquid reactions. However, the temperature ΔT across the film increases much faster than the corresponding decrease in activation energy as the value of the Thiele modulus increases. Thus, for a strongly diffusion controlled reaction with the activation energy in the range of 3-5 kcal/gm mole, it is not uncommon to have a temperature difference of 20°C across the film. In a situation of this kind, the effectiveness factor tends to be higher than unity. The results obtained in this analysis, though approximate, indicate that it is not advisable to treat the rate constant as independent of temperature under such conditions [as is done in many gas-liquid reactions] and lends support to the use of the more general boundary condition [4.80].

For the case when $\theta >> m_1^2$, i.e. the reaction is exclusively occurring on the surface, the first term has a negligible influence and Equation [4.139] reduces to

$$\eta_{non} = 1 \qquad [4.141]$$

This is quite obvious since the definition of η is based on the condition at the interface. For the intermediate case when $\theta \sim m_1^2$, Equation [4.139] should be used.

For the case where pseudo first order behaviour cannot be assumed Equation [4.136] should be used. The modulus $\frac{\theta}{m_1}$ appearing in this equation represents the ratio of surface reaction to reaction in the liquid $\frac{\theta}{m_1} = \frac{k_s}{k_v \delta}$ and hence is a measure of the contribution to the total reaction from the entire liquid volume as well as surface. As the value of this parameter increases [i.e. more surface reaction occurs], the concentration of the liquid phase component $[w_B]$ decreases at the interface and hence from Equation [4.139] the ratio of effectiveness factors also decrease. This is consistent with the fact that the rise of temperature at the interface lowers the equilibrium concentration at the interface, leading to a lower mass flux of component A and hence a lower effectiveness factor. This effect is analogous to the effect of a volatile liquid where a certain mass flux is lost to the gas-phase at the gas-liquid interface.

NOTATION

a	interfacial area, cm^2/cm^3
a_1-a_6	constants defined by Equation [4.90]
C_A	concentration of i^{th} species, g mole/cm^3
C_1-C_6	constants as defined by Equation [4.132]
D_i	diffusivity of the i^{th} species, cm^2/sec
E	enhancement factor
Ea	enhancement at infinite time
F	hypergeometric series
f[z]	defined by Equation [4.103]
G[l]	defined by Equation [4.118]
G[z]	defined by Equation [4.117]
I	defined by Equation [4.111]
k_1	rate constant, cm^3/g mole sec
k_e	effective thermal conductivity, cal/sec cm^2 °C/cm
k_L	mass transfer coefficient, cm/sec
k_s	surface rate constant, cm/sec
k_v	volumetric rate constant, cm^3/g mole sec
l	distance parameter used in the transformations and as defined by Equations [4.105], [4.115]
M	modulus defined as $\sqrt{\frac{D_A\, k_2\, B_o}{k_L}}$
m	Thiele modulus

n	order of reaction
$P[z]$	defined by Equation [4.104]
P_1	defined by Equation [4.117]
Q	liquid hold up, cm^3/cm^3
r	diffusivity ratio D_B/D_A
s	defined by Equation [4.118]
T	temperature, ^oK
t	dimensionless temperature or time
U_n	transformed variable defined by Equation [4.106]
u	transformed variable defined by Equations [4.116], [4.128], [4.129]
v	transformed variable defined by Equations [4.110], [4.116]
w_A, w_B	dimensionless concentration
x	dimensionless distance
y	distance parameter, cm
z	transformed distance parameter defined by Equation [4.100]
z_1	value of z at $y = 1$

Greek symbols

β	dimensionless parameter defined as $\frac{1}{a\delta}$
γ	dimensionless parameter based on heat of solution $\frac{[-\Delta H_s]\ D_A\ C_A^*}{k_e\ T_1}$

γ	thermicity parameter defined as $\frac{[-\Delta H]\ D_A\ C_A^*}{k_e\ T_i}$
δ	film thickness, cm
θ	modulus based on surface reaction rate defined by Equation [4.82]
ΔH	heat of reaction, cal/g mole
ΔH_s	heat of solution, cal/g mole
ϵ	defined by Equation [4.119]
$\psi[s]$	defined by Equation [4.121]
η	effectiveness factor
$\psi[x]$	dimensionless concentration variables defined by Equation [4.60]
τ	Residence time, sec
θ_1	dimensionless residence time

<u>Subscripts</u>

i	condition at the interface
o	condition in the bulk of liquid

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CHAPTER 5

CHLOROHYDRINATION OF ETHYLENE: EXPERIMENTAL INVESTIGATION

5.1 INTRODUCTION

The chlorohydrination of olefins involves simultaneous absorption of the olefinic compound and chlorine in a reacting medium [water], and the sequence of reaction steps conforms to the scheme

$$C_2H_4 + Cl_2 \rightarrow C_2H_4Cl_2 \text{ [EDC]} \qquad [i]$$

$$Cl_2 + H_2O \rightleftarrows HOCl + HCl \qquad [ii]$$

$$C_2H_4 + HOCl \rightarrow C_2H_4OHCl \text{ [ECH]} \qquad [iii]$$

where ethylene is chosen to represent the olefins. The formation of ether is not considered in this scheme, since at low concentrations of chlorohydrin, which represents the practical situation, the formation of ether is known to be negligible.

In Chapter 2 a mathematical model for the simultaneous absorption of two gases accompanied by a complex chemical reaction scheme as mentioned above was presented. A knowledge of the kinetics of the individual steps [i], [ii] and [iii] is essential for the experimental verification of the proposed model and for predicting the probable mechanism of overall absorption; The hydrolysis of chlorine has been well studied [1-3] and the kinetics of step [ii] is also known. The absorption of ethylene in chlorine water has been studied by Akehata and Johnson [4] and Dunn and Wood [5, 6]. The reaction between ethylene and hypochlorous acid is reported to be infinitely fast in presence of chloride ions and that between ethylene and chlorine is comparatively slow. In view of the various chlorinating species involved and the simultaneous occurrence of different reactions, it is difficult to analyse the results obtained. Hence in this work it was decided to study the individual reaction [uninfluenced by the others] between hypochlorous acid and ethylene.

5.2 MECHANISM OF CHLORINATION BY HYPOCHLOROUC ACID

A great deal of confusion exists in the literature as regards the mechanism of chlorination. The term positive halogen is used to denote the covalently bonded compounds in which the halogen is in +1 oxidation state and are categorised as [1] neutral or negatively charged species [hypohalous acids and their anions], [2] a species with unit positive charge $H_2O\ X^+$, and [3] simple cations X^+. Various investigators have explained the observed results on the basis of mechanisms involving the simple cations. However the thermodynamic considerations presented by Bell and Gelles [7] and Arotsky and Symons [8] invalidate the participation of these cations in the reaction. The reaction has been explained by de la Mare et al [10-15] as proceeding through the protonated hypohalous acids and experimental evidence [17] shows this to be the probable mechanism. At higher concentrations of hypochlorous acid, Israel et al [16] have suggested chlorine monoxide as the chlorinating species. The reactions of organic compounds with hypochlorous acid investigated by various workers lends support to either of these mechanisms suggested; their findings are presented in Table 5.1 along with the rate expressions obtained

5.3 DEVELOPMENT OF A MATHEMATICAL MODEL

Based on the analysis of the reaction presented in the earlier section, it can be concluded that the reaction goes through the following sequence of steps when the concentration of hypochlorous acid used is greater than 0.001 M:

$$\begin{array}{ccccccc} 2\,HOCl & \underset{k_2}{\overset{k_1}{\rightleftharpoons}} & Cl_2O & + & H_2O & & [iv] \\ [A] & [x] & [A_1\ x] & & & & \end{array}$$

$$\begin{array}{ccccccc} Cl_2O & + & C_2H_4 & \underset{k_4}{\overset{k_3}{\rightleftharpoons}} & [carbonion] & + H_2O & [v] \\ [A_1\ x] & & [A_2] & & [A_1\ A_2\ x] & & \end{array}$$

$$\begin{array}{ccccc} [Carbonion]^{+} & + [OH]^{-} & \xrightarrow{k_5} & Product & [vi] \\ [A_1\ A_2\ x] & & & [A_1\ A_2] & \end{array}$$

The overall reaction may be represented as

$$\begin{array}{cccccc} HOCl & + & C_2H_4 & \xrightarrow{k} & C_2H_4OHCl & [vii] \\ [A_1] & & [A_2] & & [A_1\ A_2] & \end{array}$$

with the rate of product formation given by

$$R = k [A_1]^m [A_2]^m = k_5 [A_1 A_2 x]^+ \qquad [5.1]$$

At steady state the following rate equations can be written from the steps [iv - vi]

$$-\frac{d [A_1 A_2 x]}{dt} = -k_5 [A_1 A_2 x] - k_4 [A_1 A_2 x] + k_3 [A_1 x] [A_2] = 0 \qquad [5.2]$$

and

$$-\frac{d [A_1 x]}{dt} = -k_3 [A_1 x] [A_2] + k_4 [A_1 A_2 x] - k_2 [A_1 x] + k_1 [A_1] [x] = 0 \qquad [5.3]$$

From Equations [5.2] and [5.3] the following expressions for the concentrations can be derived:

$$[A_1 A_2 x] = \frac{k_3 [A_1 x] [A_2]}{[k_4 + k_5]} \qquad [5.4]$$

$$[A_1 x] = \frac{k_4 [A_1 A_2 x] + k_1 [A_1] [x]}{k_2 + k_3 [A_2]} \qquad [5.5]$$

Substituting Equation [5.5] in [5.4]

$$[A_1 A_2 x] = \frac{k_1 k_3 [A_1] [A_2] [x]}{k_2 [k_4 + k_5] + k_3 A_2 k_5} \qquad [5.6]$$

The rate of reaction can then be written as

$$R = k_5 [A_1 A_2 x]$$

$$= \frac{k_1 [A_2] [A_1] [x]}{\frac{k_2 k_4}{k_3 k_5} + \frac{k_2}{k_3} + A_2} \qquad [5.7]$$

When $\frac{k_2 k_4}{k_3 k_5} + \frac{k_2}{k_3} << 1$, i.e. when steps [v] and [vi] are much faster than the reversible step [iv], Equation [5.7] gets simplified to

$$R = k_1 A_1 x = k_1' A_1 \qquad [5.8]$$

Thus the rate becomes independent of the concentration of component A_2. In many reactions reported in the literature [see Table 5.1] the rate was observed to be independent of the concentration of the olefinic compound, thus suggesting a reactive olefinic compound.

Equation [5.7] for the case of reaction between HOCl and C_2H_4 can now be written as

$$R = \frac{k_1 [HOCl]^2}{1 + \frac{k_2}{k_3 [C_2H_4]}} \qquad [5.9]$$

This rate model was found to fit the experimental data satisfactorily, as shown below.

5.4 EXPERIMENTAL DATA

The selection of a suitable reactor is one of the important considerations in any experimental programme associated with gas-liquid reactions. The preliminary experiments show the reaction between ethylene and hypochlorous acid to be quite slow, and as recommended for such reactions an all-glass stirred reactor with provision for temperature control was employed in this work.

The reactant gas, ethylene, was prepared in the laboratory by the catalytic dehydration of ethyl alcohol on basic alumina as catalyst in a fixed bed reactor at a temperature of 350-390°C. Ethylene of 99.5% purity thus obtained was collected over water in a gas holder and then compressed in a cylinder. The gas was tested for its purity in a gas-chromatographic apparatus.

The hypochlorous acid was also prepared in the laboratory using bleaching powder and boric acid as and when required. Boric acid decomposes to a considerable extent the calcium hypochlorite in bleaching powder. Consequently when bleaching powder is distilled with boric acid, there is practically no chlorine evolved and pure hypochlorous acid can be obtained. This method has thus the distinct advantage over the methods which use chlorine in the preparation of hypochlorous acid.

About 15 grams of bleaching powder was thoroughly mixed with about 2-3 times its weight of boric acid and about 300 ml water. The mixture was distilled and about 50-100 ml of distillate collected. The strength of the solution obtained this way was usually 0.1 to 0.2 N hypochlorous acid.

Hypochlorous acid undergoes continuous decomposition and Figure 5.1 shows the rate of decomposition against time. In view of the large time required for a significant decomposition compared to the reaction time employed, this change in concentration of hypochlorous acid can be neglected in analysing the data.

The relatively unreactive hypochlorous acid gets converted to more reactive species by catalytic anions. Thus Cl^- ion gives rise to molecular chlorine, ClO^- to chlorine monoxide, etc. In order to avoid complications arising out of such possibilities, a known amount of perchloric acid and silver perchlorate was added to the solution during its preparation to suppress the ClO^- and Cl^- catalysis. The solution of hypochlorous acid thus prepared was stored in the dark to avoid decomposition.

About 150 ml of hypochlorous acid was charged to the stirred reactor and ethylene was then bubbled through it. Cooling water was passed through the outer jacket to maintain the temperature. After a sufficiently long time samples were withdrawn [such that the overall concentration change involved was negligible] into 10 ml of freshly prepared KI solution at known intervals. The liberated iodine was titrated against thio solution, the exact normality of which was determined using standard dichromate solution.

In order to attempt a detailed kinetic analysis of the reaction, a number of experiments were carried out covering the following ranges of variables:

Temperature: 15-35°C

Ethylene concentration: $5 \times 10^{-6} - 4 \times 10^{-7}$ gm mole/ml

Hypochlorous acid concentration: 0.001 to 0.005 N
$[1 \times 10^{-6} - 5 \times 10^{-6}$ gm mole/ml$]$

Ethylene concentration was varied using different flow rates of nitrogen. Additional experiments to study the effect of silver perchlorate and perchloric acid concentrations were carried out to justify that AgCl $[K_D = 2 \times 10^{-6}$ gm mole/lit$]$ formed in the solution does not act as a chlorinating species or source thereof.

The physical solubility of ethylene in aqueous hypochlorous acid solution may be calculated from the known value of the solubility in water and using the following expression:

$$\log \frac{A_s}{A_w} = - k_s I \qquad [5.10]$$

where A_s and A_w represent the solubilities in the solution and water respectively; I and k_s, the ionic strength of the solution and salting out parameter respectively may be obtained from

$$I = \frac{1}{2} \sum C_i Z_i^2$$

$$k_s = i_+ + i_- + i_g \qquad [5.11]$$

where C_i is the concentration of ions of valency Z_i and i_+ and i_- represent the positive and negative ions in the solution.

The liquid phase diffusivity of ethylene in HOCl solution may be predicted from the value of 1.6×10^{-5} cm^2/sec [30] obtained at 25°C for ethylene in water, by correcting for temperature and viscosity of the solution according to the Stokes-Einstein relation:

$$\frac{D_A \mu}{T} = \text{constant} \qquad [5.12]$$

where μ is the viscosity of the solution and T the absolute temperature.

5.5 RESULTS AND DISCUSSIONS

The results of the experimental investigation are plotted in Figures 5.1 to 5.5. Figure 5.1 shows the rate of decomposition of HOCl at various temperatures and initial hypochlorous acid concentrations. The stirrer speed used varied from 100 to 400 rpm and showed no effect on decomposition. Figure 5.2 shows the effect of stirrer speed on the rate of absorption at various concentrations of HOCl. The constant rates of absorption obtained point to the reaction being independent of any diffusional influence. The effect of partial pressure of ethylene and concentration of hypochlorous acid on the rate are expressed in Figures 5.3 and 5.4. The results show a small dependence on ethylene partial pressure

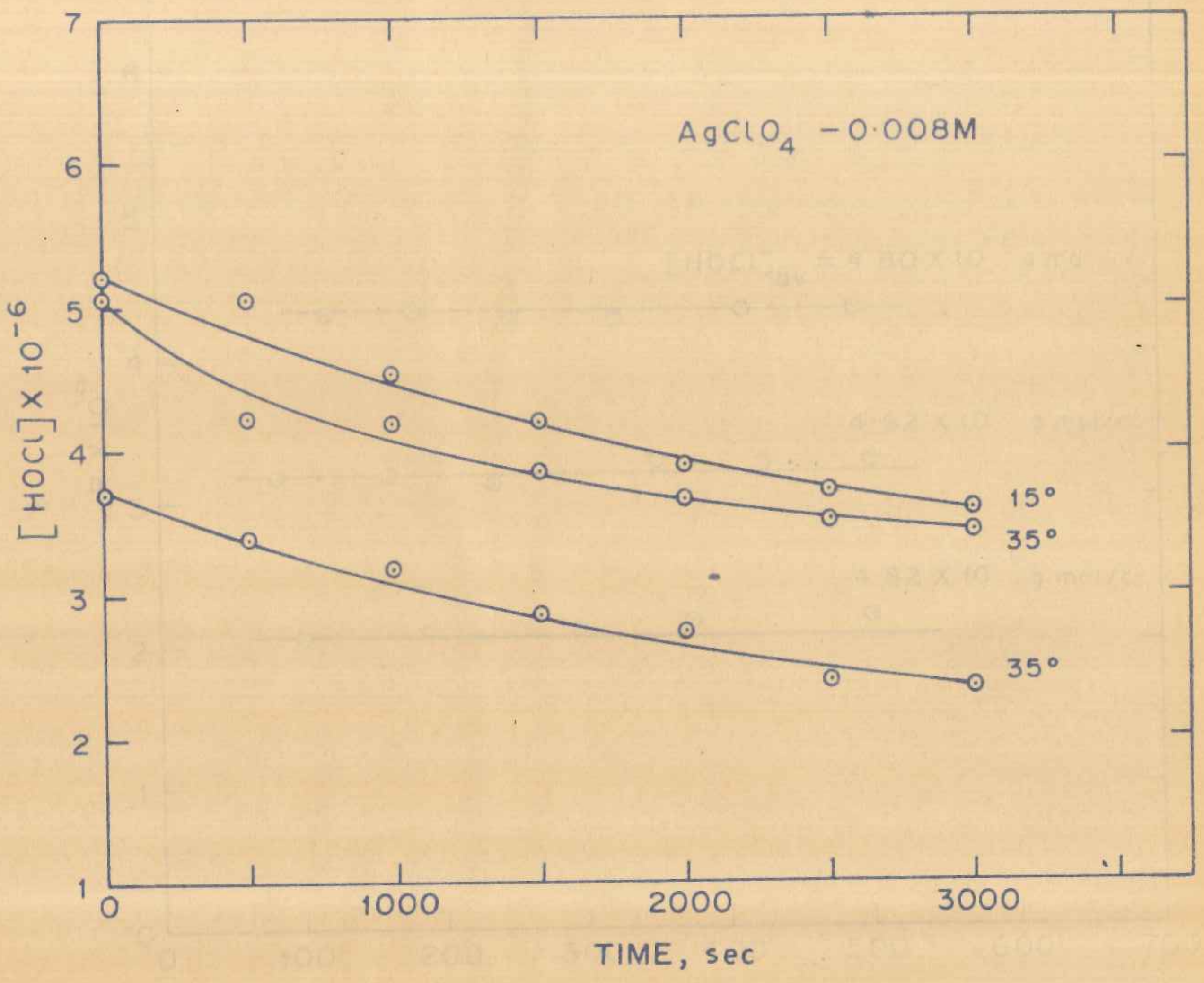

FIGURE 5·1: DECOMPOSITION OF HOCl WITH TIME IN PRESENCE OF SILVER PERCHLORATE

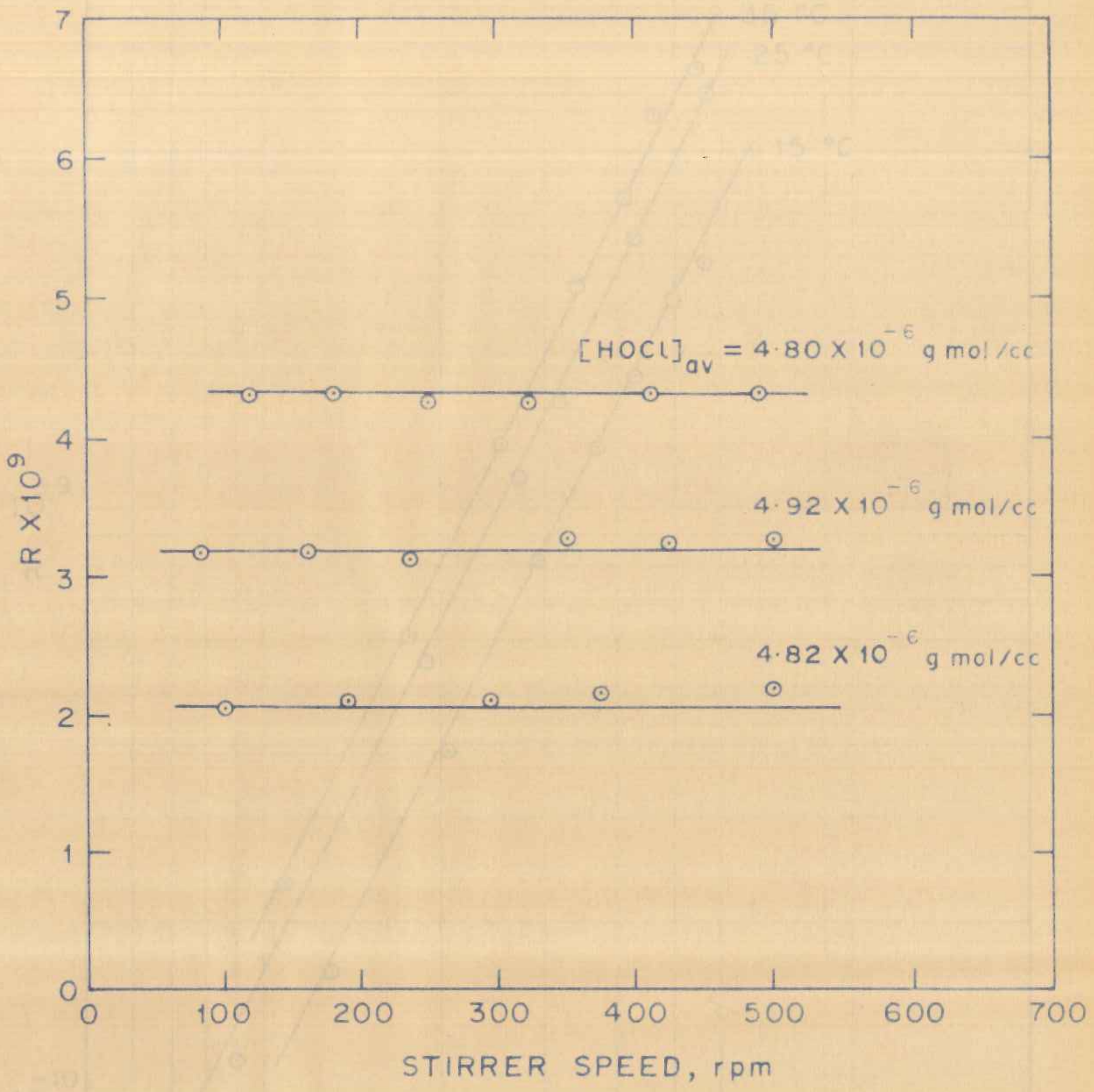

FIGURE 5·2: EFFECT OF STIRRER SPEED ON THE RATE

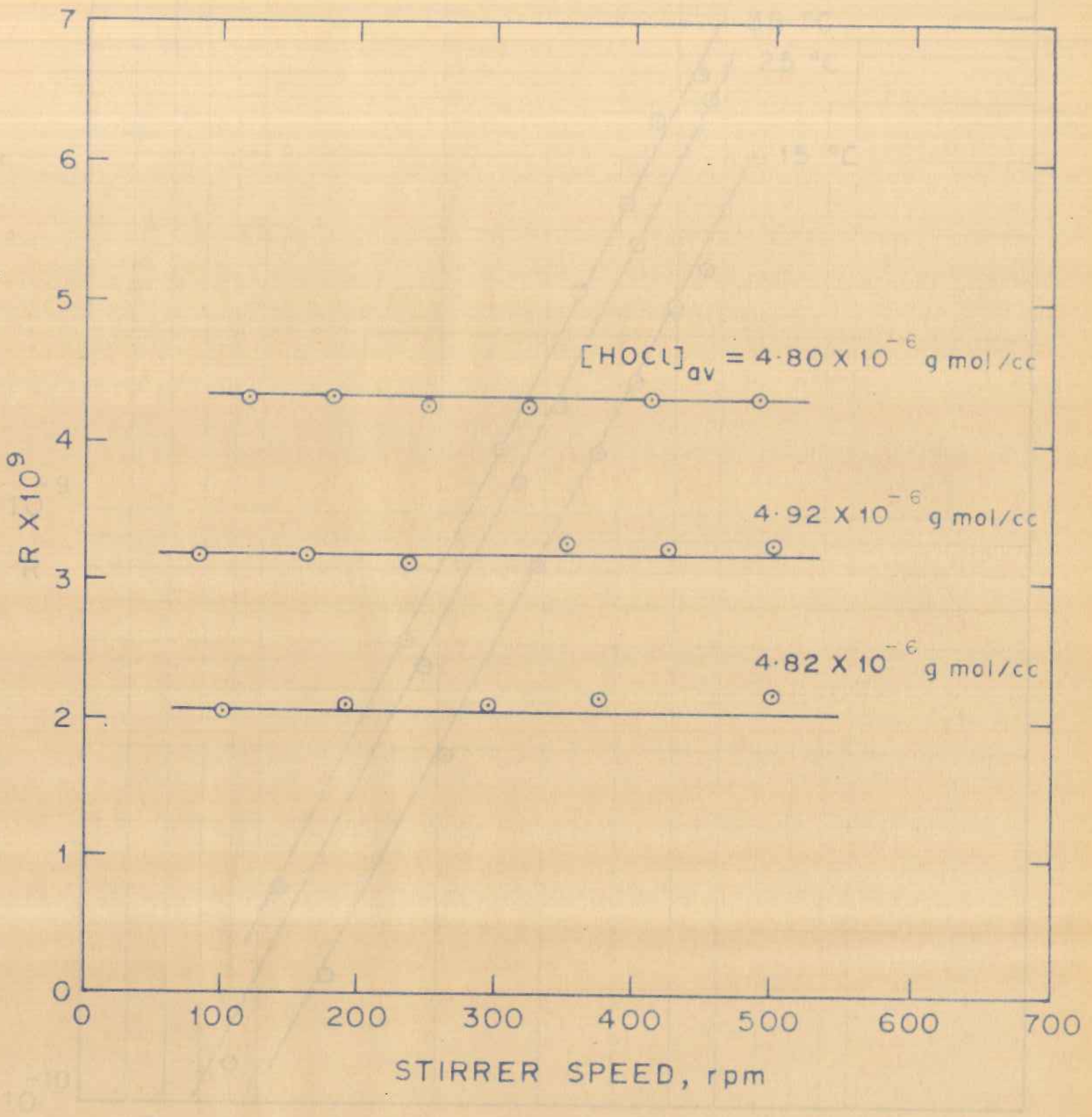

FIGURE 5·2 EFFECT OF STIRRER SPEED ON THE RATE

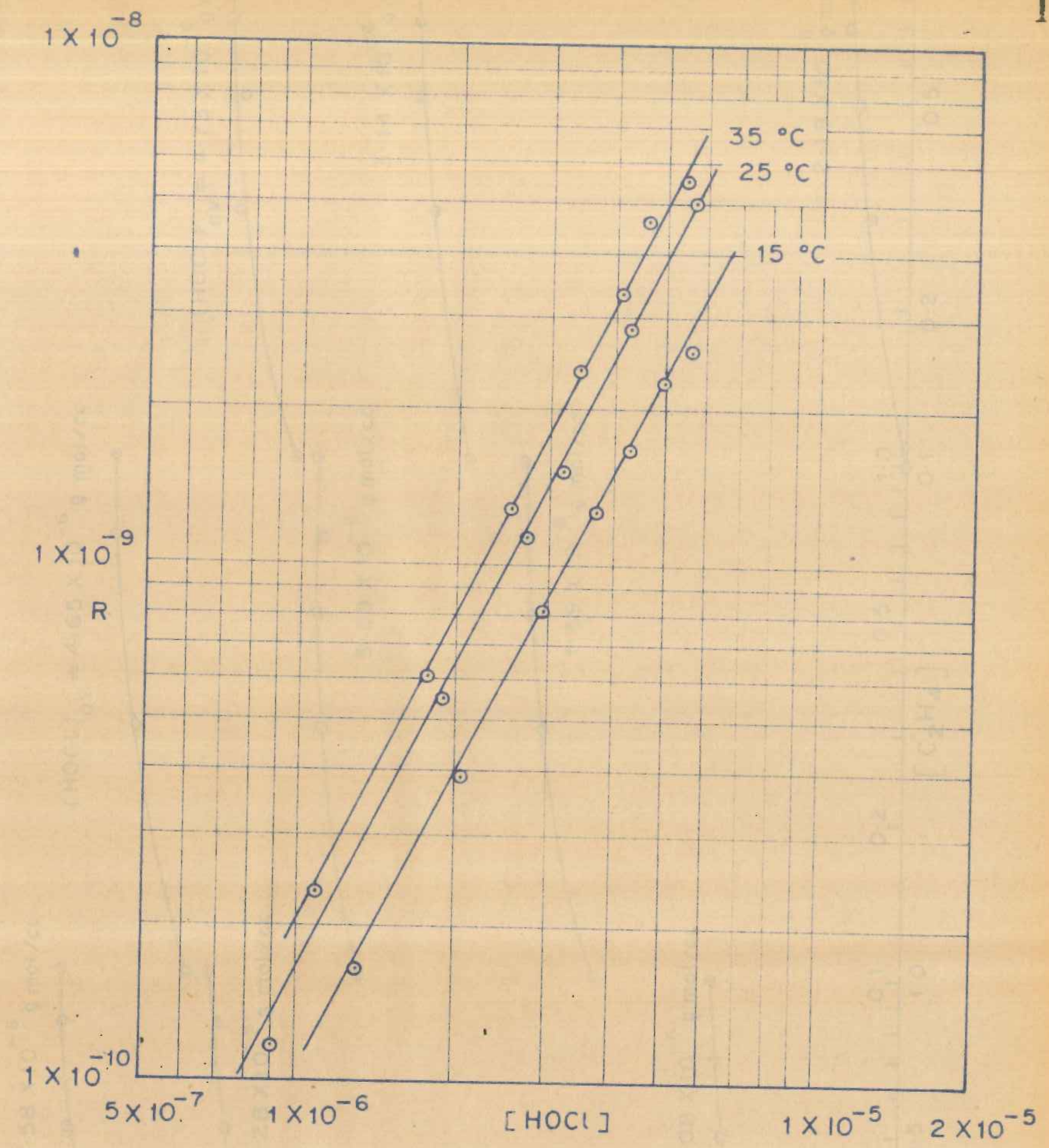

FIGURE 5·3: EFFECT OF CONCENTRATION OF HYPOCHLOROUS ACID ON THE RATE

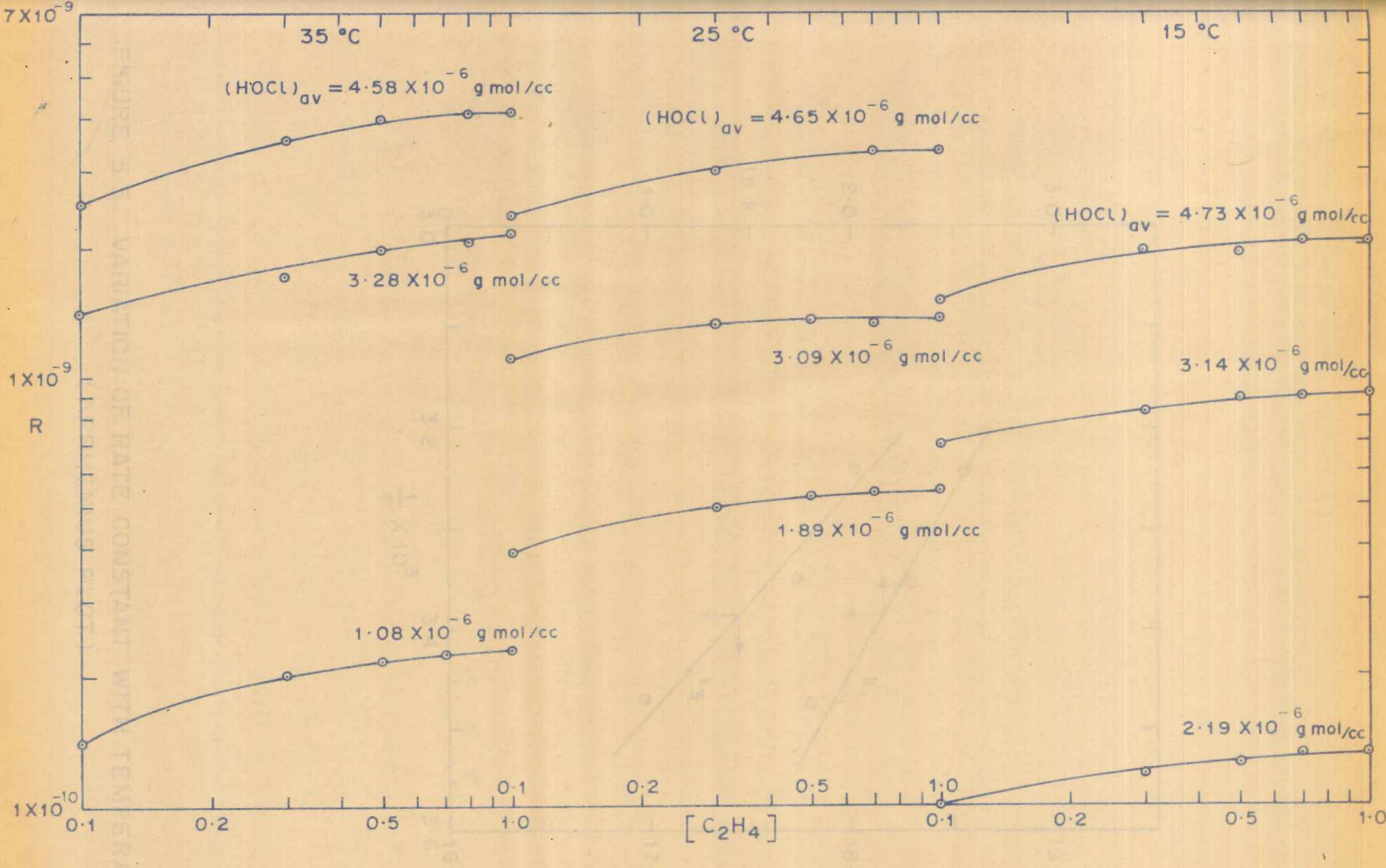

FIGURE 5·4: EFFECT OF PARTIAL PRESSURE OF ETHYLENE ON RATE OF ABSORPTION

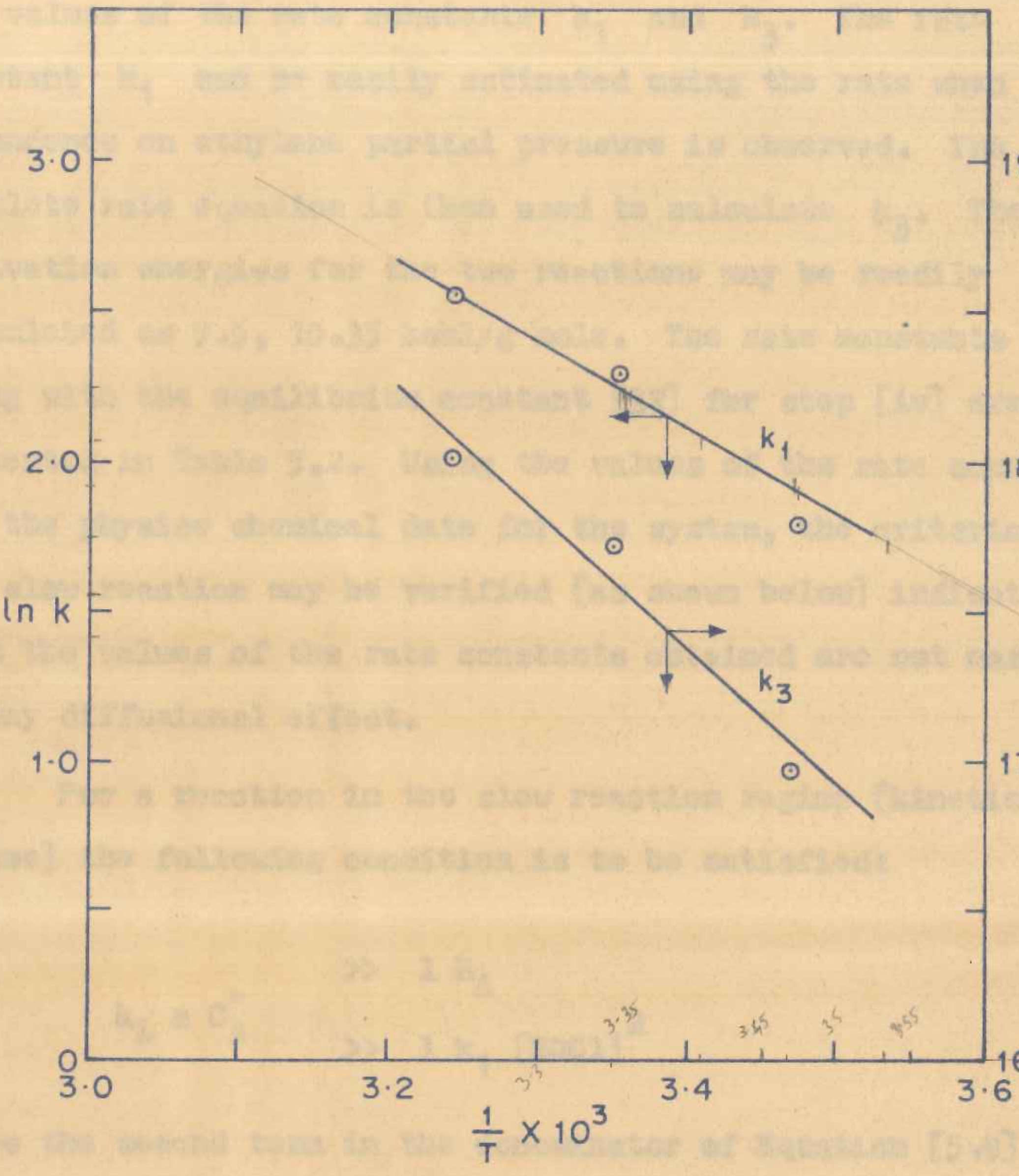

FIGURE 5·5: VARIATION OF RATE CONSTANT WITH TEMPERATURE (ARRHENIUS PLOT) in the lower range whereas a second order dependence on hypochlorous acid is observed.

The experimentally observed rate may be used to calculate the values of the rate constants k_1 and k_3. The rate constant k_1 can be easily estimated using the rate when no dependence on ethylene partial pressure is observed. The complete rate equation is then used to calculate k_3. The activation energies for the two reactions may be readily calculated as 7.5, 10.35 kcal/g mole. The rate constants along with the equilibrium constant [32] for step [iv] are presented in Table 5.2. Using the values of the rate constant and the physico chemical data for the system, the criterion for slow reaction may be verified [as shown below] indicating that the values of the rate constants obtained are not masked by any diffusional effect.

For a reaction in the slow reaction regime [kinetic regime] the following condition is to be satisfied:

$$k_L a C_A^* \begin{array}{l} >> 1 R_A \\ >> 1 k_1 [HOCl]^2 \end{array} \qquad [5.13]$$

where the second term in the denominator of Equation [5.9] is usually negligible. The k_La values in a stirred tank reactor with the stirrer speeds employed would be in the range 2-5 x 10^{-3} sec^{-1}. Assuming a conservative value of 5 x 10^{-3} sec^{-1} and substituting the numerical values for the concentrations and calculated rate constants, we have

$$5 \times 10^{-3} \times 5 \times 10^{-6} >> 0.8 \times 2.0 \times 10^2 [1 \times 10^{-6}]^2$$
$$2.5 \times 10^{-8} >> 1.6 \times 10^{-10}$$

Thus Equation [5.13] is seen to be satisfied.

The results of the experiments indicate that in spite of the low diffusivity and solubility of ethylene the reaction is not diffusion controlled. The rate controlling step is the conversion of hypochlorous acid to chlorine monoxide. The observed value of the rate constant k_1 closely corresponds to the rate constant reported for this reaction [8.2 lit/g mole min] and confirms the rate controlling step.

TABLE 5.1

Kinetic rate expressions for the reaction of hypochlorous acid with organic compounds

System(s)	Kinetic rate expression	Reference
1	2	3
HOCl+crotonic acid	$k[K = k][HOCl][Cl^-]$ $k[HOCl]^2[C_4H_6O_2]$ $k_1[HOCl][k][HCl]$ + $k_2[HOCl][k_1][HCl]$	
HOCl + ethylene	$k_2[HOCl]^2$ $k_3[C_2H_4][HOCl]^2$ $k_1[HOCl][H^+][Cl^-]$	Shilov *et al* [21]
HOCl+2 butene 1-4 diol	$k_3[HOCl]^2[C=C]$ $k_1[HOCl][H^+][Cl^-]$ $k[HOCl][OCl^-][C=C]$	Shilov *et al* [20]
HOCl+ethylene	-	Shilov *et al* [22]
HOCl+ethylene	-	Shilov *et al* [23]
HOCl+ethylene	-	Shilov *et al* [24]
HOCl+ethylene	-	Shilov *et al* [25]
Sodium anisole sulphate + HOBr	$k[HOBR][ArH]$	Shilov *et al* [26]
2 butene, 1-4 diol, crotonic acid, etc.	$k[HOCl][H^+][ArH]$	Shilov *et al* [ ]

1	2	3
Anisole + HOCl [0.003 to 0.01M]		de La mare *et al* [11, 12]
Quinol + dimethyl ether [0.004M] + HOCl	k[HOCl]	
Phenol [0.003 to 0.008M] + HOCl		
Allyl ethyl ether + HOCl	k[HOCl][ArH]	
Allyl fluoride [< 0.004M] + HOCl		
Phenol + HOCl		de La mare *et al* [13]
Mesitylene + HOCl		
Methyl-m-tolyl ether + HOCl	$k[HOCl]+k'[HOCl][H^+]$	
Methyl-p-tolyl ether + HOCl		
	$k[HOCl]+k'[HOCl][H^+]$ $+ k''[HOCl][ArH]$	
Allyl alcohol + HOCl	$k^I[HOCl][C_3H_5OH]$ $+ H^{II}[HOCl]^2$	Israel *et al* [16]
Allyl acetate + HOCl		
Allyl alcohol + HOCl in presence of sod. acetate-acetic acid buffer [constant pH]	$k_2^I[HOCl][C_3H_5OH] +$ $[k_2^{III} + k_3^{II} HOAc]$ $[HOCl]^2 + k_2^{II}[HOCl][HOAc]$	Israel *et al* [14, 15]
Tiglic acid + HOCl	$k_2^I[HOCl][R\ CO_2H]+[R\ CO_2^-]$ $+ k_2[HOCl]^2$	Israel *et al* [18]
Crotonic acid + HOCl in buffered solution at 25°, 35°C.	$k_2^I[HOCl][RCO_2]+[RCO_2^-]$ $+ k_2^{II}[RCO_2H][HOCl]^2$	Cran [27, 29]
Crotonic acid + HOCl		

1	2	3
Ethyl crotonate + HOCl Sod. acetate + acetic acid buffer of constant pH	k_2^{I} [HOCl][EtR] + k_3^{II} $[HOCl]^2$ [EtR] + k_3^{III} [HOCl][HOAc][EtR]	Israel *et al* [29]
Anisole + HOCl	$k^{7}[HOCl]^2 + k''[H_3O^+]$ $[HOCl]^2 + k'''$ [ArH] $[H_3O^+]$ [HOCl]	Swain *et al* [17]

Table 5.2

Rate constants for reaction steps [iv] and [v]

Temperature, ^{o}C	k_1 lit/g mole min	k_3 lit/g mole min	K eq. step [iv]
15	5.81	23.7×10^6	1.01
25	9.67	55.2×10^6	1.419
35	12.80	66.9×10^6	2.013

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CHAPTER 6

DEACTIVATION STUDIES IN CATALYST

6.1 INTRODUCTION

Catalyst deactivation often plays an important role in determining the overall kinetics of a catalytic reaction. Just as the intrinsic kinetics can be altered by diffusional effects, catalyst deactivation can also play a decisive role in determining the regime of a reaction in a catalyst pellet. The study of catalyst deactivation can be considered to involve three main steps. The first is concerned with the chemical nature of deactivation, the second involves the behaviour of a pellet under conditions of catalyst deactivation, and the third [based on the analysis of a deactivating catalyst pellet] relates to the problem of reactor design. Thus, analysis of the role of catalyst deactivation on the course of a chemical reaction in a catalyst pellet has been the central feature of many investigations reported in this field. Various aspects of catalyst deactivation have been reviewed by Maxted [1] and Butt [2].

In the first two sections of this chapter the effect of catalyst deactivation is considered under the following situation: one dimensional nonisothermal [adiabatic] with internal diffusion for a first order reaction, and [2] two dimensional isothermal reactor with internal diffusion for a general order reaction. In the third section, nonuniform distribution of catalyst activity is considered for a general order reaction and conclusions regarding the suitability of nonuniform deposition of catalyst for a consecutive reaction are drawn.

6.2 NONISOTHERMAL REACTOR WITH NO DIFFUSION

The nonisothermal reactor is more commonly encountered in practice than the isothermal reactor. Hence in this section the behavious of a deactivating reactor under nonisothermal conditions [in the absence of diffusion] is presented. It is assumed that deactivation occurs as a result of a second [carbon forming] reaction either in parallel with the main reaction or as a consecutive reaction. These may be described as

$$A \xrightarrow{k_{v1}} B \qquad \text{Parallel}$$

$$A \xrightarrow{k_{v2}} C$$

$$A \xrightarrow{k_{v1}} B \xrightarrow{k_{v2}} C \qquad \text{Consecutive}$$

In order to describe the progress of a chemical reaction in a nonisothermal reactor an energy balance equation is necessary in addition to the conservation equations of the reactant and carbon. These continuity equations can be written in nondimensional form as

$$\frac{\partial w_A}{\partial z} = -\alpha\, r_A \qquad [16.1]$$

$$\frac{\partial w_c}{\partial t_D} = \alpha f_B r_c \qquad [6.2]$$

$$\frac{\partial T}{\partial z} = \beta r_A \qquad [6.3]$$

where

$$\alpha = \frac{\rho_B d_p}{G}, \quad \beta = \frac{[-\Delta H] \rho_g d_p}{G T_o C_p M}$$

and

$$t_D = \frac{G}{\rho_g f_B d_p}\left[t - \frac{f_B \rho_g}{G} L\right] \qquad [6.4]$$

The time variable defined by Equation [6.4] has been used in writing Equations [6.1] - [6.3] to eliminate the time dependent terms.

To solve Equations [6.1] - [6.3], expressions for the rates r_A and r_c must be known. These rates for the case of consecutive and parallel fouling are described by:

parallel:

$$r_A = k_{v1} w_A + k_{v2} w_A = k_{v1} w_A, \text{ if } k_{v2} \ll k_{v1} \qquad [6.5a]$$

$$r_c = k_{v2} w_A \qquad [6.5b]$$

consecutive:

$$r_A = k_{v1} w_A \qquad [6.6a]$$

$$r_c = k_{v2} [1 - w_A] \qquad [6.6b]$$

Restricting our attention to parallel fouling and assuming inverse proportionality $[a = \frac{1}{w_c}]$, we have $k_{v1} = \frac{K_1}{w_c}$ and $k_{v2} = \frac{K_2}{w_c}$. Equation [6.1] - [6.3] can now be recast as

$$\frac{\partial w_A}{\partial z} = - \alpha K_1 \left(\frac{w_A}{w_c} \right) \qquad [6.7]$$

$$\frac{\partial w_c}{\partial t_D} = f_B \alpha K_2 \left(\frac{w_A}{w_c} \right) \qquad [6.8]$$

$$\frac{\partial T}{\partial z} = \beta K_1 \left(\frac{w_A}{w_c} \right) \qquad [6.9]$$

Equations [6.7] - [6.9] have to be solved simultaneously. From Equations [6.7] and [6.9] the following relationship between concentration and temperature can be obtained:

$$T = T_o + \frac{\beta}{\alpha} \quad [w_{Ao} - w_A] \qquad [6.10]$$

Using this result in Equations [6.7] and [6.8] and neglecting the higher order terms in the expansion, we get

$$\frac{\partial w_A}{\partial z} = \alpha \; k_{v1}^{o} \; \exp \left[\beta_R \; (w_{Ao} - w_A) \right] \frac{w_A}{w_c} \qquad [6.11]$$

and

$$\frac{\partial w_c}{\partial t_D} = \alpha \; f_B \, k_{v2}^{o} \; \exp \left[\beta_f \, (w_{Ao} - w_A) \right] \frac{w_A}{w_c} \qquad [6.12]$$

where

$$\beta_R = \frac{E\,\beta}{\alpha\,R_g\,T_o^2}, \quad \beta_f = \frac{E_f\,\beta}{\alpha\,R_g\,T_o^2} \quad \text{and} \qquad [6.13]$$

$$k_{v1}^{o} = A_1 \exp\left[-E/R_g\,T_o\right], \quad k_{v2}^{o} = A_2 \exp\left[-E_f/R_g\,T_o\right]$$

Following Bischoff [3] the solution to Equations [6.11] and [6.12] is assumed to be given by

$$w_A\,[z,\,t_D] = \frac{w_c\,[z,\,t_D] - w_c\,[0]}{w_c\,[0,\,t_D] - w_c\,[0]}\; w_{Ao}\,[t_D] \qquad [6.14]$$

Using Equations [6.14] in [6.11] and [6.12] and after some algebraic manipulations, the following equations are obtained:

$$\int_{w_c\,[0,0]}^{w_c\,[0,\,t_D]} w_c\; d\,w_c = \frac{\alpha_R\,f_B\,k_{v2}^{o}}{1} \int_0^{t_D} w_A\,[t_D]\; d\,t_D \qquad [6.15]$$

and

$$z = \int_{w_c\,[0,\,t_D]}^{w_c\,[z,\,t_D]} \frac{w_c\,[z,\,t_D]}{\alpha_R\,k_{v1}^{o}\left[w_c\;z,\;t_D - w_c\,[0]\right]} \qquad [6.16]$$

$$\times \exp\left\{-\beta_R\left[w_{Ao} - \frac{w_c\,[z,\,t_D] - w_c\,[0]}{w_c\,[0,\,t_D] - w_c\,[0]}\; w_{Ao}\,[t_D]\right]\right\} d\,w_c$$

At constant feed rate $y_A\,[0,\,t_D] = y_{Ao}$, and for zero initial position $w_c\,[z, 0] = 0$. Under these conditions Equations 6.15 and 6.16 reduce to

$$w_c\,[0, t_D] = [2\,\alpha_R\, f_B\, k^o_{v2}\, t_D\, w_{Ao}]^{1/2} \qquad [6.17]$$

and

$$z = \frac{\exp\,[-\beta_R]}{\alpha_R\, k^o_{v1}} \int_{w_c\,[0,\, t_D]}^{w_c\,[z,\, t_D]} \exp\left[\beta_R\, \frac{w_c\,[z, t_D]}{w_c\,[0, t_D]}\right] d\,w_c \qquad [6.18]$$

Equation [6.18] can now be integrated to give the profiles for carbon. The reactant and temperature profiles are then obtained using Equations [6.14] and [6.10] respectively. These profiles are presented in Table 6.1. It can be seen from the equations that the maximum temperature and the distance at which it occurs are functions of time.

6.3 TWO-DIMENSIONAL ISOTHERMAL REACTOR WITH INTERNAL DIFFUSION

In many gas-solid catalytic reactions the activity of the catalyst decreases with time-on-stream. Such deactivation might be the result of a number of side reactions, or presence of poison in the feed stream itself. Numerous studies [3-6], both experimental and theoretical, have been reported in the literature on this subject. In the evaluation of the performance of a fixed bed reactor with catalyst deactivation, a knowledge of the single pellet effectiveness factor is necessary. This quantity depends upon time, intraparticle diffusion and reaction parameters, and is a measure of the activity of the catalyst pellet. The analysis of an isothermal two dimensional fixed bed reactor is carried out here using the effectiveness factors obtained for a general order reaction in a single pellet. The useful assumption that the rate of the main reaction is much faster than that of the fouling reaction is made to simplify the analysis.

6.3.1 Formulation of the problem

The conservation equations for the reactant and carbon are as follows:

External field equations

$$- u \frac{\partial C_f}{\partial z} + \frac{D_f}{r_t} \frac{d}{d r_t} r_t \frac{\partial C_f}{\partial r_t} - \frac{1 - f_B}{f_B} R [C_s] = \frac{\partial C_A}{\partial t} \qquad [6.22]$$

$$z = 0, \quad C_f = C_{fo}, \quad R < r < 0, \quad t > 0 \qquad [6.23]$$

$$\left.\begin{aligned} r_t &= 0, \quad \frac{\partial C_f}{\partial r_t} = 0 \\ r_t &= R, \quad \frac{\partial C_f}{\partial r_t} = 0 \end{aligned}\right\} L < z < 0, \quad t > 0 \qquad [6.24]$$

$$t = 0, \quad L < z < 0, \quad R < r < 0, \quad C_f = 0 \qquad [6.25]$$

Internal field [spherical pellet] equations

reactant balance

$$\frac{1}{r_s^2}\ De\ \frac{d}{d\, r_s}\left(r_s^2\ \frac{\partial C}{\partial r_s}\right) = R\ [C_s] + \frac{\partial C}{\partial t} \qquad [6.26]$$

$$C = C_s = C_f\ [r,\ z,\ t],\quad r_s = b \qquad [6.27]$$

use flux term instead.

$$\frac{\partial C}{\partial r_s} = 0,\quad r_s = 0 \qquad [6.28]$$

$$t = 0,\quad b < r_s < 0,\quad C = 0 \qquad [6.29]$$

carbon balance

$$\frac{\partial}{\partial t}\left(\frac{a_p}{A_w}\right) = k_2\ [a_o - a_p]\ C_A + k_3\ [a_o - a_p]\ C_B$$

$$= R_w \qquad [6.30]$$

where a_o, a_p represent the initial and poisoned areas and A_w represents the area poisoned per mole of poison produced. Equation [6.30] can also be written in terms of the amount of carbon deposited as,

$$\frac{\partial w_c}{\partial t} = R_w \qquad [6.31]$$

$$t = 0,\quad w_c = w_{co} = 0 \qquad [6.32]$$

Equations [6.22] - [6.32] represent the mathematical description of the process occurring in a fixed bed reactor operated isothermally with catalyst deactivation. In fixed bed reactors with slow poisoning of catalyst, the time dependent terms in Equations [6.22] and [6.26] can be neglected, and Equations [6.22] - [6.32] transformed into dimensionless formsas follows.

External fluid phase equations

$$-\frac{\partial y}{\partial x} + \frac{1}{Pe_f} \frac{\partial y}{\partial p^2} - \frac{3\,[1 - f_B]}{f_B} \frac{1}{Pe_f} \left.\frac{d\,w}{d\,\xi}\right|_{\xi = 1} = 0 \qquad [6.33]$$

This equation can also be written in terms of the effectiveness factor of the pellet as

$$-\frac{\partial y}{\partial x} + \frac{1}{Pe_f} \frac{\partial y}{\partial p^2} - \frac{1 - f_B}{f_B}\, \eta_d \left(\frac{b\,k_{v1}}{U}\right) y^n = 0 \qquad [6.34]$$

$$x = 0, \quad y = 1, \quad \frac{R}{b} < p < 0 \qquad [6.35]$$

$$\left.\begin{aligned} p = 0, \quad \frac{\partial y}{\partial p} &= 0 \\ p = \frac{R}{b}, \quad \frac{\partial y}{\partial p} &= 0 \end{aligned}\right\} \quad \frac{L}{b} < x < 0 \qquad [6.36]$$

Internal [spherical pellet] equations

$$\frac{d^2\,v}{d\,\xi^2} + \frac{2}{\xi} \frac{d\,v}{d\,\xi} - \phi^2\, a\, v^n = 0 \qquad [6.37]$$

$$\xi = 1, \quad v = \frac{C_f}{C_{fo}} \xi = y \qquad [6.38]$$

$$\frac{d\,v}{d\,\xi} = 0, \quad \xi = 0 \qquad [6.39]$$

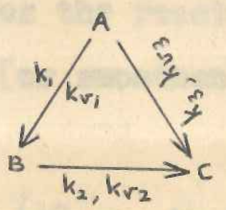
carbon

$$\mu\, v_A \left(1 - \frac{k_3}{k_2}\right) + \mu \left(\frac{k_3}{k_2}\right) [v_A + v_B] = - \frac{\partial \mu}{\partial \gamma} \qquad [6.40]$$

where

$$\mu = \left(1 - \frac{a_p}{a_o}\right) \quad \text{and} \quad \gamma = k_2\, C_{As}\, A_w\, t \qquad [6.41]$$

In writing Equation [6.40], the triangular self poisoning scheme is assumed:



where k_1, k_2 and k_3 are the surface rate constants [cm/sec], and k_{v1}, k_{v2} and k_{v3} are [as before] the volume based constants [1/sec].

6.3.2 Solution of the pellet equations

For obtaining the expression for effectiveness factor required in Equation [6.34], the pellet equations [6.37] - [6.41] have to be solved simultaneously, and for this purpose numerical methods have to be employed. Following Bischoff [3],

however, a solution of the form

$$v\,[\xi\,,\,t] = \left[\frac{w_c\,[\xi\,,\,t] - w_c\,[0]}{w_c\,[0,\,t] - w_c\,[0]}\;y_o\right]^{1/m} \qquad [6.43]$$

[where m is the order of the deactivating step], can be used. Also, inverse proportionality between activity a and carbon content of catalyst may be assumed. Thus, Equation [6.37] becomes

$$\frac{d^2\,v}{d\,\xi^2} + \frac{2}{\xi}\,\frac{d\,v}{d\,\xi} - \phi^2\left(\frac{y_o}{w_c\,[0,\,t]}\right)v^{n-m} = 0 \qquad [6.44]$$

If the main reaction is n^{th} order and the deactivation is m^{th} order, the resultant system behaves as a $[n - m] = q^{th}$ order reaction. Deactivation may therefore be regarded as a step which reduces the reaction order; in other words it tends to decrease [or smoothen] the effect of reactant concentration.

Equation [6.44] can be transformed into the following form:

$$\frac{d^2\,u}{d\,s^2} - \phi_1^2\,u^q = 0 \qquad [6.45]$$

using the transformations

$$v\,\xi = \upsilon$$

and

$$\xi = s\,[1 - \sqrt{n-m-1}]^{1 - \sqrt{n-m-1}} \qquad [6.46]$$

with the boundary conditions

$$s = \frac{1}{[1 - \sqrt{n-m-1}]}, \quad u = y \qquad [6.47]$$

$$s = 0, \quad \frac{d\,u}{d\,s} = 0, \quad u = y_o \qquad [6.48]$$

Equation [6.45] is integrated twice making use of the substitution $\psi = 1 - \left(\frac{y_o}{u}\right)^{q+1}$ and expressing the results in terms of incomplete β functions [or hypergeometric series] as

$$u = \left[\frac{\left(\frac{2}{q+1}\right)^{-1/2} [1 - \psi]^{-\frac{1-q}{2[1+q]}} \; \phi_1 \left(\frac{1}{1 - \sqrt{n-m-1}}\right)}{\psi_s \; F_1 \left[\frac{1}{2}, \frac{1}{2} + \frac{1}{q+1}; \frac{3}{2}, \psi_s\right] - \psi_o^{1/2} \; F_1 \left[\frac{1}{2}, \frac{1}{2} + \frac{1}{q+1}; \frac{3}{2}, \psi_o\right]} \right]^{\frac{2}{1-q}}$$

and [6.49]

$$\frac{d\,u}{d\,s} = \sqrt{\frac{2}{q+1}} \; \phi_1 \; [u]^{\frac{q+1}{2}} \left[1 - \left(\frac{y_o}{u}\right)^{q+1}\right]^{1/2} \qquad [6.50]$$

The effectiveness factor for the pellet under deactivation can then be found as

$$\eta = \frac{-3\,D_e \left.\frac{\partial C}{\partial r_s}\right|_{r=b}}{k_1 \, [C_s]^n_{r=b} \, . \, b}$$

$$\eta = \frac{3}{\phi}\ \frac{2}{q+1}\ \frac{y_o}{w_c\,[0,\ t]}\ \psi_1^{1/2}\ \frac{\psi_s^{-1/2}\ F_1\ [\frac{1}{2},\ \frac{1}{2} + \frac{1}{q+1}\ ;\ \frac{3}{2},\ \psi_s}{[1 - \psi_s]^{\frac{1-q}{2(1-q)}}\qquad \phi_1\ \frac{1}{\sqrt{n-m-1}}} - \frac{1}{\phi}$$

[6.51]

where y is obtained from Equation [6.50] and $w_c\,[0,\ t]$ can be found from Equation [6.30] and [6.43].

For parallel fouling,

$$w_c\,[0,\ t] = [2\ y_o\ k_2\ t\ C_{fo}]^{1/2} = [2\ y_o\ \tau\ ]^{1/2} \qquad [6.52]$$

If we now make the assumption: $q = 1$, this equation reduces to

$$\eta = \frac{3\ y^{1-n}}{\phi^2}\ \phi \left(\frac{y_o}{w_c\ [0,\ t]}\right)^{1/2}\ \coth\ \phi\ \frac{y_o}{w_c\ [0,t]} - 1$$

[6.53]

The asymptotic solution of Equation [6.53] can be obtained as

$$\eta = \frac{3\ y^{1-n}}{\phi}\ \left(\frac{y_o}{2\ \tau}\right)^{1/4} \qquad [6.54]$$

Equation [6.54] is plotted in Figure 6.1 for various values of the parameter ϕ.

The plots of effectiveness factor are similar to any normal plot for the η . The η decreases with increase in

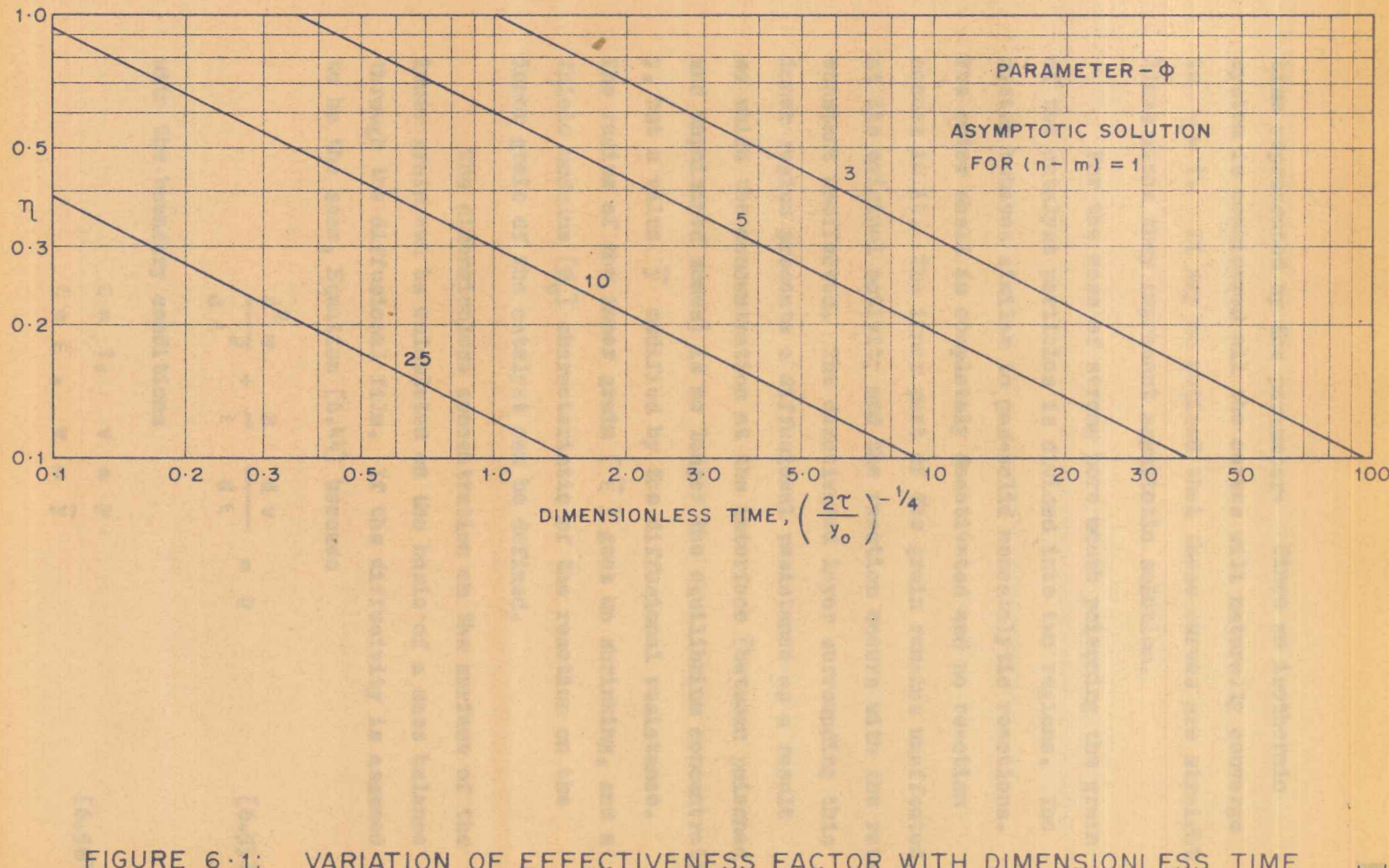


FIGURE 6·1: VARIATION OF EFFECTIVENESS FACTOR WITH DIMENSIONLESS TIME FOR VARIOUS VALUES OF THIELE MODULUS time represented by the parameter. Since an isothermic system is considered all the curves will naturally converge to $\eta = 1$. It may be noticed that these curves are straight lines since they represent asymptotic solution.

For the case of strong pore mouth poisoning the grain of the catalyst particles is divided into two regions. The system behaves similar to gas-solid noncatalytic reactions. The outer shell is completely deactivated and no reaction occurs in it. The inner part of the grain remains unaffected at its original activity and the reaction occurs with the rate constant unaffected. The deactivated layer surrounding this inner region presents a diffusional resistance as a result of which the concentration at the interface [between poisoned and unpoisoned zones] is no longer the equilibrium concentration y, but a value $\bar{y}$ modified by the diffusional resistance. The radius of the inner grain [$\bar{\xi}$] goes on shrinking, and a Thiele modulus [ϕ_s] characteristic of the reaction on the inner grain of the catalyst can be defined.

The dimensionless concentration on the surface of the inner grain can be calculated on the basis of a mass balance through the diffusional film. If the diffusivity is assumed to be the same, Equation [6.44] becomes

$$\frac{d^2 v}{d \xi^2} + \frac{2}{\xi} \frac{d v}{d \xi} = 0 \qquad [6.55]$$

with the boundary conditions

$$\xi = 1, \quad v = y$$
$$\xi = \bar{\xi}, \quad v = \bar{y} \qquad [6.56]$$

The effectiveness factor for the pellet can then be calculated as

$$\eta = \frac{3}{\phi^2} \quad \frac{\bar{\xi}\,[y - \bar{y}\,]}{[1 - \bar{\xi}\,]\,y} = \frac{3}{\phi^2} \quad \frac{\bar{\xi}\,[1 - \bar{y}^{1}]}{[1 - \bar{\xi}\,]} \qquad [6.58]$$

Equation [6.58] can then be solved by a trial and error method.

In the process of deactivation, the effectiveness factor continuously decreases with time, so that the reaction passes from the kinetic regime [initially] to a strongly diffusion influenced regime. The apparent order of reaction changes as a result of the transition. Tartarelli and Morelli [7] have obtained an expression for the variation of the apparent order of reaction with Thiele modulus. Following Wheeler [8] the apparent order can also be written as

$$\bar{n} = n + \frac{n - 1}{2} \quad \frac{d \ln \eta}{d \ln \phi} \qquad [6.59]$$

Thus if the relationship between η and ϕ is known Equation [6.59] can be used to calculate the apparent order of reaction.

6.3.3 Solution of the external field equation

Equation [6.34] can be rewritten as

$$- \frac{\partial y}{\partial x} + \frac{1}{Pe_f} \frac{\partial y}{\partial p^2} - \frac{[1 - f_B]}{f_B} D_a \, \eta \, y^n = 0 \qquad [6.60]$$

We seek the solution to this equation subject to the boundary conditions [6.35] and [6.36], in the form

$$y\,[x,\,p] \;=\; \sum_{j=1}^{\infty} X_j\,[x]\,\cos\,\frac{j\,\pi\,p\,b}{R} \qquad [6.61]$$

so that the boundary conditions [6.35] and [6.36] are automatically satisfied.

Let us suppose that the function $\eta\,[x,\,p,\,t]$ regarded as a function of p can be expanded in a Fourier series:

$$[x,\,p,\,t] \;=\; \sum_{j=1}^{\infty} \eta_j\,[x,\,t]\,\cos\,\frac{j\,\pi\,p\,b}{R} \qquad [6.62]$$

Substituting Equation [6.60] in [6.61] and utilising the result in Equation [6.62], we get

$$\sum_{j=1}^{\infty} \Bigg[-\,X_j'\,[x,\,t] \;+\; \frac{1}{Pe_f}\,[-\,X_j]\,\left(\frac{j\,\pi\,b}{R}\right)^2$$

$$-\;\frac{1-f_B}{f_B}\,D_a\,\eta_j\,[x,\,t]\,X_j^{\,n}\,\cos^{\,n-1}\frac{j\,\pi\,p\,b}{R}\Bigg]\,\cos\,\frac{j\,\pi\,p\,b}{R}$$

$$[6.63]$$

Equation [6.63] can be solved when the order of the main reaction [n] is known. Solutions are presented here for second and first order reactions.

For the second order case Equation [6.63] becomes

$$X' \;+\; \frac{\gamma}{Pe_f}\,X \;-\; \delta\,X^2 \;=\; 0 \qquad [6.64]$$

where

$$\delta = \frac{f_B - 1}{f_B} D_a \eta_d \cos^{n-1}\left(\frac{\pi p b}{R}\right) \qquad [6.65]$$

Equation [6.64] can be identified with the Riccati equation the solution of which is obtained as

$$y[x, p] = \frac{\frac{\gamma}{Pe_f} \cos \gamma}{\frac{1 - f_B}{f_B} D_a \eta_d \cos^{n-1}\left(\frac{\gamma}{Pe_f}\right)}$$

$$\times\left[\frac{\left(1 - \frac{1}{1 - \exp\left(-\gamma L/b\, Pe_f\right)}\right)\exp\left(-\frac{\gamma x}{Pe_f}\right)}{\left(1 - \frac{1}{1-\exp\left(-\gamma L/b\, Pe_f\right)}\right)\exp\left(-\frac{\gamma x}{Pe_f}\right) + \frac{1}{1 - \exp\left(-\frac{\gamma L}{b\, Pe_f}\right)}}\right]$$

$$[6.66]$$

A relatively simple solution is obtained for the case of a first order main reaction. Equation [6.63] becomes

$$X' + \left(\frac{\gamma}{Pe_f} - \delta\right) X = 0 \qquad [6.67]$$

the solution to which is

$$y[x, p] = \sum_{j=1}^{\infty} \exp\left[-\frac{j \pi p b}{R\, Pe_f} + \frac{1 - f_B}{f_B} D_a \eta_d\right] \times$$

$$[6.68]$$

Equation [6.68] under conditions of no fouling reduces to the well known simple form for a plug flow reactor:

$$y\,[x,\,p] \;=\; \exp\left(-\,\frac{k_v'' \, l}{u}\right) \qquad [6.69]$$

Equations [6.66] and [6.68] represent the concentration profiles in a fixed bed reactor for second and first order main reaction and are plotted in Figures 6.2 to 6.4.

The curve obtained for $\eta = 1$ coincides with the curve obtained by Masamune and Smith [9] at zero time. We have previously obtained effectiveness factor as a function of time [Equation [6.51], [6.54]] which shows that the effectiveness factor continuously falls with time, hence the different curves obtained with various values of the effectiveness factor really correspond to the curves obtained by Masamune and Smith at different values of the time. Thus if the time from the start of reaction is known, the effectiveness factor can be read from Figure 6.1 and for the corresponding value of η the concentration can be obtained using Figure 6.4.

The concept of an effectiveness factor can thus be successfully employed in the analysis of a two dimensional reactor. The concentration profiles obtained are more realistic than can be obtained using the one dimensional model.

6.3.4 <u>Consecutive reaction</u>

The selectivity of product B in a consecutive reaction A → B → C occurring in a fixed bed reactor operating

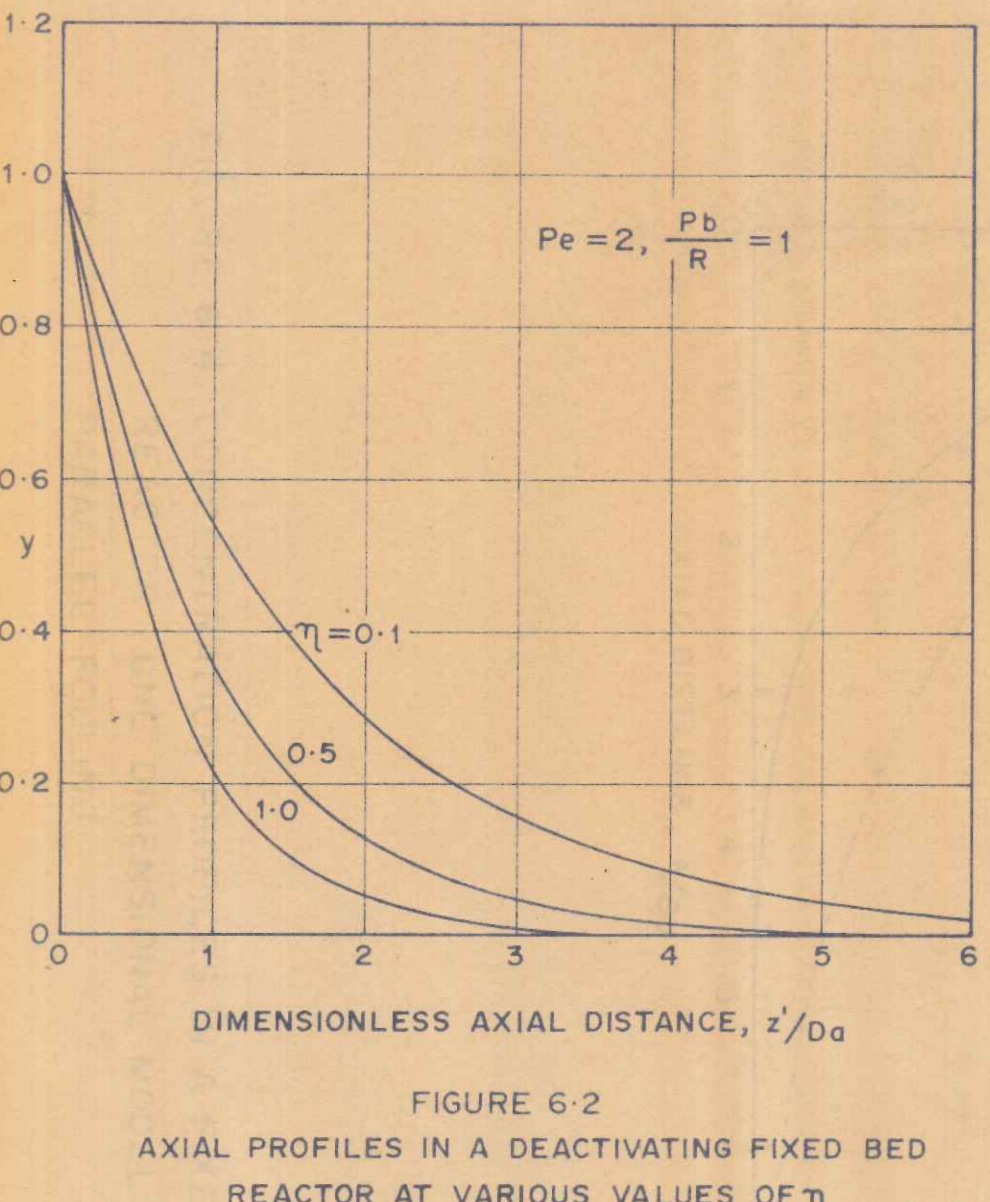


FIGURE 6·2
AXIAL PROFILES IN A DEACTIVATING FIXED BED
REACTOR AT VARIOUS VALUES OF η

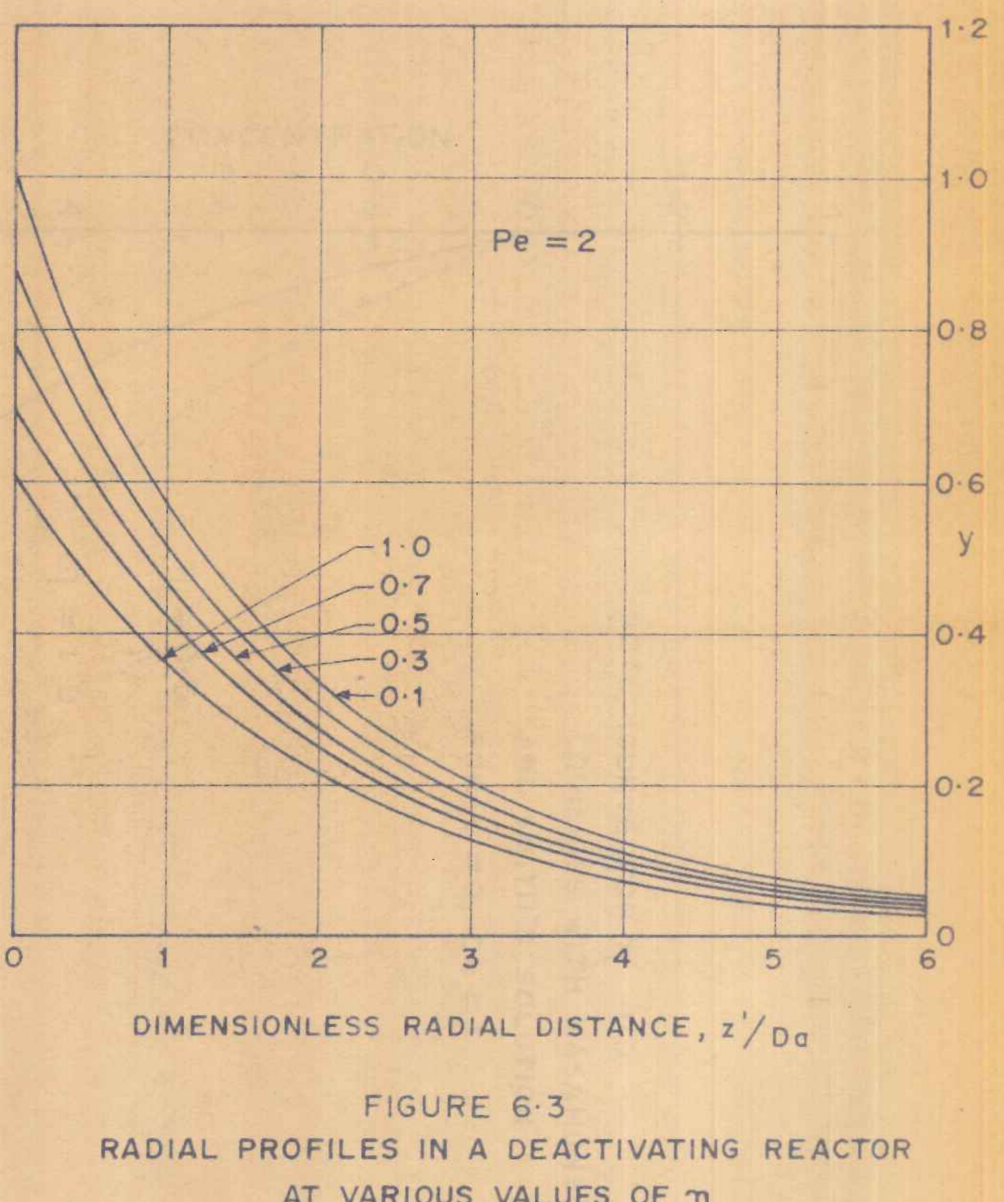


FIGURE 6·3
RADIAL PROFILES IN A DEACTIVATING REACTOR
AT VARIOUS VALUES OF η

FIGURE 6·2, 6·3: CONCENTRATION PROFILES IN A DEACTIVATING REACTOR
FOR THE CASE OF PARALLEL FOULING

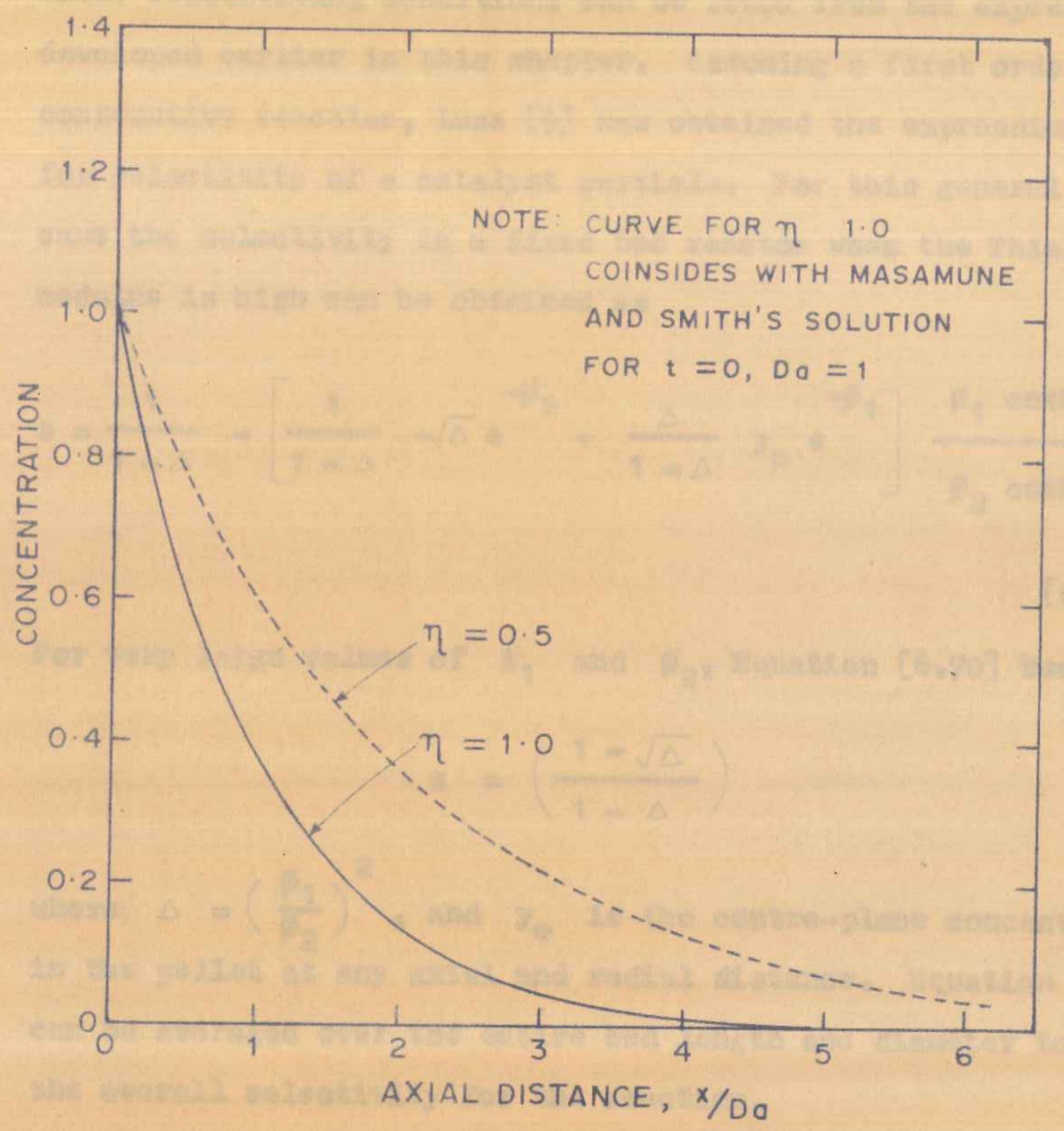


FIGURE 6·4: CONCENTRATION PROFILES IN A FIXED BED REACTOR (ONE DIMENSIONAL MODEL) FOR PARALLEL FOULING under deactivating conditions can be found from the expressions developed earlier in this chapter. Assuming a first order consecutive reaction, Luss [9] has obtained the expression for selectivity of a catalyst particle. For this general case the selectivity in a fixed bed reactor when the Thiele modulus is high can be obtained as

$$s = \frac{1}{1-\Delta} - \left[\frac{1}{1-\Delta} + \sqrt{\Delta}\, e^{-\phi_2} + \frac{\Delta}{1-\Delta}\, y_o\, e^{-\phi_1}\right] \frac{\phi_1 \coth \phi_1 - 1}{\phi_2 \coth \phi_2 - 1} \qquad [6.70]$$

For very large values of ϕ_1 and ϕ_2, Equation [6.70] becomes

$$s = \left(\frac{1-\sqrt{\Delta}}{1-\Delta}\right)$$

where $\Delta = \left(\frac{\phi_1}{\phi_2}\right)^2$, and y_o is the centre-plane concentration in the pellet at any axial and radial distance. Equation [6.70] can be averaged over the entire bed length and diameter to get the overall selectivity for the reaction.

6.4 INFLUENCE OF DISTRIBUTED CATALYST ACTIVITY ON THE PERFORMANCE OF A SINGLE PELLET WITH GENERAL ORDER KINETICS; AN APPROXIMATE SOLUTION

The influence of diffusion [a transport phenomenon] on the intrinsic kinetics of a reaction [a chemical phenomenon] on porous catalysts has been discussed extensively [for example, 10-12] in the literature. A uniform distribution of catalyst activity in the pellet was assumed in most of these developments.

Many industrially important reactions are however carried out on catalysts having a spatially nonuniform activity distribution. Thus Minhas and Carberry [13] reported the use of a partially impregnated catalyst for sulphur dioxide oxidation over supported platinum catalyst. Their results indicated the definite improvements in space-time-yield for the partially impregnated catalysts. Oxidation of o-xylene to phthalic anhydride and hydrogenation of acetylene in the presence of a large excess of ethylene are some of the other reactions carried out on catalysts having nonuniform activity distributions [14, 15].

The problem of evaluating the changes in performance of a supported catalyst with changes in the distribution of catalytically active material on an inert porous support has been analysed by Yazdi and Petersen [16] and Corbett and Luss [17]. The exponential variation of catalyst activity with the activity decreasing towards the centre of the pellet, and the rate constant density functions were employed in their analysis and linear kinetics was assumed. The general conclusions are in favour of the selectivity for a consecutive reaction though concentrating the activity in the external shell yields minimal resistance to deactivation. The specific deactivation mechanism, the rates of the main and the fouling reactions and the diffusional resistances involved have a marked influence on the activity profile. Further the cost of regeneration of catalyst goes a long way in deciding on the optimum activity profile. Neverthless the general conclusions seem to be in favour of catalyst with nonuniform catalyst deposition.

In the analysis presented in this section, general order kinetics, which is more commonly encountered than linear kinetics, is considered. Exponential variation of catalyst activity, with the activity decreasing with increasing distance from the surface, is assumed. The governing equations for slab geometry are then transformed into Emden-Fowler type of equations and asymptotic solutions are presented which extend the validity of the conclusions stated above to general order reactions as well.

6.4.1 Formulation of the problem

The mass conservation equation for the reactant A for the case of diffusion and reaction through a pellet with varying activity takes the general form

$$D_A \frac{d^2 C_A}{d x^2} = k_{v1} C_A^n a [x] \qquad [6.71]$$

$$C_A = C_A^* , \quad x = L \qquad [6.72]$$

$$\frac{d C_A}{d x} = 0, \quad x = 0 \qquad [6.73]$$

If the activity profile 'a' in the pellet is known, then Equation [6.71] can be solved for a specific case. Thus Yazdi and Petersen [16] have considered the exponential variation in activity and solved the equation for a first order consecutive reaction. Kasaoka and Sakata [18] have considered various other activity profiles and Corbett and Luss [17] have employed the rate constant density function with a first order main reaction. In this analysis a general order reaction is considered. In general the activity distribution in a pellet can be expressed as $\left(\frac{X}{L}\right)^{\alpha}$, where α is some exponent, as indicated in ref. [16]. Thus Equation [6.71] is more general and describes the physical situation for a variety of reactions. The asymptotic behaviour of this equation is examined here which verifies the previously known conclusions.

Equation [6.71] can be transformed into dimensionless form as

$$\frac{d^2 w}{d y^2} - \phi^2 w^n y^m = 0 \qquad [6.74]$$

$$w = 1, \quad y = 1 \qquad [6.75]$$

$$\frac{d w}{d x} = 0, \quad y \to \alpha \qquad [6.76]$$

where $m = -[4 + \alpha]$

A solution to this equation is assumed in the form

$$w = \phi C y^{u} \qquad [6.77]$$

where C and u are constants. Substituting Equation [6.77] in [6.74], these constants are evaluated as

$$\phi\, C = \left[\frac{[m+2]\,[m+n+1]}{[n-1]^2}\right]^{1/n-1} \phi^{-\frac{2}{n-1}} \quad , \quad n \neq 1$$

$$u = -\frac{[m+2]}{[n-1]} \qquad [6.78]$$

The solution to Equation [6.74] then becomes

$$w = \left[\frac{[m+2]\,[m+n+1]}{[n-1]^2}\right]^{1/n-1} y^{-\frac{m+2}{n-1}} \phi^{-\frac{2}{n-1}} \qquad [6.79]$$

Since only the real continuous solutions are considered, the arithmetic nature of n [order of the main reaction] will have considerable influence upon the possible types of 'proper solutions.' It is clear that, in general, because of the presence of the term u^n, the solutions must be positive. As can be seen from Equation [6.78], the solution [6.79] to Equation [6.74] exists only if $[m+2]\,[m+n+1] > 0$. Various other asymptotic solutions are obtained for different values of the exponents [n, m] and are given below.

[1] If $m + n + 1 < 0$:

$$w = \left[\frac{[m+2]\,[m+n+1]}{[n-1]^2}\right]^{\frac{1}{n-1}} y^{-\frac{m+2}{n-1}} \phi^{-\frac{2}{n-1}} \qquad [6.80]$$

[2] If $m + 2 < 0 < m + n + 1$:

$$w \approx \left[a + \frac{\phi^2 a^n y^{m+2}}{[m + 1]\,[m + 2]}\,[1 + 0\,(1)]\right] \qquad [6.81]$$

[3] If $m + 2 > 0$:

$$w \approx \left[\frac{[m + 2]\,[m + n + 1]}{[n - 1]^2}\right]^{\frac{1}{n-1}} y^{-\frac{m+2}{n-1}}\ \phi^{-\frac{2}{n-1}} \qquad [6.82]$$

Most of the practical systems follow Equation [6.81]:

The effectiveness factor for the pellet can now be calculated as

$$\eta = \frac{1}{\phi^2}\left.\frac{d\,w}{d\,y}\right|_{y=1} = \frac{1}{\phi^2}\left[a_2^n \frac{\phi^2}{m + 1} + 0\,[1]\right] \qquad [6.83]$$

where a_2 can be found from the equation

$$\frac{a_2^n\ \phi^2}{[m + 1]\,[m + 2]}\,[1 + 0\,(1)] + a_2 - 1 = 0 \qquad [6.84]$$

The asymptotic expression for the case of a general order reaction with uniform catalyst activity can be used to study the effect of various other activity profiles. The result can be expressed as the ratio

$$\frac{\eta_{\text{nonuniform}}}{\eta_{\text{uniform}}} = -\frac{3}{m + 1} = \frac{3}{\alpha + 3} \qquad [6.85]$$

Equation [6.85] shows that with increase in the exponent α

the effectiveness factor for nonuniform catalyst decreases, i.e. concentrating the activity in the exterior shell of the catalyst weakens the resistance to deactivation.

6.4.2 Self fouling reactions

The conservation equations for a self deactivating general order reaction A → B → C can be written in dimensionless form with the boundary conditions as

$$\left.\begin{aligned} &\frac{d^2 w_A}{d y^2} - \phi_A^2 \; y^m \, [1 - w_c] \, w_A^n = 0 \\ &\frac{d^2 w_B}{d y^2} - \phi_A^2 \; y^m \, [1 - w_c] \, w_A^n = 0 \\ &\frac{d^2 w_c}{d \theta} - y^m \, [1 - w_c] \, w_B = 0 \end{aligned}\right\} \qquad [6.86]$$

$$\left.\begin{aligned} &\frac{d w_A}{d y} = \frac{d w_B}{d y} = 0, \quad y \rightarrow \alpha \\ &w_A = 1, \quad w_B = 0, \quad y = 1 \\ &w_c = 0, \quad \theta = 0 \end{aligned}\right\} \qquad [6.87]$$

Equation [6.86] can be solved subject to boundary conditions [6.87] for large values of α $[\alpha > 0]$, when w_c can be assumed to be independent of the distance parameter to give

$$w_A = a_2 + \frac{\phi_s^2 \, a_2^n \, y^{m+2}}{[m+1]\,[m+2]} \Big[1 + O\,[1]\Big]$$

$$w_B = 1 - w_A \qquad [6.88]$$

and

$$[1 - w_c] = \exp\left[- \frac{2 + \alpha}{[\alpha - 1]\,[1 + 2\alpha]} \; \frac{[1 - a_2]}{Y} \; \theta\right]$$

where $$\phi_s = \phi\sqrt{1 - w_c} \qquad [6.89]$$

Since α is always a positive quantity, $[1 - w_c]$ decreases with time θ.

The effectiveness factor for the system can be defined as

$$\eta = \frac{a_2^n}{m+1} \; \exp\left[- \frac{2 + \alpha}{[\alpha - 1]\,[1 + 2\alpha]} \; \frac{1 - a_2}{Y} \; \theta\right] \qquad [6.90]$$

The following relationship between the effectiveness factors for nonuniform and uniform activity can be readily written:

$$\frac{\eta_{\text{nonuniform}}}{\eta_{\text{uniform}}} = \left\{ \exp\left(\frac{1 - a_2}{Y}\right)\theta \; \left[2 - \frac{2 + \alpha}{[\alpha - 1]\,[1 + 2\alpha]}\right]\right\}$$

$$[6.91]$$

As the value of α increases, the effectiveness factor with nonuniform catalyst activity decreases, indicating again that ~~with~~ the resistance to deactivation is minimised by increasing α.

The conclusion that the resistance to deactivation is minimised by concentrating the activity in the exterior shell of the catalyst is thus verified for the case of a general order reaction. The expressions developed earlier were restricted to the first order reaction system and this analysis extends the validity to a general order scheme.

Table 6.1

Carbon, reactant and temperature profiles in a nonisothermal [adiabatic] fixed bed reactor with deactivation

Profile	Solution	Remarks
1	2	3
Carbon	$w_c\,[0,\,t_D] = [2\,f_B\,k^o_{v2}\,y_{Ao}\,t_D]^{1/2}$	
	$w_c\,[z',\,t_D] = \dfrac{w_c\,[0,\,t_D]}{M_R\,t_D\,y_{Ao}}\left[\dfrac{w_c\,[1,\,t_D]}{w_c\,[0,\,t_D]}\,M_R\,t_D\,y_{Ao} + p\,z' + p\,M_R\,t_D\,y_{Ao}\log z' - p\right]$	For large values of z'
	$w_c\,[z',\,t_D] = \dfrac{w_c\,[0,\,t_D]}{M_R\,t_D\,y_{Ao}}\left[C\,z'^{-p} + \dfrac{p\,z'}{p+1} - M_R\,t_D\,y_{Ao}\right]$	For small values of z'
	where $p = -\dfrac{M_1\,M_R\,t_D\,k^o_{v1}\,y_{Ao}}{w_c\,[0,\,t_D]}$, and $M_R = \dfrac{M_2\,E}{M_1\,R_g\,T_o^2}$	

1	2	3
Reactant	$\frac{y_A [z', t_D]}{y_{Ao}} = \frac{1}{M_R\, t_D\, y_{Ao}} \left[\frac{w_c [1, t_D]}{w_c [0, t_D]}\, M_R\, t_D\, y_{Ao} + p\, z' \right.$	For large value of z'
	$\left. + p\, M_R\, t_D\, y_{Ao} \log z' - p \right]$	
	$= \frac{1}{M_R\, t_D\, y_{Ao}} \left[L^p \left(M_R\, t_D\, y_{Ao} - \frac{p\, L}{p+1} \right) z'^{-p} \right.$	
	$\left. + \frac{p\, z'}{p+1} - M_R\, t_D\, y_{Ao} \right]$	For small values of z'
Temperature	$T [z', t_D] = T_o - \frac{M_2}{M_1} \left(\frac{t_D}{z'} \right) y_{Ao} \left(\frac{y_A}{y_{Ao}} - 1 \right)$	
	$T_M = T_o + \frac{M_2}{M_1}\, \frac{t_D\, y_{Ao}}{1} \left[\frac{2\, M_R\, t_D\, y_{Ao}}{[1+p]} + \frac{1}{L^p\, [M_R\, t_D\, y_{Ao} - \frac{p\, L}{p+1}]} \right]^{1/p} \left(\frac{y_A}{y_{Ao}} - 1 \right)$	Maximum temperature

1	2	3
	$z'_M = \frac{2\, M_R\, t_D\, y_{Ao}}{[1 + p]} \left[\frac{1}{L^p \left(M_R\, t_D\, y_{Ao} - \frac{p\, L}{p + 1} \right)} \right]^{-1/p}$	The distance at which maximum in temperature occurs

NOTATION

a_o, a_p	initial and poisoned area, cm^2
Aw	area poisoned per mole of poison, cm^2/g mole
b	particle diameter, cm
C_A, C_B	concentration of A and B species, g mole/cm^3
C_f	concentration of fluid, g mole/cm^3
C_s	concentration in the solid, g mole/cm^3
D_a	Damkohler number
D_e	effective diffusivity, cm^2/sec
D_f	diffusivity in fluid phase, cm^2/sec
f_B	void fractions
F	hypergeometric series
G	mass flow rate, g/sec
k_{v1}, k_{v2}, k_{v3}	volume based rate constants, sec^{-1}
k_1, k_2, k_3	surface rate constants, cm/sec
m,n	orders of reactions
Pe_f	fluid Peclet number
p	dimensionless radial parameter
R[c]	rate of reactions
r_s	radial parameter for solid phase, cm
r_t	radial parameter of reactor, cm

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s	dimensionless parameter defined by Equation [6.47]
S	selectivity defined by Equation [6.70]
v	dimensionless concentration in the solid phase
w_c	dimensionless carbon concentration
y	dimensionless concentration in fluid phase
x	dimensionless axial distance parameter
z	distance parameter, cm
X'	defined by Equation [6.61]

Greek symbols

μ and τ	defined by Equation [6.41]
ϕ	Thiele modulus
η	effectiveness factor
ξ	dimensionless radial parameter in solid
ψ	defined by Equation [6.49]
δ	defined by Equation [6.65]
Γ	$\frac{j \pi Pb}{R}$

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APPENDIX - A

APPLICATION OF THE KINETIC BOUNDARY CONDITION TO DECOURSEY'S PROBLEM [1974]

Consider the case of absorption of gas A in a liquid B, where an irreversible reaction $A + z\,B \rightarrow Y\,P$ takes place. This problem has been analysed by Decoursey, using the conventional boundary conditions, in the light of Danckwerts theory. Using the kinetic boundary condition at the interface and following Decoursey [1974] the following equations can be written:

$$D_A \frac{\partial^2 \mu}{\partial x^2} - \frac{\partial \mu}{\partial t} = 0 \qquad [A.1]$$

$$t = 0, \quad x > 0, \quad \mu = \mu_o = B_o - z\,A_o \qquad [A.2]$$

$$t > 0, \quad x = \alpha, \quad \mu = \mu_o \qquad [A.3]$$

$$t > 0, \quad x = 0, \quad A = A_i, \quad \frac{d\,u}{d\,x} = \frac{k_s\,A_i\,B_i}{D_B} - z\,\frac{d\,A}{d\,x} \qquad [A.4]$$

$$\mu = B - z\,A \qquad [A.5]$$

The solution to this equation can be obtained as

$$\bar{\mu} = \mu_o \left[E\,[A_i - A_o] + \frac{k_s}{k_L}\,\frac{D_A}{D_B}\,A_i\,\bar{B}_i \right] \exp\left(-\,\frac{x\,k_L}{D_A}\right) \qquad [A.6]$$

where bar denotes the Lapkke transformed quantity.

Equation [A.6] evaluated at the interface can be rearranged using the equality

$$\frac{B_o}{z\,A_i} = E_a - 1 \qquad [A.7]$$

to give

$$\frac{\overline{B}_i}{B_o} = \frac{1}{1 + \frac{k_s}{k_L}\,\frac{D_A}{D_B}\,A_i \exp\left(-\,\frac{x\,k_L}{D_A}\right)}\left[1 - \frac{z\,A_o}{B_o}\left[1 - \frac{E}{z}\exp\left(-\,\frac{x\,k_L}{D_A}\right)\right]\right.$$

$$\left. + \frac{1}{E_a - 1}\left[1 - \frac{E}{z}\,\exp\left(-\,\frac{x\,k_L}{D_A}\right)\right]\right] \qquad [A.8]$$

Expressing the concentration of B in the film as $\frac{\overline{B}_i}{B_o}\,B_o$, the enhancement factor is obtained as

$$E = \left[1 + M\,\frac{\overline{B}_i}{B_o}\right]^{1/2} \qquad [A.9]$$

which can be rearranged to give

$$E = \left\{1 + \frac{M}{\emptyset\,r\exp[-sh]}\left[1 - \frac{z\,A_o}{B_o}\left(1 - \frac{E}{z}\,\exp[-sh]\right)\right.\right.$$

$$\left.\left. + \frac{1}{E_a - 1}\left(1 - \frac{E}{z}\,\exp[-sh]\right)\right]\right\}^{1/2} \qquad [A.10]$$

For $sh \to \alpha$, this equation reduces to

$$E = \left[1 + M\left(\frac{E_a - E}{E_a - 1}\right)\right]^{1/2} \qquad [A.11]$$

which is the equation obtained by Decoursey [1974].

APPENDIX B

APPLICATION OF THE LIE THEORY TO THE SOLUTION OF NONLINEAR EQUATIONS

The equation

$$\frac{d^2 w}{d x^2} + \frac{2}{x} \frac{d w}{d x} - \phi^2 w^n = 0 \qquad [B.1]$$

represents a number of physical situations occurring in chemical engineering. An analytical solution to Equation [B.1] can be given for a simple first order reaction. For a nonlinear reaction source term, analytical solution to Equation [B.1] is not possible and hence numerical evaluation becomes necessary. Equation [B.1] is an ordinary nonlinear differential equation which can be reduced to a different form of the first order equation. In the event the first order differential equation cannot be solved in terms of the elementary functions, which is frequently the case, its direction field can be sketched in the phase plane and qualitative information about the solutions can be obtained from the study of the singularities and integral curves of these first order differential equations. In the phase plane analysis, particularly useful for autonomous differential equations, the dependent variable and its first derivative are used as coordinates. The independent variable does not appear explicitly. The phase plane however loses much of its importance when the equation studied is not autonomous. We employ here an alternative method based on the Lie theory of one parameter group.

This method is based on the fact that when an invarient u and a first differential invariant v are substituted in the original nonlinear equation, the resulting equation in u and v is first order. The invariant v of the group is a function of [w, x], and the first differential invariant v, a function of [w, w' and x]. The invariant u and the first differential invariant v are tabulated for systems of differential equations [Cohen, 1971] and for the Equation under consideration can be obtained as

$$u = [x]^{-2/1-n} w$$
$$v = [x]^{n+1/n-1} \frac{d w}{d x} \qquad [B.2]$$

Differentiating Equation [B.2] and dividing one by the other gives

$$\frac{d v}{d u} = \frac{\frac{n+1}{n-1} [x]^{2/n-1} \frac{d w}{d x} + [x]^{\frac{n+1}{n-1}} \frac{d^2 w}{d x^2}}{\frac{2}{n-1} [x]^{n-3/1-n} w + [x]^{-2/1-n} \frac{d w}{d x}} \qquad [B.3]$$

Substituting for $\frac{d^2 w}{d x^2}$ from Equation [B.1], Equation [B.3] can be rearranged as

$$\frac{d v}{d u} = \frac{3-n}{2} \left[\frac{v + \frac{n-1}{3-n} \phi^2 u^n}{u + \frac{n-1}{2} v} \right] = \frac{f_1 [u,v]}{f_2 [u,v]} \qquad [B.4]$$

Equation [B.4] is a first order differential equation and can be plotted in the u v plane. We search for all the points through which the trajectories will have the same slope. If this slope is s then

$$\frac{3-n}{2}\left[\frac{v+\frac{n-1}{3-n}\,\phi^2 u^n}{u+\frac{n-1}{2}\,v}\right] = s \qquad [B.5]$$

represents all points at which the slope should be s. The integral curves can then be drawn on a $u\,v$ plane. For specific values of n, it is sometimes possible to integrate Equation [B.4] analytically and an explicit relationship can be obtained between the dependent and independent variables.

For $n = 2$, Equation [B.2] can be written as

$$\frac{v}{u^{3/2}} = \frac{d\,w/d\,x}{w^{3/2}} = w^{-3/2}\,\frac{d\,w}{d\,x} \qquad [B.6]$$

The term $[w/u^{3/2}]$ can be treated as constant, in the neighbourhood of a singularity and thus can be integrated to give after some manipulation

$$v = 2\,u \qquad [B.7]$$

Equation [B.4] can now be simplified to give

$$6\,x^4\,w^2 - 2\,\phi^2\,x^6\,w^3 + 3\,x^6\left(\frac{d\,w}{d\,x}\right)^2 = b \qquad [B.8]$$

where b is a constant of integration. For finite values of b, as $x \to 0$, all the terms in Equation [B.8] cannot vanish and no matter which term we choose the relation $w = x^{-2}$ holds as $x \to 0$. Thus

$$u = x^2 y = \text{constant} \quad \text{as} \quad x \to 0$$

and the value of u can be obtained from Equation [B.8] as

$$[18 - 2\phi^2 u]\, u^2 = b \qquad [B.9]$$

In the case when analytical integration of Equation [B.4] is not possible, qualitative information like Equation [B.9] can be obtained to aid the analysis.

Alternatively Equation [B.4] can be transformed into a more suitable form by using the transformations

$$Y = \frac{u\, dw/dx}{x\, w^2} \quad , \quad X = \frac{v}{x^2\, w} \qquad [B.10]$$

as

$$\frac{dY}{dX} = \frac{Y}{X}\, \frac{3 + nX - \phi^2 Y}{\phi^2 Y - 1 - X} = \frac{Y}{X}\, \frac{aX + bY + C}{a'X + b'Y + C'} \qquad [B.11]$$

Equation [B.11] is of the standard type studied by Poincare and has been discussed by Jones [1953].

The singular points for $n = 2$, can be obtained as

$x = 0,\ w = 0$ Saddle [-1]

$x = 0,\ w = 3/\phi^2$ Saddle [-1]

$x = -1,\ w = 0$ Node [+1]

$$\left.\begin{aligned} x &= -\frac{2\phi^2}{[2\phi^2 + 3]} \\ w &= -\frac{5}{[2\phi^2 + 3]} \end{aligned}\right\} \quad \text{Saddle } [-1]$$

$x = \alpha, \quad w/x = 0 \qquad \text{Node } [+1]$

$x = \alpha, \quad w/x = 3/2\,\phi^2 \qquad \text{Node } [+1]$

$x/w = 0, \quad w = 0 \qquad \text{Node } [+1]$

When, for a particular value of n, all the singularities are determined the integral curves can be sketched relatively easily and qualitative information like the oscillatory nature of the solution, their stability, asymptotic limits, roots and singularities, can be obtained.

For specific values of n and ϕ these curves can be traced following the method described by Jones [1953].

The application of the Lie theory of one parameter group is demonstrated here to the solution of a general equation which describes a number of physical situations in chemical engineering.

Jones, P. C., Proc. Roy. Soc., 'A', <u>212</u>, 327 [1953].