MODEL REDUCTION OF FIXED BED

CATALYTIC REACTORS.

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in

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by

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under the direction of

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ABSTRACT

With the increasing demand for optimal control and operation of plant, in particular chemical reactors, the need for detailed models which can be solved by computer in a reasonable time is apparent. Clearly, since the model is used repeatedly in each iteration of the computation, this will normally mean that it must be relatively simple. Unfortunately, this results in loss of detailnecessary to take full advantage of the optimisation.

A technique for model reduction, suitable for the two-dimensional heterogeneous catalytic reactor has been developed, which results in substantial reduction in dimensionality of the system, but which retains the essential detail. A general reaction scheme with first order kinetics has been considered. Furthermore, it is possible to relate the well defined physical parameters, e.g. transport coefficients and rate constants, etc. to the parameters in the reduced model. Significant savings in computation time are made which makes it feasible to use the reduced model in optimisation and control schemes.

ACKNOWLEDGMENTS.

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A plausible impossibility is always preferable to an

inconvincing possibility.

ARISTOTLE. (384 - 322 BC)

"Contrariwise," continued Tweedledee, "if it was so, it might be; and if it were so, it would be; but as it isn't, it ain't. Thats logic."

Through the looking glass. LEWIS CARROLL.

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1. Relation of the thesis to the work of the Leeds fixed bed reactor group.

The principle aim of the group, under the supervision of Dr. C. McGreavy, is the computer control of a fixed bed catalytic reactor in which strongly exothermic reactions, such as the partial oxidation of benzene to maleic anhydride, are occurring. The group is split up into three sections, (1) practical experimental work to derive the physical data for the system, i.e. for heat and mass transfer and chemical kinetics, and to build and operate the pilot reactor; (2) the development of optimisation methods and automatic control schemes for the reactor, directed towards optimal design and operation of the pilot reactor through a computer; (3) the development of mathematical models which can reliably predict the performance of the reactor in real time situations in order that they may be included in the optimisation and control algorithms. This thesis is concerned with the latter section which is now considered in more detail.

Both Cresswell[27] and Thornton[35], in this Department, developed methods of modelling the fixed bed reactor, for simple and complex reaction schemes respectively, and identified the minimum degree of complexity called for in the model. Although the mathematical models generate an adequate prediction of performance and description of the system, the computation times are excessive with respect to practical optimisation and control studies. It was therefore necessary that a method should be developed which would produce models with a radically reduced computation time which replaced the original complex models. This introduced the concept of simplifying the models while retaining the essential detail in terms of physically identifiable properties, and is referred to as model reduction.

The development of these techniques forms the basis of the work presented in this thesis, and applies specifically to the fixed bed reactor.

2. Recommendations for future work.

This study has been restricted to the steady state and has considered only first order kinetic systems. In order to render the work more practically applicable, model reduction must be applied to non-first order and non-integer order kinetic system to determine whether or not the reduced model and its associated profiles and pseudo-parameters maintain their same general form.

As control studies are associated with the unsteady state, it will also be necessary to apply the technique to the unsteady state models. One approach could consider the fact that the unsteady state can be represented by a series of pseudo-steady states; or another possibility the capacitance effects on the form of the profiles and pseudo-parameters.

Another possible objective is to further reduce the steady state model to a completely algebraic system by considering the various limiting conditions of the model; and a consideration which has not yet been made is the problem of applying the model of a single tube to a multi-tubular environment for which the extra-tubular conditions are a function of the position in the overall reactor.

Model reduction has been formally defined and specifically applied

to the fixed bed reactor, although it is the author's opinion

that the techniques could be applied to any distributed system.

CHAPTER 1

INTRODUCTION

To meet the increasing demand for the optimal control and operation of fixed bed reactors, detailed mathematical models are required which can be solved by computer in a reasonable time. The model should be as comprehensive as possible and based on a mathematical interpretation of the physical processes taking place. This will result in all the model parameters being physically identifiable and capable of independent measurement or an estimation from accepted correlations.

The level of sophistication demanded of the model will usually depend on the context of the problem, eg. design, optimisation and/or control, and should be consistent with its desired objectives. For example, if it is to be used in an optimisation algorithm, it must predict the performance of the reactor more accurately than the expected improvement and accommodate all the problem constraints.

1.1 Development of the Fixed Bed Reator Model.

Consider the fixed bed reactor in more detail. The reactor normally consists of a number of cylindrical tubes packed with catalyst particles with the gaseous reactants passing through the tubes. Many of the chemical reactions which occur in equipment of this type are associated with large heats of reaction. In order to retain control of the reactor and to prevent irreversible damage to the catalyst, external cooling around the tubes is utilised. In such a situation radial temperature gradients exist (i.e. perpendicular to the direction of reactant flow), in

addition to the axial gradient due to convective flow.
Therefore, the mathematical model for a non-isothermal reactor
would be expected to be at least two-dimensional. However, the
design of fixed bed reactors has generally been based on a one
dimensional model, for which gradients are assumed to occur only
in the axial direction, and the radial transport of heat and mass
in the reactor assumed to be unimportant, i.e. the resistance to
heat transfer being effectively lumped at the tube wall. In
fact, substantial radial temperature gradients and, consequently,
concentration gradients can occur which have an appreciable
effect on the overall predicted performance of the reactor.

With the advent of high speed computers, it has become
possible to consider models of a greater complexity than the one-
dimensional system, so that more reliable predictions of the
performance can be made. Froment [1] has considered a quasi-
homogeneous two-dimensional model in which he assumed radial
transport occurs by effective diffusive and conductive processes.
Axial diffusion of heat and mass can generally be neglected for
the normal high rates of throughput experienced in a practical
reactor. The effective radial diffusivity and conductivity of
the fixed bed can be easily determined from correlations of Peclet
numbers for mass and heat transfer respectively and Reynold's
number, and for the normal turbulent conditions the Peclet numbers
are essentially constant. But, although Froment dealt
extensively with the global transport phenomena he made no
attempt to distinguish between the reacting fluid and solid
catalyst phases, i.e. resulting from the assumption of a quasi-
homogeneous system. Such models which take no account of the

potential rate controlling mechanisms such as fluid film and particulate heat and mass transfer, are characterised by a susceptability to temperature 'run-away', which often occurs near to the practical operating region of the reactor, i.e. reactors normally operate in a region in which the rate of reaction and particulate modes of heat and mass transfer are comparable. Unfortunately, inclusion of all the additional physical processes produces an almost intractable problem from the point of view of obtaining a solution in a time sufficiently short for routine design and optimisation studies. Extensive studies have been carried out in order to represent the overall rate of reaction occuring inside the catalyst pellets in terms of the fluid field observables [2-13], and normally the results are expressed in terms of an effectiveness factor. It has been the practice to assume the surface temperature and concentration of the catalyst pellet are equal to those of the gas stream. Except in the case of the method given by Petersen [11], the effort involved in solving the equations is equivalent to the numerical solution of the fully distributed problem. However, Petersen's solution is an asymptotic expression which has limited application for general problems. Recently McGreavy and Cresswell [14], have reduced the distributed parameter intra-particle field equations to an algebraic lumped parameter form. The result is an expression for the effectiveness factor with a definition which is based on observables in the bulk fluid phase in the presence of inter-phase as well as intra-phase heat and mass transfer resistances. All evidence seems to indicate that the overall rate process is dominated by mass transfer, resulting from high

film resistance to heat transfer, and the particle essentially operates at isothermal conditions, although the temperature is not that of the fluid. So far only a simple first order irreversible reaction has been considered, but McGreavy and Thornton [15] have extended the above treatment to more complex reaction schemes which in general are more practically applicable.

At this point it may be advantageous to the reader to be familiar with the relation computing times of the various types of steady state model. The three types are, (1) the fully distributed model which takes account of all transport phenomena in the reactor and the catalyst pellet, (2) the two-dimensional reactor model which uses the isothermal pellet approximation for the effectiveness factor and (3) the corresponding one-dimensional model. The relative computing times for (1) : (2) : (3) are 720 : 20 : 1. The time for the most complex model is approximately three hours on an I.C.L. K.D.F.9 computer, programming in Algol 60. It may be noted that a transient state model can be considered as a series of steady states, from which it can be easily seen that both models (1) and (2) would be computationally intractable especially when considering real time situations.

1.2 The Necessity for Model Reduction.

In the above terms adequate models for the fixed bed catalytic reactor are available which fulfill the constraints of accuracy, general reliability and description as discussed at the beginning of this chapter. They are essentially two dimensional and direct simplification to a one-dimensional system is not generally acceptable, because of the important effects of the radial gradients. This generally means that dynamic reactor

studies cannot be made as the resulting three-dimensional model is intractable. Further, the steady state two-dimensional model is not suitable for optimisation studies etc., because of the iterative nature of the procedure which becomes computationally excessive. In order to avoid this difficulty most workers [16-20] have made gross simplifying assumptions and considered special cases in order to justify the use of a one-dimensional model, by assuming that the radial gradients are flat. No-one has made any attempt at rational analysis to take account of the effect of the radial gradients in the one-dimensional model except Shah [21] who used an approach which was a compromise between the exact solution of the model equations and a completely arbitrary regression-type model. Although the formulation of the model is empirical, it is based on the asymptotic behaviour of the basic differential equations of the physical system. This approach along with the statistical methods employed in developing regression models are not generally applicable and the results cannot be extrapolated.

It is obvious that some method is required to produce a less computationally demanding procedure which has a general applicability and bears all the features of the fully distributed model. There are several alternatives of approach which can be adopted. (i) A statistical approach has already been rejected, and normally assumes the existence of an operational plant. (ii) A method which would increase the efficiency of the numerical technique used to solve the two-dimensional model. This is not really feasible as the existing methods are restricted by the non-linear nature of the model. Simplifying the

numerical methods would lead to unreliable solutions.   (iii) A

lumped parameter approach which accounts for the existence of the

radial gradients would favourably improve the existing one-

dimensional models, but knowledge of the radial gradients is lost;

and as, for example, the temperature at the tube axis is a

parameter necessary for control and optimisation of the reactor,

the lumped parameter model would have limited application.

However, it is to be noted that substantial reduction of

computational load of a model is generally coupled with reduction

of the dimensionality.

Therefore a technique is required which will both reduce the

dimensionality of the model and retain some knowledge of the

behaviour of the radial profile.   A satisfactory method has

already been outlined by McGreavy and Turner [22] which is

suitable for a fixed bed reactor in which a simple first order

irreversible reaction is taking place.

1.3 Research Objectives

Until now, no attempt has been made to develop a generally

applicable and reliable reduced model of the fixed bed reactor.

The analysis entails examining the solutions of the exact

distributed model for reaction schemes of increasing complexity,

and to decide upon a reliable lumped parameter approach to reduce

the dimensionality of the reactor model.   A second and coupled

objective is to develop solutions for the radial profiles of

temperature and concentration which are related to the original

reactor model in their application and have a sufficiently simple

form for easy manipulation to minimise the computation time.

Overall, the reduced model replaces the original model rather

than becomes an approximation to it.

(NOTE: This work has been restricted to the steady state and to first order reaction systems, then in order that the generality of the approach be extended (i) non-integer and second order reactions must be considered, and (ii) an analysis of the unsteady state must be made by future work in the new field of model reduction.)

CHAPTER 2

DETAILED OBJECTIVES AND PHILOSOPHY OF MODEL REDUCTION

2.1 Definition of Model Reduction

In order to know what is implied by model reduction, it is necessary to define a mathematical model. While it may be intuitively obvious to see how it has relevance to the problems in which it will be used, it is both convenient and necessary to have a formal definition. For the purpose of this thesis, a mathematical model will be regarded as a set of mathematical equations, describing all essential characteristics quantitatively, while using parameters which relate to the physically identifiable phenomena which characterise the process. Generally the model cannot be solved analytically, but making use of high speed computers, numerical solutions are feasible. For example, if the model is in the form of a set of differential equations, efficient finite difference techniques are available. Invariably the computational load of the solution of the model is prohibitive for use in optimisation and control algorithms, so that some method is needed which will reduce the computing time, eg. a less complex form of the model which can be solved more quickly. It is this phase which may be referred to as model reduction. It is a procedure which attempts to substantially reduce the time of computation of the process model, whilst retaining the features described above, namely, those of accuracy and description and still making use of the physical parameters if only implicitly. Consider as an example the use of a reduced model in an optimisation algorithm. It should be capable of predicting the

performance more accurately than the expected improvement and at the same time describe the process adequately in order that all the relevant constraints may be applied. This must be possible without the repeated use of the algorithm being a limitation with respect to computation time. A similar criterion also applies for use of reduced models in control and design algorithms. It is to be expected that reduction of computational load will generally be related to a reduction in the dimensionality of the model.

2.2 The General Approach.

Suppose we have a mathematical model of some process which exhibits all the essential features described above, but which is computationally time consuming. Even if an analytical solution exists for the model, it does not necessarily follow that it is quicker to evaluate the resulting analytic expression, than to solve the original model equation by a numerical method. For example, this is often true where a series solution may not be rapidly convergent, as in the case of the transient fixed bed heat exchanger model [23], for which the analytical solution model is very complex. The evaluation of the solution requires more computational effort than the numerical solution of the original model. In both cases the computation time is excessive. Where it is feasible, the most direct way of overcoming the difficulties is to reduce the dimensionality of the model.

2.3 Generalised Reduction.

As noted, the first stage is to reduce the dimensionality of the model. The most convenient method is to 'lump' the effects

in one or more dimensions. Choice of the dimensions will depend

on the characteristics of the process, and the method of condensing

the dimensions will depend on the most useful form of the result.

The reduced model must be described by terms which may necessitate

the definition of certain pseudo-parameters in the resulting

equations.

In lumping distributed variables some of the original

constraints of the model are usually violated. Normally some

loss of description of the model results from such simplification

and many of the new model pseudo-parameters will not relate to

physically identifiable phenomena. Compensation for these

violations can be made by suitable analysis of the original model

by obtaining solutions to each of the model dimensions. The

pseudo-parameters should be expressed in terms of the reduced

model by carrying out numerical simulations on the original model

over the practical operating range.

Special cases which may occur must be avoided, by taking care

in the choice of data. Sensitivity tests must be carried out on

parameters so that the resulting expressions are valid over the

practical operating region of the process. Although such a

rigorous analysis is tedious, it need only be carried out once for

a particular type of process. Modification of the reduced model

for a process of the same general type need only mean

reassessment of coefficients in a solution, the structure of which

is already known.

2.4 Regeneration of Description.

In regenerating the detailed description of the original

model, it is necessary to examine the constraints, since in solving the original model to provide the required description, some redundant information will be produced. For example, the case often arises that the complete solution along a dimension is produced because of the structure of the numerical method used to solve the complex model, when in fact only a part of the solution is required. Therefore an extra bonus in reduction of computing time can be gained by providing the minimum of information for solving the model.

To regenerate the physical detail, the reduced model, solutions must be constructed for the dimensions which have been eliminated. The structure of these solutions is restricted in order to comply with the general philosophy of model reduction. As stated above, the solutions must be generally applicable over the whole of the practical operating range. They should be of the simplest algebraic form possible for ease of manipulation and to minimise the computing time. For example, in a computational procedure it is less time consuming to calculate terms to an integer power than a non-integer power, i.e. x^2 may be expressed as $x \times x$ which is one operation but $x^{1.3}$ is evaluated from $1.3 \log x$ and subsequently determining the antilog. Each operation requires the summation of a series. Therefore, in order to minimise computational effect it would be better to consider integral powers only.

Over a practical range of the model parameters, the solutions are examined for the relevant dimensions to gain some insight as to their basic structural properties for the proposing suitable

algebraic expressions.

This particular aspect of the numerical approach belongs to the same class of methods as Galerkin and collocation, and in particular to the more recently developed technique of cubic splines [36], for two point boundary value problems for ordinary differential equations.

The Galerkin and collocation [31] methods represent the solution for the dependent variable, Θ by a finite sum of trial functions Ω_i,

$$\Theta \sim \Theta^{(m)} = \sum_{i=1}^{m} a_i^{(m)} \Omega_i + \Omega_0 \qquad 2.00$$

For a problem of dimension P, the $a_i^{(m)}$ are constants or functions of 1, 2, ... P-1 of the independent variables, depending on the number of independent variables that are included in the functions Ω_i. For parabolic partial differential equations the usual choice is to let the $a_i^{(m)}$ be functions of one independent variable and the Ω_i be functions of the remaining independent variables. The method which is used represents a solution for the dependent variable Θ by,

$$\Theta \sim \Theta^{(m)} = \Omega_0 \prod_{i=1}^{m} (a_i^{(m)} \Omega_i + 1) \qquad 2.01$$

which can be satisfied by definition of Ω_{i+1} of the form,

$$a_{i+1}^{(m)} \Omega_{i+1} = \left\{ \frac{\Theta - \Theta^{(i)}}{\Theta^{(i)}} \right\} \qquad 2.02$$

where $\Theta^{(i)}$ is the i-th order approximation to Θ. If the problem is of dimension P , then the $a_i^{(m)}$ are constants or functions of (P-1) of the independent variables, or alternatively, a function of the dependent variables and system coefficients.

The trial function, Ω_o is the first approximation to Θ, and fulfills the boundary conditions in the dimension considered. Therefore the first derivatives of the Ω_i at the boundary limits are consequently zero. The Ω_i are functions of the independent variable in the dimension being considered. Normally, it will be expected that the $a_i^{(m)} \Omega_i$ will be small and the integer $i \leqslant 2$.

The basic difference between the proposed method and the method of orthogonal collocation is that the latter is merely an alternative numerical method of solution to the finite difference methods (eg. Crank – Nicolson [33]), whereas the former produces a generally applicable reduced model. Both methods are superficially similar, they propose the use of trial functions which satisfy the boundary conditions and ultimately both require the solution of a set of simultaneous ordinary differential equations. But, for the case of orthogonal collocation an ordinary differential equation must be solved along the principal dimension at each collocation point, whereas there is only one for the reduced method. Hence the comparison of computation times will depend on the number of collocation points used. The use of only one collocation point effectively produces a lumped parameter system with a resultant loss of description. In addition, the coefficients used in the collocation method are arbitrary whereas in the reduced method they are related to the physical processes occuring. An outline of the method of orthogonal collocation is given in appendix 4.

2.5 Formulation of the Pseudo-parameters.

There is no general method for the formulation of the

pseudo-parameters in the reduced equations, although some of
the techniques involved are well known   .   Any theoretical
analysis, no matter how coarse, is performed to provide some
information as to the general form of the pseudo-parameter.   The
functional forms (which include the $a_i^{(m)}$) may, for example
represent asymptotic forms which will be established along the
dimension to which the model has been reduced, to be referred to
as the principal dimension.   The gradual transition of the
pseudo-parameter $a_i^{(m)}$ from its initial value, $a_{oi}^{(m)}$ to its
asymptotic form, $a_{ai}(m)$ is represented by a development term along
the principal dimension,

$$a_i^{(m)} = a_{oi}^{(m)} \exp(-b_i^{(m)}) + a_{ai}^{(m)} (1 - \exp(-b_i^{(m)}))\quad 2.03$$

where the $b_i^{(m)}$ are constants or functions of the dependent or
independent variables.

From the coarse analysis, the parametric groups are
determined which it will be necessary to correlate in order to
calculate the constants of the function which describes the
pseudo-parameters.   Additional information is gained by
observing the behaviour of the pseudo-parameter at the limiting
values, so that logical argument may be used to suggest the
functional dependence of these on each system coefficient.   A
detailed analysis is carried out to cover all the model
coefficients, so that the resulting expression is generally
applicable in any practical operating region of the process.
Once this analysis has been completed for the process (or type of
process), it is not necessary to repeat it.

This approach, although not formally developed in this

manner, is often used in the solution of a wide range of
chemical engineering problems for which an analytical solution
does not exist (eg. boundary layer theory, the determination of
pressure drop in a pipe; heat transfer from fluids flowing
through pipes; etc.) For the case of boundary layer theory [24],
arbitrary profiles are assumed but the included coefficients are
not related to the physical parameters of the system.

2.6 Further Simplification of the Reduced Model.

Once a reduced model which is generally applicable, has been
developed, (and in fact replaces the original more complex model)
it may be possible to simplify it even further for ranges of
operation in which some effects become unimportant, thus giving
further savings in computing time.

Normally extensive simplification cannot be made if the
accuracy is to be retained, although, in certain cases an
approximate model could be used during, say, the initial approach
work of an optimisation problem. Then in the region of the
optimum a more sophisticated model is used, resulting in an overall
increase in speed.

The Specific Problem.

So far in the chapter, model reduction has been discussed
with respect to a quite general system. The fixed bed catalytic
reactor in which a highly exothermic reaction is taking place is
a typical case to which model reduction could profitably be
applied. The model is a set of coupled partial differential
equations (see Chapter 4) which contain highly non-linear terms
(i.e. the reaction rate terms due to the Arrhenius rate expression).
There is no analytical solution for the model due to the coupled

non-linear nature of the system. In the succeeding chapters the fixed bed reactor is considered in increasing complexity about which the techniques of model reduction are illustrated and developed. It is convenient to reduce the fixed bed reactor in three stages, firstly considering the fixed bed heat exchanger model (in the next chapter) i.e. a reactor for which there is no heat source. The analysis is subsequently extended to the case of a simple irreversible first order reactor with a heat source and finally more complex reaction schemes are considered. Each stage is used as the first approximation to the next.

CHAPTER 3

REDUCTION OF THE FIXED BED HEAT EXCHANGER MODEL

3.1 Introduction.

The data used for this particular analysis is related to the reactor situations to be considered later and in chapter four a discussion of this choice will be made. The particular set of data about which the conditions are varied is listed in table 3.01. The flow through the reactor is turbulent so that the Peclet numbers for heat and mass transfer can be assumed constant at a value of 10. Froment [16] has shown that the model is not particularly sensitive to this parameter. The inside wall film heat transfer coefficient, h_w is calculated according to Yagi and Wakoa [25], and the composite heat transfer coefficient, U for the whole tube wall is calculated in the normal way. The data available for h_w is not particularly reliable and as in the reactor situation the model is particularly sensitive to its value, the data should be eventually 'trimmed' by comparison of predicted and practical heat exchanger performance.

3.2 The Model

A cylindrical heat exchanger, length L and radius L is considered packed with spherical pellets, radius b. The fluid is assumed to pass through the bed in plug flow and axial dispersion terms are neglected. The modes of heat transfer considered are axial convection and radial conduction. Heat from the bed is transferred through the tube wall to a coolant fluid which is at constant temperature. The model state equation may be written:

Table 3.01

Reactor Data		Heat Transfer Data	
G_o	= 0.449 g/cm.^{2}/sec.	U = 4. 4 x 10^{-2} j./cm.^{2}/sec./$^{\circ}$K	
ρ_f	= 5.68 x 10^{-3} g./cm.^{3}	λ_f = 4.62 x 10^{-2} j./cm./sec./$^{\circ}$K.	
σ_f	= 2.45 j./g./$^{\circ}$K		
e	= 0.4	Dimensionless Groups	
b	= 0.21 cm	Pe_T = 0.84	
B	= 2.1 cm	NU = 2.0	
L	= 125 cm	t_{mo} = 1.18	
T_{mo}	= 590°K		
T_w	= 500°K		

$$- G_o \sigma_f \frac{\partial T}{\partial x} + \lambda \frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial T}{\partial r} \right) = 0 \qquad 3.01$$

where the boundary conditions are,

$$T = f\left(T_{mo}, r\right) \qquad x = 0 \quad 0 \leqslant r \leqslant B$$

$$\frac{\partial T}{\partial r} = 0 \qquad r = 0 \quad 0 \leqslant x \leqslant L \qquad\qquad 3.02$$

$$-\lambda \frac{\partial T}{\partial r} = U\left(T - T_w\right) \quad r = B \quad 0 \leqslant x \leqslant L$$

The model is shown diagramatically in fig. 3.01.

The inlet temperature profile is here expressed as an arbitrary function of the radial mean inlet temperature, T_{mo} and the radial coordinate; a discussion of the inlet profile will be given in section 3.45.

The complete set of model equations are rendered dimensionless
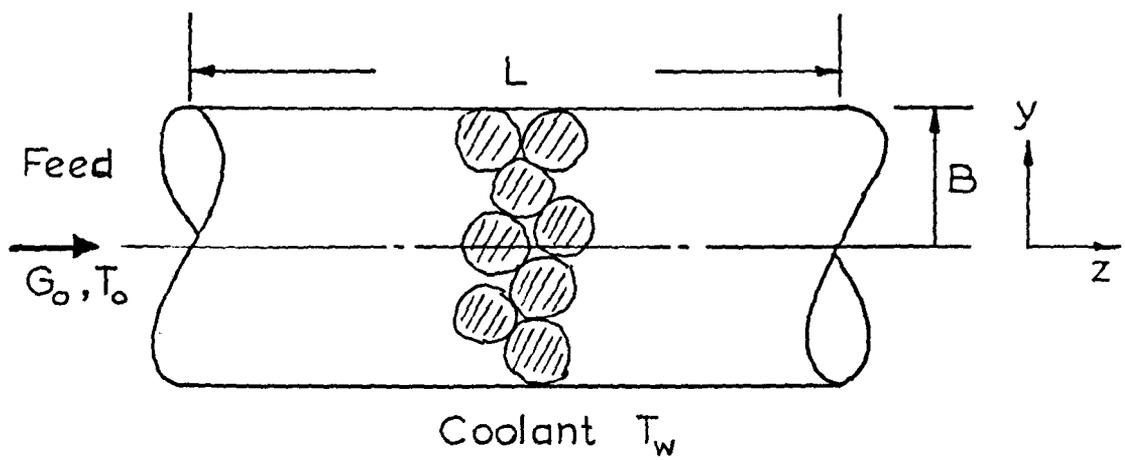
Figure 3.01 . Diagram of the fixed bed heat exchanger.

so that the model is characterised by two dimensionless groups,
Pe_T and NU defined below:

$$- Pe_T \frac{\partial t}{\partial z} - \frac{1}{y} \frac{\partial}{\partial y} \left(y \cdot \frac{\partial t}{\partial y} \right) = 0 \qquad 3.03$$

where the boundary conditions are,

$$t = f (t_{mo}, y) \qquad z = 0 , \quad 0 \leq y \leq 1$$

$$\frac{\partial t}{\partial y} = 0 \qquad y = 0 , \quad 0 \leq z \leq 1 \qquad 3.04$$

$$- \frac{\partial t}{\partial y} = NU (t - 1) \qquad y = 1 , \quad 0 \leq z \leq 1$$

The characteristic groups are defined in the usual way

Effective Peclet number for heat transfer, $Pe_T = \left(\dfrac{Go \, \sigma_f \, B^2}{L} \right)$

fluid Nussalt number $= \left(\dfrac{RU}{\lambda_f} \right)$ $\Bigg]$ 3.06

The remaining dimensionless variables are,

$$t = \frac{T}{Tc} , \quad z = \frac{X}{L} , \quad y = \frac{r}{B} \qquad 3.07$$

Equations 3.03, 4 are usually non-linear and so analytical solution is not possible but they can be conveniently and efficiently solved by a Crank - Nicolson finite difference scheme using the Thomas method for the resulting algebraic equations (see Appendix 2); it is only in very special circumstances that an analytical solution is possible.

3.3 The Analytic Solution.

In those cases where it is possible to solve equations 3.03, 4 analytically, a separable solution is assumed,

$$(t - 1) = Y \cdot Z$$

$$Y = Y (y) \ , \ Z = Z (z) \tag{3.08}$$

By substitution in equation 3.03, and separation of the variables,

equation 3.03 becomes,

$$\frac{Y''}{Y} + \frac{1}{y}\frac{Y'}{Y} = Pe_T \frac{Z'}{Z} = - q^2 \tag{3.09}$$

where q is a constant. The partial differential equation has now

been separated into two ordinary differential equations, which can

be solved analytically [26].

$$y^2 Y'' + y Y' + q^2 y^2 Y = 0 \tag{3.10}$$

$$Z' + \frac{q^2}{Pe_T} Z = 0 \tag{3.11}$$

The combined solution of 3.10, 11 is

$$(1 - t) = 2NU \sum_{n=o}^{\infty} \frac{Jo (\lambda_n y) \cdot e^{-\left(\frac{\lambda_n^2}{Pe_T} z\right)}}{(\lambda_n^2 + NU^2) J_o (\lambda_n)} \tag{3.12}$$

In solving equation 3.10, the inlet temperature profile is assumed

to be flat, i.e. $t_o (y) = t_{mo}$.

3.4 <u>Generalised Reduction of the Model.</u>

The structure of the analytical solution for the heat transfer

model is unsuitable for extension to the reactive case due to the

series nature of the expression. There is no computational

advantage gained in solving the model analytically rather than

numerically as the computing times are similar.

A lumped parameter approach may be used to reduce the model

and the description lost can be regenerated by constructing a

solution in the dimension which is eliminated.

Keeping in mind that the heat exchanger model is to be used as the first approximation for the reactor model with respect to the choice of the principal dimension and the terms in which the reduced model equations are to be expressed, the principal dimension is chosen as the axial direction and the reduced model will be expressed in terms of radial mean values. The radial mean value, Θ_m of a dependent variable $\Theta_{(y)}$ is defined by,

$$\Theta_m = \frac{\int_0^1 \Theta_{(y)} \cdot y \cdot dy}{\int_0^1 y \cdot dy} = 2 \int_0^1 \Theta_{(y)} \cdot y \cdot dy \qquad 3.13$$

Considering the state equation 3.03, multiply each term by $2y \cdot dy$ and integrate over the bed radius.

$$-\int_0^1 2 \, Pe_T \, \frac{\partial t}{\partial z} \cdot y \cdot dy + \left[2y \, \frac{\partial t}{\partial y} \right]_0^1 = 0 \qquad 3.14$$

Assuming that,

$$\int_0^1 2 \, Pe_T \, \frac{\partial t}{\partial z} \, y \, dy = Pe_T \, \frac{d}{dz} \left(\int_0^1 2 \, t \cdot y \cdot dy \right) \qquad 3.15$$

then substituting for the boundary conditions (equations 3.04) in in equation 3.14.

$$- Pe_T \, \frac{dt_m}{dz} - 2NU \, (\, t \, (1) - 1 \,) = 0 \qquad 3.16$$

A pseudo-parameter the effective Nusselt number NU' is defined, such that,

$$NU' = NU \left(\frac{t \, (1) - 1}{t_m - 1} \right) \qquad 3.17$$

The model is now expressed in terms of the radial mean temperature only:

$$Pe_T \ \frac{dt_m}{dz} \ + \ 2NU' \ (\ t_m \ - \ 1 \ ) \ = \ 0 \qquad 3.18$$

It will be shown that NU' is independent of t_m, so that equation 3.18 can be solved analytically.

$$(\ t_m \ - \ 1 \ ) \ = \ (\ t_m \ - \ 1 \ ) \bigg|_{z \ = \ 0} \ e^{- \left(\frac{2 \ NU'}{Pe_T} \right) z} \qquad 3.19$$

In order to evaluate the effective Nusselt number, NU', a knowledge of the radial temperature profile is required.

3.5 The Radial Temperature Profile.

3.5.1 General Analysis.

The radial temperature profile is examined for a practical range of values of Pe_T, NU in order to gain some insight as to its basic general structure for the purpose of suggesting a suitable approximate form. Further information can be derived by inspecting the analytical solution of the model (summarised in section 3.2), that the radial solution is separable from the axial solution, hence it should be possible to base the radial solution on a temperature at a specific radial position; the analytical solution considers the temperature difference between fluid and coolant rather than the absolute value of fluid temperature, and a similar policy will be used here.

3.5.2 The First Approximation

From the above analysis, the radial temperature is assumed to be approximately represented by an even order polynomial function, of which the second degree is taken as a first approximation. By

applying the boundary conditions (equation 3.04) to the function,

$$(t (y)_p - 1) = w_0 + w_1 y + w_2 y^2 \qquad 3.20$$

where $t (y)_p$ is the radial temperature profile given by the approximation, it can be shown that

$$(t (y)_p - 1) = (1 + 0.5 \, NU (1 - y^2)) (t(1) - 1) \qquad 3.21$$

where $t (1)$ is the temperature at the tube wall, obtained by differentiating equation 3.20 with respect to y and substituting for the boundary conditions to evaluate the coefficients w_i.
The function $(t (y)_p - 1)$ represents Ω_0 in equation 2.01.
In the next stage a $a_1^{(m)} \Omega_1$ is considered, where

$$a_1^{(m)} . \Omega_1 = \frac{\Theta - \Theta^{(o)}}{\Theta^{(o)}} \qquad 3.22$$

from equation 2.02, and $\Theta^{(o)}$ is equivalent to Ω_0.

3.5.3 Profile Correction

From equation 3.22 a correction function $f_1 (y)$ is defined by

$$f_1 (y) = \left[\left(\frac{t_{ht} - 1}{t_p - 1} \right) - 1 \right] \qquad 3.23$$

which will be a radially dependent function. Fig. 3.02 shows the typical form of the correction function, which has the boundary conditions,

$$f_1 (1) = 0$$
$$f_1' (o) = f_1' (1) = 0 \qquad 3.24$$

An acceptable functional form for $f_1 (y)$ is,

$$f_1 (y) = w_3 (1 - 3y^2 + 2y^3) \qquad 3.25$$
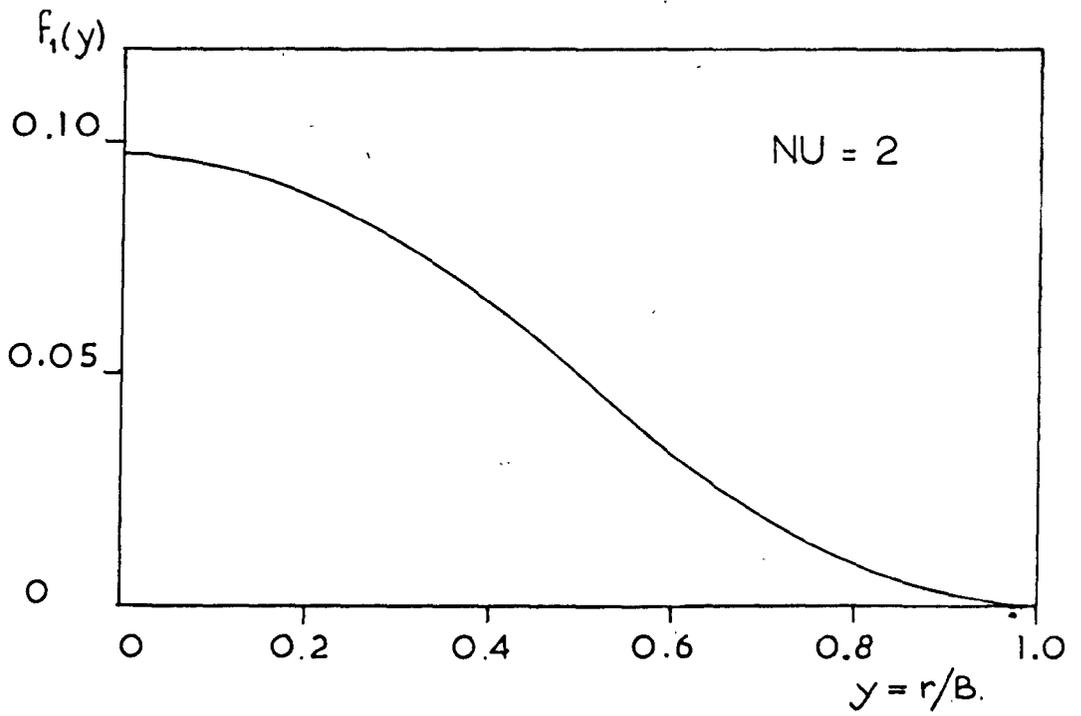
Figure 3.02 . Typical form of the correction function $f_1(y)$

For particular values of Pe_T and NU, irrespective of the form of the inlet temperature profile, the function f_1 (y) tends to an asymptotic form, i.e. the value of f_1 (y) for $o \leqslant y \leqslant 1$ is independent of axial position; therefore w_3 is a function of Pe_T and NU only.

3.5.4 Determination of w_3

By carrying out a sensitivity test, w_3 is found to be independent of Pe_T, and hence is a function only of NU. Fig. 3.03 shows the relationship of w_3 to NU obtained by plotting on logarithmic co-ordinates. From the curve it can be seen that $\lim_{NU \to \infty} W_3 =$ constant and $\lim_{NU \to 0} w_3 =$ constant x NU^2, so that a relationship would be expected of the form,

$$w_3 = \left(\frac{NU}{u_1 \cdot NU + u_2} \right)^2 \qquad \qquad 3.26$$

By expanding equation 3.26 we have,

$$(NU / \sqrt{w_3}) = u_1 NU + u_2$$

then if $(NU / \sqrt{w_3})$ and NU are plotted on cartesian co-ordinates, the result is a straight line, gradient u_1 and intercept u_2, which is demonstrated in figure 3.04, hence w_3 is written,

$$w_3 = \left(\frac{NU}{1.2 \ NU + 4} \right)^2 \qquad \qquad 3.27$$

It is interesting to note the similarity of this coefficient and the coefficient in the analytical solution. (equation 3.12)

The correction function, f_1 (y) is not exactly and generally described by equation 3.25 and although the difference is small, it must be examined. The variation of the form of f_1 (y)

$$\frac{w}{3}$$

-24-
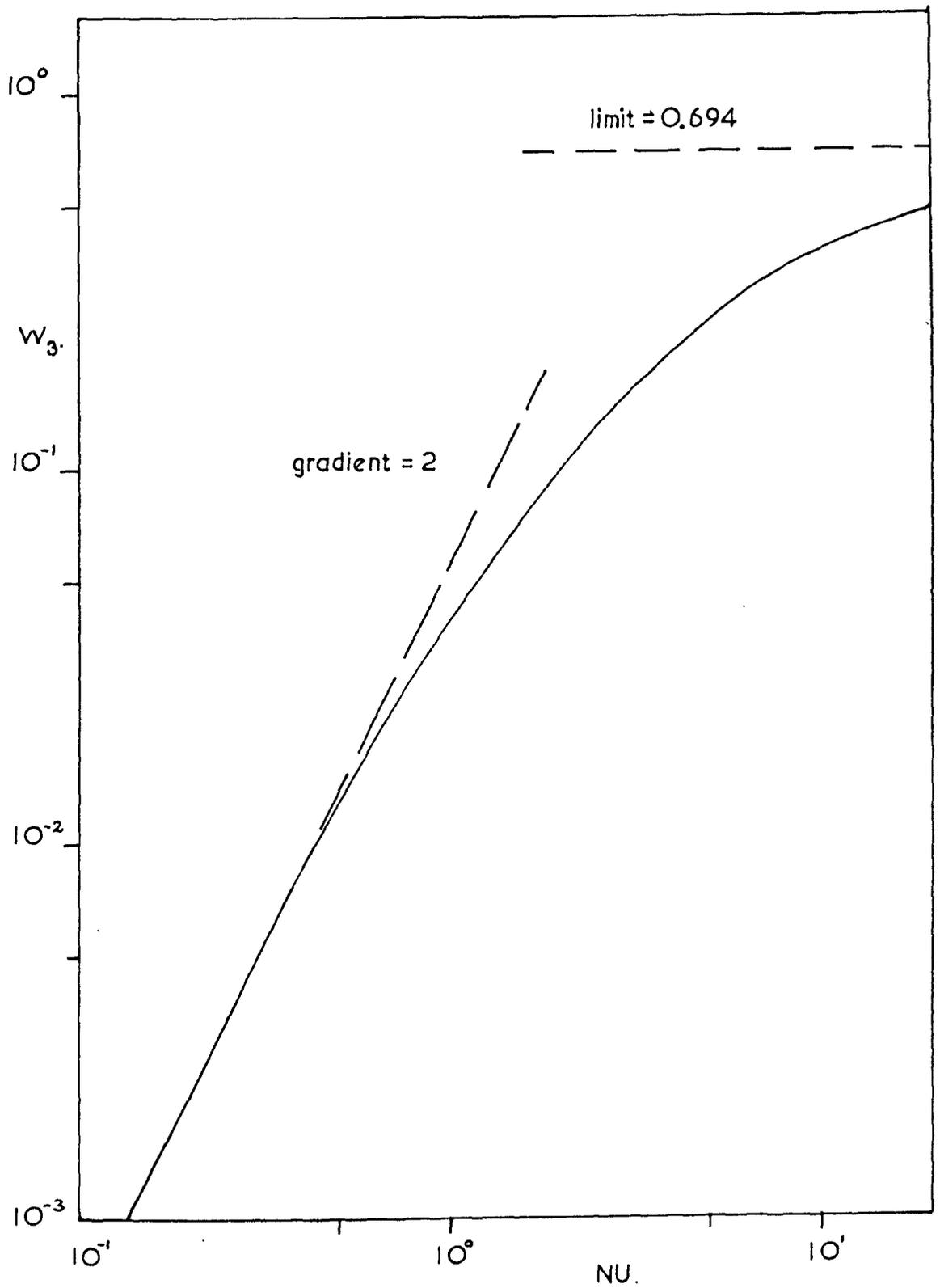
Figure 3.03 . The variation of the coefficient w_3 with respect to the Nusselt number Nu.
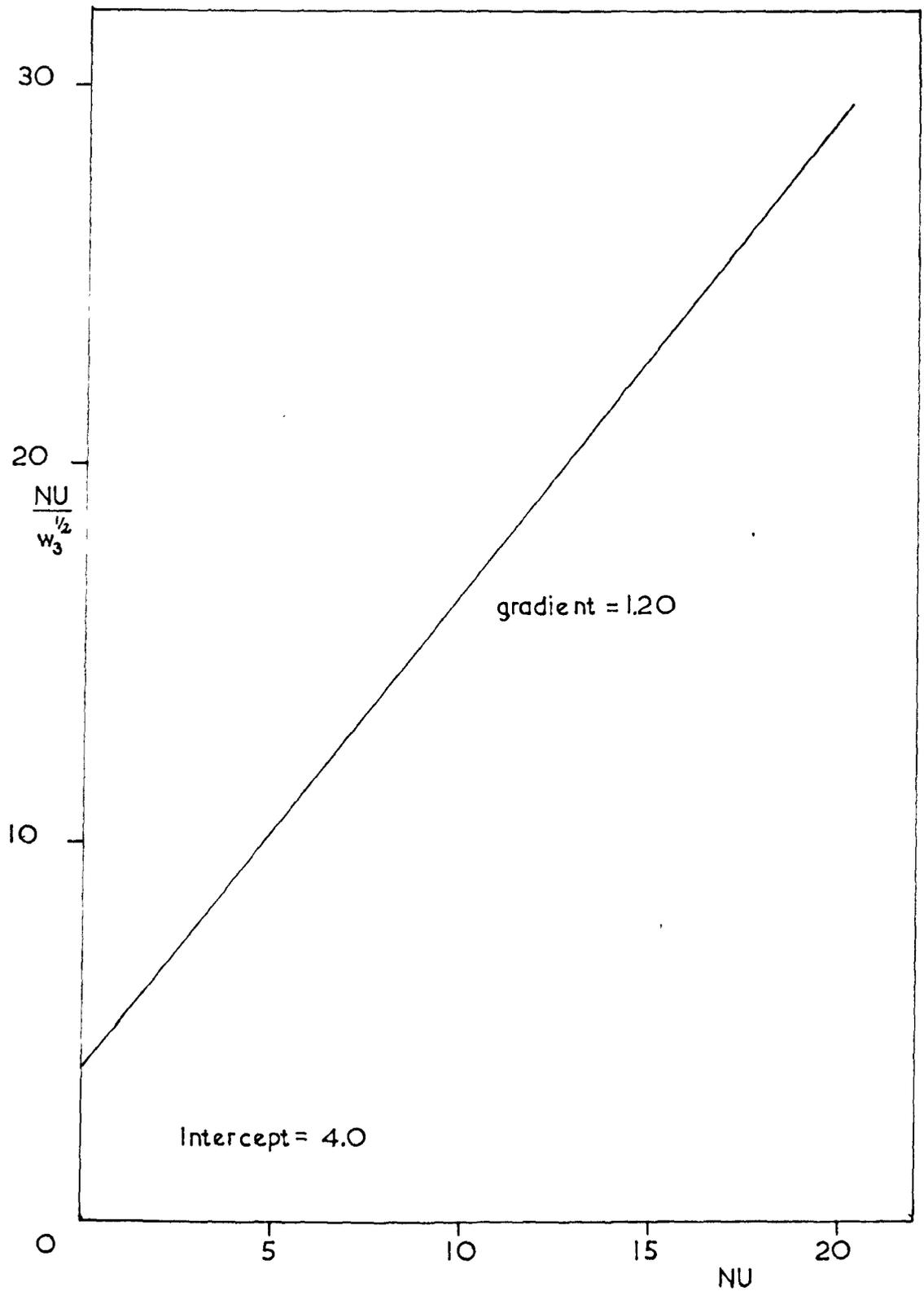
Figure 3.04 . Determination of the exact form of the
coefficient w_3.

is shown in fig. 3.05. The parametric analysis of this error is described in Appendix I; for a secondary correction function defined by,

$$\Omega_{II} = \left[\frac{f_1(y)}{w_4(1 - 3_y{}^2 + 2_y{}^3)} - 1 \right] \qquad 3.28$$

then Ω can be satisfactorily represented by,

$$\Omega_{II} = 0.4y^2 \left[\frac{(1 - 0.5 \, y \, (2 - y)) \, NU + 1}{1 + 0.5 \, NU \, (1 - y^2)} \right] \qquad 3.29$$

The major contribution of Ω_{II} is in the region of the tube wall and hence in the value of the effective Nusselt number; its contribution is zero in the prediction of the axis temperature $t(o)$.

3.5.5 The Radial Temperature Profile.

The radial temperature profile may be represented by,

$$(t(y)_{ht} - 1) = \left[w_3 (1 - 3y^2 + 2y^3)(1 + \Omega_{II}) + 1 \right] \left[1 + 0.5NU (1 - y^2) \right] (t(1) - 1 \qquad 3.30$$

where w_3 and Ω_{II} are defined by equations 3.27, 3.29 respectively. The secondary correction function, Ω_{II} need not necessarily be included in the expression unless a great emphasis is placed on accuracy. As stated above, the effect of Ω_{II} is zero at the tube axis $(y = o)$ and is also zero at the tube wall as $f_1(1) = 0$, although its effect is greatest in the region of the tube wall. Therefore the error in excluding Ω_{II} is best seen by considering its effect on the effective Nusselt number rather than on the prediction of the temperature profile, which will be discussed in section 3.5.

Examining equation 3.30, it is clear that the axially dependent reference temperature difference $(t(1) - 1)$ may be
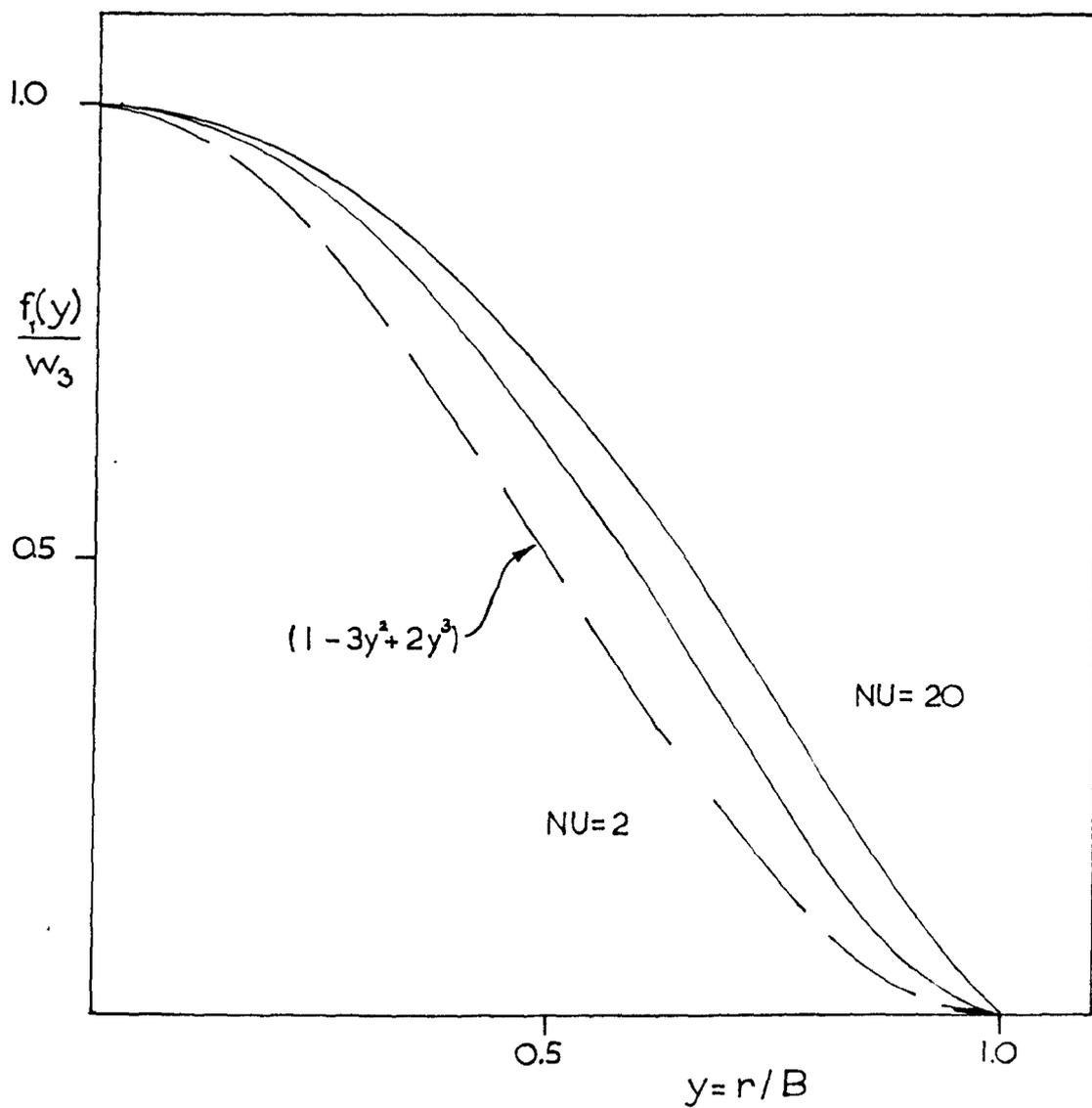
Figure 5.05 . The deviation of $f_1(y)$ from its predicted form.

replaced by a reference temperature $(t(Y) - 1)$ at any value of

$y = Y$; in this case the reference temperature is the mean radial

temperature. The advantage of equation 3.30 over the analytical

solution, equation 3.12, is that the expression is simple and

finite so that the profiles are easily computed. Equation 3.30

is in a form which can be used as the trial function for the

reactor with an exothermic reaction.

3.5.6 The Inlet Temperature Profile.

Normally, in the literature it has been assumed that the

inlet temperature profile is flat, which in a real situation is

unlikely. Numerically this assumption produces a discontinuity

at the tube wall, and this causes difficulties with the numerical

solution in the region of the inlet. Figure 3.06 shows how

sensitive the resulting axial profile is to the assumed inlet

radial temperature profile. Since the peak temperature is often

near the inlet region it is apparent that some care is needed in

specifying the appropriate inlet radial profile if the peak

axial temperature is to be specified with any accuracy. A

distributed inlet temperature profile, which fulfills the radial

boundary conditions, is physically more reasonable than the usual

flat inlet profile and will produce a more reliable solution in

the inlet region. Therefore, in view of this, all cases, except

where stated otherwise, are solved for the distributed inlet

profile, described by equation 3.30.

3.6 The Effective Nusselt Number.

The effective Nusselt number was defined in equation 3.17 as,

$$NU' = NU \frac{t(1) - 1}{t_m - 1}$$
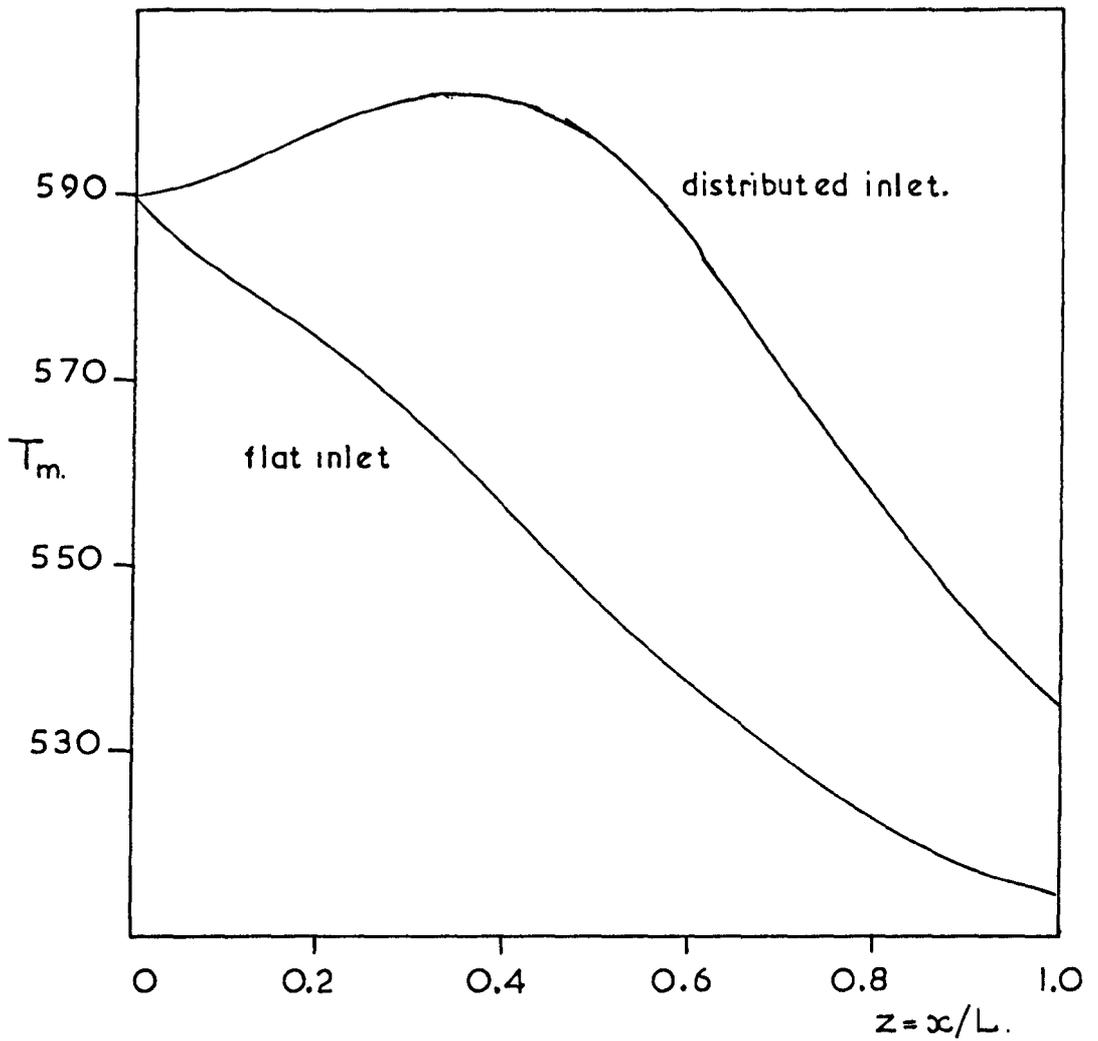
Figure 3.06 . Effect of the form of the inlet profile
on the axial temperature profile.

and $(t_m - 1)$ is defined by,

$$(t_m - 1) = 2 \int_0^1 (t\,(y)_{ht} - 1)\, y.\, dy \qquad 3.31$$

from equation 3.13. By substitution for $(t\,(y)_{ht} - 1)$ from

equation 3.30 integrating and rearranging, an expression for NU'

is derived:

$$NU' = \frac{NU}{(1 + 0.25\,NU) + w_3\,(0.3286 + 0.1545\,NU)} \qquad 3.32$$

where W_3 is given by equation 3.27. Due to the error in

estimating NU (i.e. the wall heat transfer coefficient and the

effective thermal conductivity), the constants in equation 3.32

will be expressed to the second decimal place only.

$$NU' = \frac{NU}{(1 + 0.25\,NU) + w_3\,(0.33 + 0.15\,NU)} \qquad 3.33$$

If the secondary correction function Ω_{II} is neglected (as will be

the usual case for the reactive system), then the value of the

constants change slightly

$$NU' = \frac{NU}{(1 + 0.25\,NU) + w_3\,(0.30 + 0.11\,NU)} \qquad 3.34$$

The error of estimating NU' when ignoring Ω_{II} is plotted against

NU in figure 3.07. These expressions are analogous to that

derived by Froment for the analytic solution (which is summarised

in section 3.2)

$$NU' = \frac{NU}{1 + 0.25\,NU} \qquad 3.35$$

Equation 3.35 is the expression for NU' which would be derived if
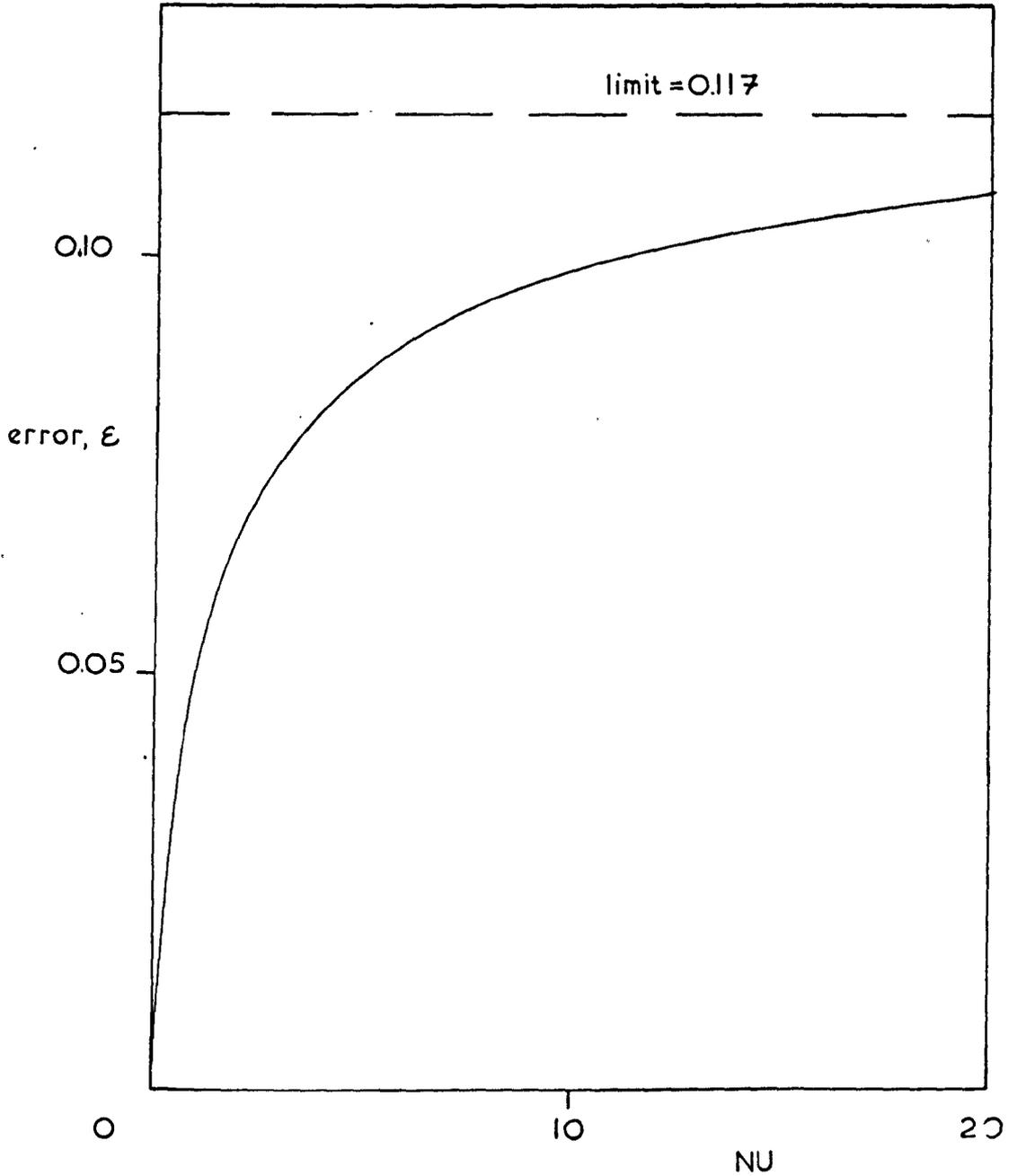
Figure 3.07 . The error of ignoring the secondary
correction function with respect to
the effective Nusselt number, NU.

a parabolic radial temperature profile is assumed i.e. $w_3 = 0$.
This is only a valid approximation for low values of NU. A
comparison of the predicted values and actual value of NU' is
given in figure 3.08; it can be seen that the predicted value
(given by equation 3.34) almost exactly coincides with the actual
value of NU', whereas the Froment prediction always overestimates
the value of NU'.

3.7 Conclusions.

The reduced model for heat transfer from a packed bed may now
be written,

$$(t_m - 1) = (t_m - 1)\big|_{z = 0} \; e^{-\left(\dfrac{2NU'}{Pe_T}\right) z}$$

$$(t(y) - 1) = \left[\left(\frac{NU}{1.2NU+4}\right)^2 (1 - 3y^2 + 2y^3) + 1\right]\left[1 + 0.5NU(1 - y^2)\right](t(1)-1)$$

$$\frac{NU'}{NU} = \left(\frac{t(1) - 1}{t_m - 1}\right) = \frac{1}{\left[(1 + 0.25\,NU) + \left(\dfrac{NU}{1.2NU+4}\right)^2(0.30 + 0.11NU)\right]}$$

A comparison of the original and reduced models is given in
figure 3.09. The above model retains the generality and
quantitative and qualitative description of the original model
described by equations 3.03, 4, while radically reducing the
computing by a factor of 60 : 1. The relative reduction of
computational load is not important for this case, as it has been
considered solely as a special case of the chemical reactor, and
because the temperature profile is used as a first approximation
for the case with exothermic chemical reaction. Nevertheless
it does indicate how effective model reduction can be.
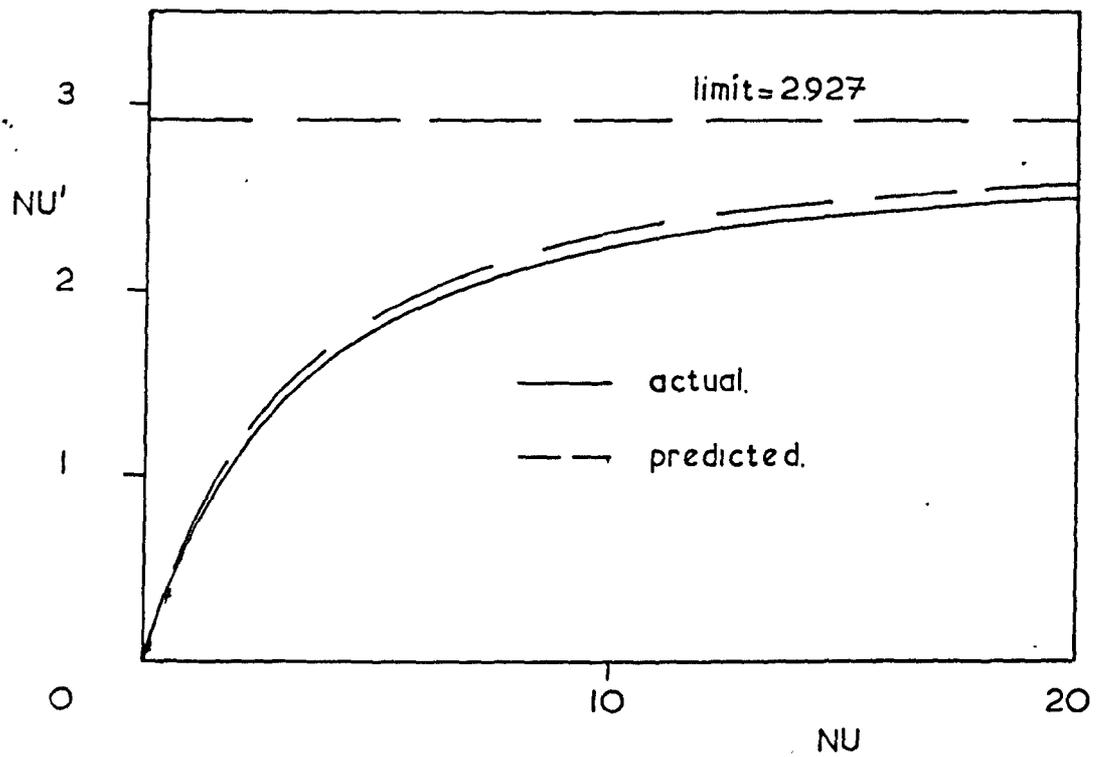
Figure 3.08 . Comparison of the actual and predicted values of the effective Nusselt number, NU.
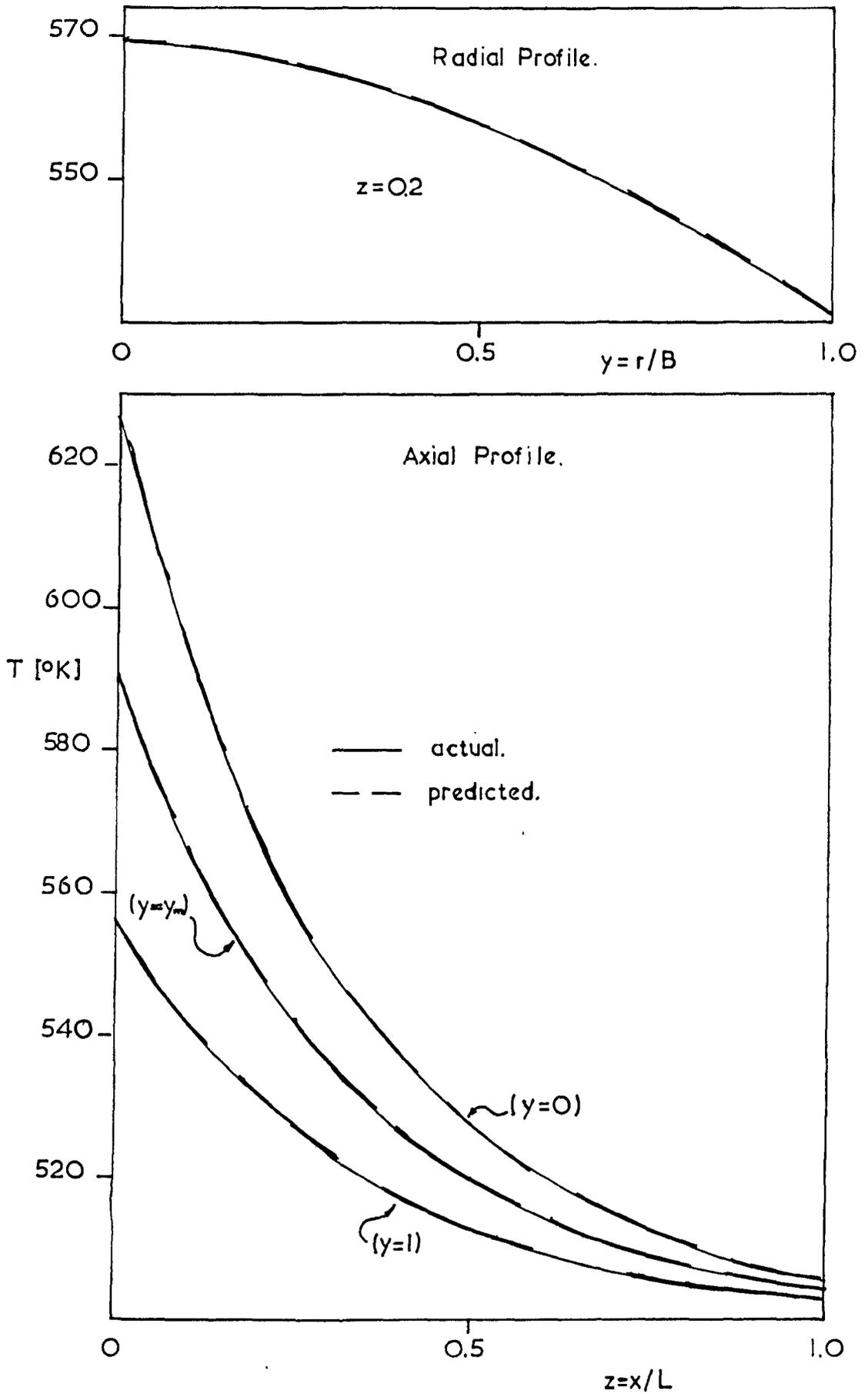
Figure 3.09 . Comparison of the actual and predicted

performance of the fixed bed heat exchanger.

CHAPTER 4

REDUCTION OF THE FIXED BED CATALYTIC REACTOR MODEL

- SIMPLE IRREVERSIBLE REACTION A ⟶ B.

4.1 Choice of Model.

The system considered is a tubular fixed bed catalytic

reactor in which the chemical change is highly exothermic. The

model is multi-dimensional in that it considers the spatial

variations of concentration and temperature in both the fluid and

solid phases. The simplifying assumptions which render the

solution tractable are amply enumerated by Cresswell [27], whose

model [14] is to be used. A conventional tubular reactor is

considered, packed with spherical catalyst pellets. (1) The

pellets are of a uniform size and both physically and chemically

identifiable. A diagramatic representation of the reactor and

pellet is given in figure 4.01. The pellets are randomly packed

to produce a homogeneous assembly having no preferred flow

directions. (2) Heat from the reactor is removed via the tube

wall to a coolant at constant temperature with respect to the

axial direction. (3) The reactant flows through the packing

in plug flow. (4) Axial dispersion in the direction of flow may

be neglected compared with the eddy diffusional processes. For

a practical range of flow rates this assumption is valid [28,29].

(5) The physical properties and heat of reaction are assumed

constant with respect to the range of concentration and

temperature in the reactor. (6) The individual pellets are

assumed to be quasi homogeneous, the internal mass and heat

transfer being by 'effective' diffusion and conduction processes,

both of which are measurable properties.
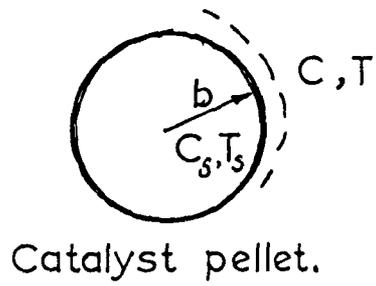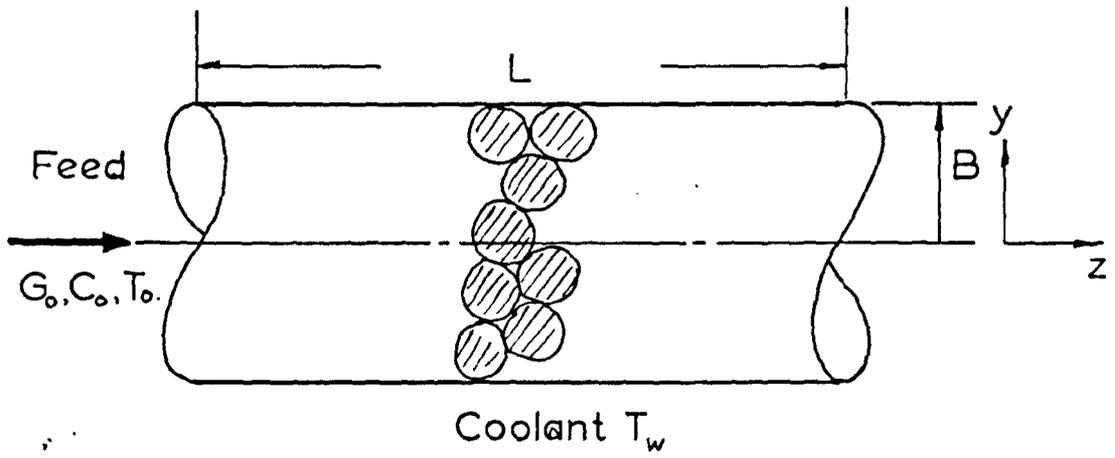
Figure 4.01 . Diagram of the fixed bed reactor.

Allowing for finite rates of heat and mass transfer across the fluid film surrounding the pellets, inside the catalyst pellets and radially in the fluid phase, the reactor state equations may be written:

Fluid:

$$-G_o \sigma_f \frac{\partial T}{\partial x} + \frac{1}{r} \lambda_f \frac{\partial}{\partial r} \left(r \cdot \frac{\partial T}{\partial r} \right) - \frac{3}{b} (1 - e) \lambda_p \frac{dT_s}{ds} \bigg|_{s=b} = 0 \qquad 4.01$$

$$-\frac{G_o}{\rho_f} \frac{\partial c}{\partial x} + \frac{1}{r} D_f \frac{\partial}{\partial r} \left(r \cdot \frac{\partial c}{\partial r} \right) - \frac{3}{b} (1 - e) D_p \frac{dC_s}{ds} \bigg|_{s=b} = 0 \qquad 4.02$$

Solid:

$$\frac{1}{s^2} \lambda p \frac{d}{ds} \left(s^2 \frac{dT_s}{ds} \right) + (-\Delta H) \, R \, (C_s, T_s) = 0 \qquad 4.03$$

$$\frac{1}{s^2} D_p \frac{d}{ds} \left(s^2 \frac{dC_s}{ds} \right) - R \, (C_s, T_s) = 0 \qquad 4.04$$

Where the boundary conditions are

$$\begin{aligned} T &= T_{ht} \, (r) \\ C &= C_o \end{aligned} \qquad x = 0, \quad 0 \leqslant r \leqslant B \qquad 4.05$$

$$\frac{\partial T}{\partial r} = \frac{\partial c}{\partial r} = 0 \qquad r = 0, \quad 0 \leqslant x \leqslant L \qquad 4.06$$

$$\frac{\partial c}{\partial r} = 0 \qquad r = B, \quad 0 \leqslant x \leqslant L \qquad 4.07$$

$$-\lambda_f \frac{\partial T}{\partial r} = U \, (T - T_w) \qquad r = B, \quad 0 \leqslant x \leqslant L \qquad 4.08$$

$$\frac{dC_s}{ds} = \frac{dT_s}{ds} = 0 \qquad s = 0$$

$$- D_p \frac{dC_s}{ds} = k_g \, (C_s - C) \qquad s = b \qquad\qquad 4.09$$

$$\begin{matrix} 0 & r & B \\ \\ 0 & x & L \end{matrix}$$

$$- \lambda_p \frac{dT_s}{ds} = h_f \, (T_s - T) \qquad s = b$$

It has been demonstrated that the pellet is essentially isothermal [14] although not at the fluid temperature, so that equations 4.03, 4, 9 can be solved analytically, and by use of an effectiveness factor, η, are replaced by algebraic expressions. The state equations are now reduced to the form:

Fluid:

$$- G_o \sigma_f \frac{\partial T}{\partial x} + \frac{1}{r} \lambda_f \frac{\partial}{\partial r}\left(r \cdot \frac{\partial T}{\partial r}\right) + \frac{3}{b} \, (1 - e) \, h_f \, (T_s - T)\big|_{s=b} = 0 \qquad 4.10$$

$$- \frac{G_o}{\rho_f} \frac{\partial C}{\partial x} + \frac{1}{r} D_f \frac{\partial}{\partial r}\left(r \cdot \frac{\partial C}{\partial r}\right) + \frac{3}{b} \, (1 - e) \, k_g \, (C_s - C)\big|_{s=b} = 0 \qquad 4.11$$

Solid:

$$- \frac{3}{b} \, h_f \, (T_s - T)\big|_{s=b} = (-\Delta H) \cdot \eta \cdot R\,(C, T) = 0 \qquad 4.12$$

$$- \frac{3}{b} \, k_g \, (C_s - C)\big|_{s=b} = \eta \cdot R\,(C, T) = 0 \qquad 4.13$$

the effectiveness factor for a first order irreversible reaction is given by,

$$\eta = \frac{3 \; Sh' \left(1 - \frac{\tanh \phi_s}{\phi_s} \right)}{2 \; \phi^2 \left\{ \left(\frac{Sh'}{2} - 1 \right) \frac{\tanh \phi}{\phi} + 1 \right\}} \qquad 4.14$$

where,

$$\phi_s = b \sqrt{\frac{k_o \; \exp \left(\frac{-E}{Rg \; Ts} \right)}{Dp}}$$

$$\qquad 4.15$$

$$\phi = b \sqrt{\frac{k_o \; \exp \left(\frac{-E}{Rg \; T} \right)}{D_p}}$$

The set of equations are conveniently and efficiently solved by the Crank-Nicolson finite difference method for equation 4.10, 11 (see Appendix 2)

The choice of reactor data is extremely important as all the characteristics of interest must be fully demonstrated. For example there must be a temperature maximum in the axial direction and appreciable radial temperature and concentration gradients. An unusually large (as far as a practical reactor is concerned) inlet temperature difference between reacting fluid and coolant is used to encourage large radial temperature and hence concentration gradients. The reactor data is summarised on table 4.01 together with the corresponding dimensionless groups.

4.2 Definition of the Required Model Description.

Before attempting to reduce the model, it is necessary to define exactly the description required of the model with respect to its uses in design, optimisation and control algorithms.

Table 4.01

Reactor Data.

G_o = 0.449 g./cm^2/sec.

ρ_f = 5.68 x 10^{-3} g./cm^3.

σ_f = 2.45 j./g./$^\circ$K.

e = 0.4

b = 0.21 cm.

B = 2.10 cm.

L = 125 cm.

T_{mo} = 590 $^\circ$K.

T_w = 500 $^\circ$K.

Transfer Data.

U = 4.4 x 10^{-2} j./cm.^{2}/sec./$^\circ$K.

λ_f = 4.62 x 10^{-2} j./cm./sec./$^\circ$K.

D_f = 3.32 cm.^{2}/sec.

Pellet Data

h_f = 7.86 x 10^{-2} j./cm.^{2}/sec./$^\circ$K.

λ_s = 3.302 x 10^{-2} j./cm./sec./$^\circ$K.

K_f = 1.45 cm./sec.

D_p = 0.05 cm.^{2}/sec.

Dimensionless Groups

Pe_T = Pe_M = 0.84

NU_s = 64.31, SH_s = 16.51.

Φ^2 = 1.697 x 10^{-2}; β = 0.6623

γ = 23.09 ; NU = 2.0

Kinetic Data

k_o = 2.27 x 10^8 sec.$^{-1}$.

E = 9.6 x 10^4 j./mole.

$-\Delta H$ = 2.27 x 10^5 j./mole.

C_o = 2.03 x 10^{-5} g./cm.^{3}.

A knowledge of the radial mean concentration along the length of the reactor is required but a description of the radial variation of concentration is not normally necessary. The description of the temperature distribution is localised at the axis where it is the radial maximum and which it is important to control in order to retain the stability of the catalyst and to prevent temperature run-away. If the problem is concerned with catalyst decay which is temperature dependent, it may be necessary to generate the complete radial temperature profile. But, as most catalyst decays over a period of years, the process is so slow that the effective catalyst activity need only be updated relatively infrequently eg. monthly.

4.3 Generalised Reduction of the Reactor Model.

In order to ease the analysis the reactor state equations are rendered dimensionless.

Fluid:

$$- Pe_T \frac{\partial t}{\partial z} + \frac{1}{y} \frac{\partial}{\partial y} \left(y \cdot \frac{\partial t}{\partial y} \right) + NU_s (t_s - t) \Big|_{y=1} = 0 \qquad 4.16$$

$$- Pe_M \frac{\partial c}{\partial z} + \frac{1}{y} \frac{\partial}{\partial y} \left(y \cdot \frac{\partial c}{\partial y} \right) + SH_s (c_s - c) \Big|_{y=1} = 0 \qquad 4.17$$

Solid:

$$- NU_s (t_s - t) = \beta \, \Phi^2 \eta \, R^* (c, t) \qquad 4.18$$

$$- SH_s (c_s - c) = \Phi^2 \eta \, R^* (c, t) \qquad 4.19$$

with boundary conditions,

$$\left. \begin{array}{l} t = t_{ht} (y) \\ c = 1 \end{array} \right\} \quad z = 0, \ 0 \leq y \leq 1 \qquad 4.20$$

$$\frac{\partial t}{\partial y} = \frac{\partial c}{\partial y} = 0 \qquad y = 0, \quad 0 \leq z \leq 1 \qquad\qquad 4.21$$

$$\frac{\partial c}{\partial y} = 0 \qquad\qquad y = 1, \quad 0 \leq z \leq 1 \qquad\qquad 4.22$$

$$-\frac{\partial t}{\partial y} = NU\,(t - 1) \qquad y = 1, \quad 0 \leq z \leq 1 \qquad\qquad 4.23$$

where

$$v = \frac{s}{b} \;;\; y = \frac{r}{B} \;,\; z = \frac{x}{L}$$

$$t = \frac{T}{T_w} \;;\; t_s = \frac{T_s}{T_w} \;;\; c = \frac{C}{C_o}$$

$$c_s = \frac{C_s}{C_o}$$

$$Pe_T = \frac{G_o\, d_f\, B^2}{\lambda_f\, L} \qquad\qquad ;\qquad Pe_M = \frac{G_o\, B^2}{\rho_f\, D_f\, L}$$

$$NU_s = \frac{3\,(1 - e)\, B^2\, h_f}{\lambda_f\, b} \qquad ;\qquad SH_s = \frac{3\,(1 - e)\, B^2\, kg}{D_f\, b}$$

$$NU = \frac{BU}{\lambda_f} \qquad ;\qquad \gamma = \frac{E}{Rg\, Tc}$$

$$\beta = \frac{(-\Delta H)\, Co\, D_f}{\lambda_f\, Tc} \;;\; \Phi^2 = \frac{(1 - e)\, B^2\, k_o\, \exp(-\gamma)}{D_f}$$

There is no general analytical solution for the fixed bed reactor model, so that approximate methods are used in order to gain some insight as to the basic structure of solution. Consider the locally linearised version of equations 4.16, 17 :

$$- \text{Pe}_T \frac{\partial t}{\partial z} + \frac{1}{y} \frac{\partial}{\partial y} \left(y. \frac{\partial t}{\partial y} \right) + at + bc + d = 0 \qquad 4.24$$

$$- \text{Pe}_M \frac{\partial c}{\partial z} + \frac{1}{y} \frac{\partial}{\partial y} \left(y \frac{\partial c}{\partial y} \right) + a't + b'c + d' = 0 \qquad 4.25$$

Froment [1] has shown that the solutions of the equations may take the form,

$$c = \sum_{n=0}^{\infty} h_n (z) \Psi_n (y) \qquad 4.26$$

$$(1 - t) = \sum_{n=0}^{\infty} g_n (z) \xi_n (y) \qquad 4.27$$

Although these are not generally applicable, it may be possible to suggest basic forms for the reduced solutions, eg. that the radial and axial solutions are separable and that it is better to consider the temperature difference with respect to the ambient temperature, rather than the absolute value of temperature.

The reactor model is reduced by a lumped parameter approach and the description is regenerated by constructing solutions in the dimensions which have been eliminated, in a similar manner to that used in the previous chapter. The principle dimension is chosen as the axial direction.

Multiplying the state equations 4.16, 17 through by 2y.dy and integrating over the bed radius,

$$- Pe_T \frac{dt_m}{dz} - 2NU (t(1) - 1) + \beta \Phi^2 (\eta R^* (c,t))_m = 0 \qquad 4.28$$

$$- Pe_M \frac{dc_m}{dz} - \Phi^2 (\eta R^* (c,t))_m = 0 \qquad 4.29$$

so long as,

$$\left(\frac{dt}{dz}\right)_m = \frac{dt_m}{dz} \quad \text{and} \quad \left(\frac{dc}{dz}\right)_m = \frac{dc_m}{dz}$$

In order that the reduced model is expressed in terms of radial mean temperature and concentration only two pseudo-parameters are defined.

The effective Nusselt number, $NU' = NU \left(\dfrac{t(1) - 1}{t_m - 1}\right)$ \qquad 4.30

and a distribution factor
for the reactor tube

$$\mathcal{D} = \frac{(\eta R^* (c,t))_m}{\eta (m) R^*(c_m, t_m)} \qquad 4.31$$

which is analogous to the effectiveness factor, η and is a local value. Satisfactory agreement between the solutions of the complex and reduced models will be dependent on reliable methods of estimating these two parameters, which will be discussed in the succeeding chapter. The resulting reduced model may now be written:

$$- Pe_T \frac{dt_m}{dz} - NU' (t_m - 1) + \beta \Phi^2 \mathcal{D} \eta (m) R^* (c_m, t_m) = 0 \qquad 4.32$$

$$- Pe_M \frac{dc_m}{dz} - \Phi^2 \mathcal{D} \eta (m) R^* (c_m, t_m) = 0 \qquad 4.33$$

where the boundary conditions are,

$$\left.\begin{matrix} t_m = t_{mo} \\ \\ c_m = 1 \end{matrix}\right\} \quad z = 0 \qquad 4.34$$

The problem is to reproduce the detailed description by constructing solutions for the radial concentration and temperature profiles.

4.4 Regeneration of Description.

4.4.1 Introduction.

Before carrying out the numerical experiments to determine the functional forms of the radial profiles, the basic model data must be chosen in order that all the general features of the model are described, eg. large radial temperature gradients, and a maximum temperature, axially, as discussion earlier in section 4.1.

4.4.2 The Radial Concentration Profile.

By observation of typical solutions of the complex model, the radial concentration profile, representing the two point boundary problem, can be adequately described by an odd power polynomial function. The simplest form of the trial function is a cubic of the form,

$$c(y) = \varepsilon_0 + \varepsilon_1 y + \varepsilon_2 y^2 + \varepsilon_3 y^3 \qquad 4.35$$

where the ε_i are axially dependent coefficients. Applying the boundary conditions of the complex model (given by equations 4.21, 2, 3) to the polynomial function, and substituting for

$$c_m = 2 \int_0^1 c(y) \cdot y \cdot dy ;$$

$$\left. \frac{\partial c}{\partial y} \right|_{y=0} = \varepsilon_1 = 0$$

$$\left. \frac{\partial c}{\partial y} \right|_{y=1} = 2\varepsilon_2 + 3\varepsilon_3 = 0 \qquad \left. \right\} \qquad 4.36$$

and,

$$c_m = \varepsilon_0 + 0.5\varepsilon_2 + 0.4\varepsilon_3 \qquad 4.37$$

then

$$c(y) = \varepsilon_3 (y^3 - 1.5 y^2 + 0.35) + c_m \qquad 4.38$$

A pseudo-parameter, the overall radial concentration difference is
defined as,

$$\Delta c = c(1) - c(0) \qquad 4.39$$

where $c(0)$ is the concentration at the tube axis and $c(1)$ the
concentration at the tube wall.   Substituting for Δc in equation
4.38 the coefficient ε_3 is eliminated from the expression.

$$c(y) = \Delta c (3_y^2 - 2_y^3 - 0.7) + c_m \qquad 4.40$$

Both Δc and c_m are axially dependent functions.   Equation 4.40
is equivalent to the type of function proposed by the Galerkin
and collocation methods, where m = 1, ie.

$$c \sim c^{(1)} = a_1^{(1)} \Omega_1 + \Omega_0 \qquad 4.41$$

where $c_m = \Omega_0$, $(3_y^2 - 2_y^3 - 0.7) = \Omega_1$ and $\Delta c = a_1^{(1)}$.

The predicted concentration profile given by equation 4.40 is
accurate to within 0.5% of the computed from the complex model,
(see fig. 4.02) so that it is unnecessary to consider any form of
correction term.

In order to use equation 4.40 in the reduced model an
expression for Δc is required which is related to radial mean
parameter values, eg. c_m, t_m, k^* (tm) etc., but discussion will be
deferred until the succeeding chapter.

4.4.3   The Radial Temperature Profile.

As stated in section 3.1, the fixed bed heat exchanger has
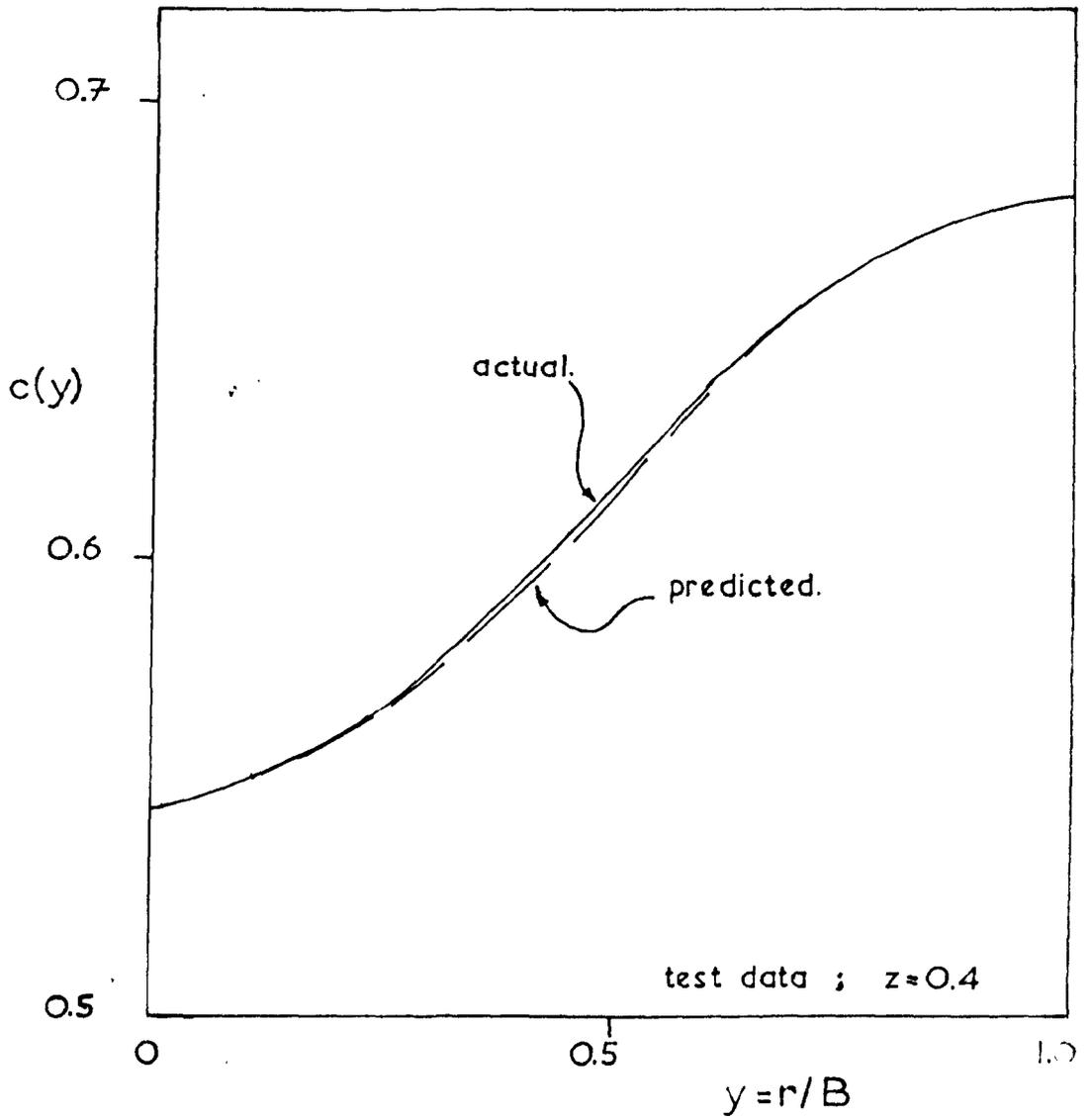
Figure 4.02 . Comparison of the actual and predicted forms
of the radial concentration profile.

been taken as a special case of the fixed bed reactor model
(ie. where $\beta = 0$), and the temperature profile which has been
developed for that model will be used as a first approximation for
the reactor model.   Graphically, it is assumed that the
temperature profile is distorted by the presence of an exothermic
chemical reaction.   If a correction function is defined by,

$$f_2\,(y) = \left[\left(\frac{t-1}{t_{ht}-1}\right) - 1\right] \qquad 4.42$$

where the reference temperature is that at the tube wall,
(ie. $t\,(1)$, where $f_2\,(1) = 0$), then $f_2\,(y)$ is similarly
constrained as $f_1\,(y)$ (see section 3.4.3)

$$\left.\begin{array}{l} f_2\,(1) = 0 \\ f_2{}'\,(0) = f_2{}'\,(1) = 0 \end{array}\right\} \qquad 4.43$$

from the boundary conditions of the original reactor model.   By
observation of the solutions for a practical range of reactor
operating condition, the correction function, $f_2\,(y)$ can be
adequately represented by a simple algebraic function:

$$f_2\,(y) = w_4\,(1 - 3_y{}^2 + 2_y{}^3) \qquad 4.44$$

It would be expected that the coefficient, w_4 would be solely a
function of the reaction terms and is in fact primarily
dependent upon the overall radial concentration difference, Δc
which could be physically interpreted as the ~~design~~ *extent* to which the
temperature profile is distorted by the presence of an exothermic
chemical reaction.   From an exhaustive analysis of the model
coefficients, the coefficient, w_4 may be adequately represented by,

$$w_4 = {}^{10}/_3\,\beta\,\Delta c \qquad 4.45$$

In figure 4.03, w_4 and $\beta\Delta c$ are correlated. As may be seen, the relationship is not exactly linear as proposed by equation 4.45 But it is always the policy of model reduction to preferably make use of simple algebraic relationships even if slightly less accurate than more complex forms. Nevertheless use of the simple relationship must be justified with respect to the error.

In the direction of increasing temperature (i.e. when approaching the temperature maximum) and in the region of the temperature maximum, which on figure 4.03 is along the line from the origin through AB, equation 4.45 holds almost exactly. But in the direction of decreasing temperature, through BC to the origin on figure 4.03, the error increases to a maximum and falls to zero. Therefore equation 4.45 always holds in the region of practical importance (i.e. up to and around the temperature maximum), and no great concern need be caused by the error in the region in which the temperature is falling as normally this is beyond the normal limits of the reactor, i.e. before this situation can occur the exit of the reactor has been reached.

When the exothermicity, β, is zero then, as would be expected, the temperature profile is that for the fixed bed heat exchanger. The radial temperature profile may be written as,

$$(t(y) - 1) = \left[{}^{10}/_3 \beta\Delta c \, (1 - 3_y{}^2 + 2_y{}^3) + 1 \right]\left[\left(\frac{NU}{1.2NU+4} \right)^2 (1 - 3_y{}^2 + 2_y{}^3) + 1 \right]$$

$$x \left[1 + 0.5 \, NU \, (1 - y^2) \right] (t(1) - 1) \qquad 4.46$$

The temperature adjacent to the wall, $t(1)$ can be eliminated from equation 4.46 by integrating with respect to $2_y \cdot d_y$ to introduce the mean radial temperature, t_m, where,
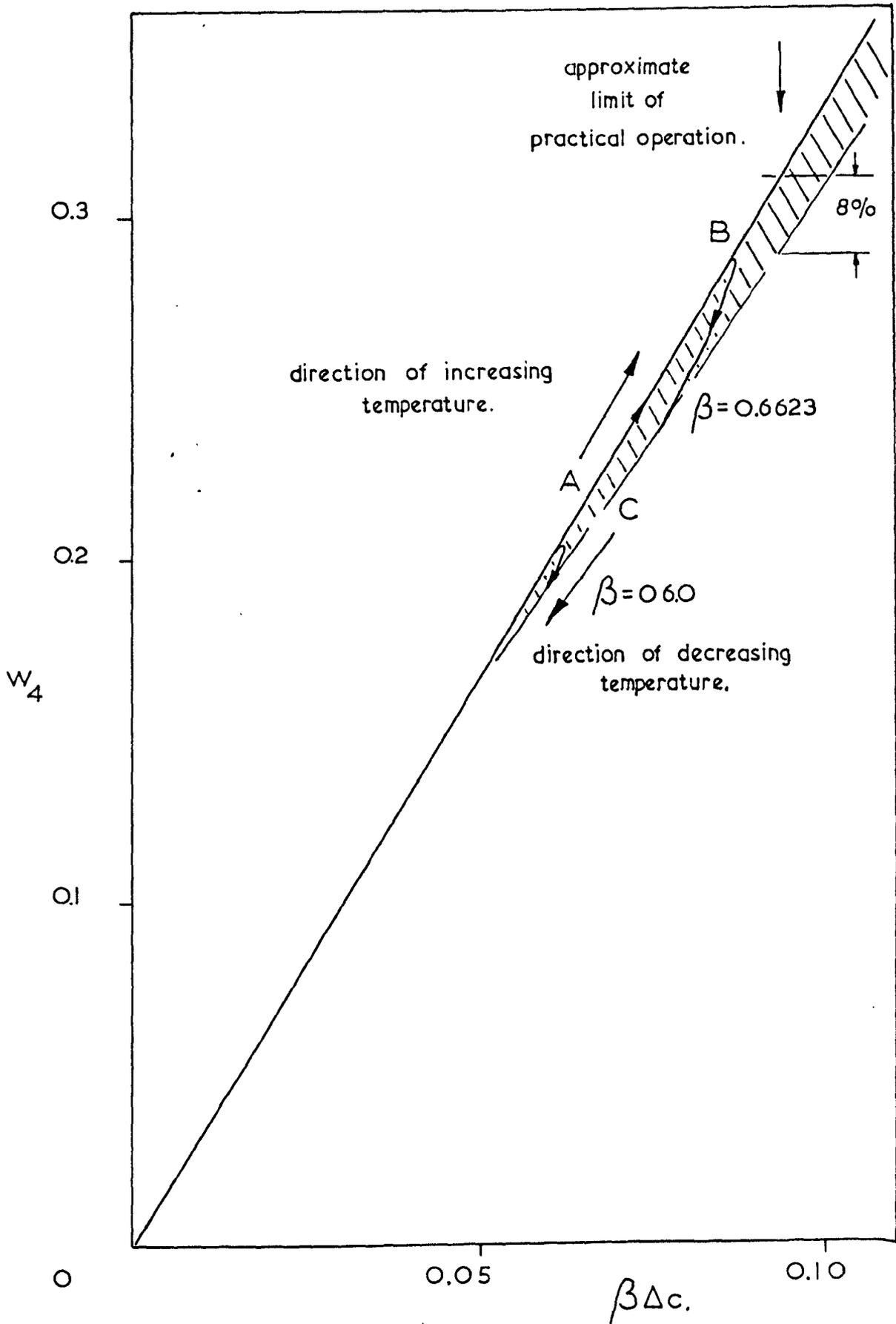
Figure 4.03 . Prediction of the coefficient w_4.

$$(t(1) - 1) = \frac{(t_m - 1)}{\left[(1+0.25NU)+(w_3+w_4)(0.11NU+0.30)+w_3w_4(0.47NU+0.17)\right]}$$

and w_3, w_4 are defined by equations 3.27, 4.45 respectively.

4.5 Conclusions

The reduced model for the exothermic fixed bed chemical reactor may now be written,

$$- Pe_T \frac{dt_m}{dz} - NU' (t_m - 1) + \beta \Phi^2 \mathcal{D} \eta(m) R^* (c_m, t_m) = 0 \qquad 4.47$$

$$- Pe_M \frac{dc_m}{dz} - \Phi^2 \mathcal{D} \eta(m) R^* (c_m, t_m) = 0 \qquad 4.48$$

and the radial profile may be obtained by using,

$$c(y) = \Delta c (3_y{}^2 - 2_y{}^3 - 0.7) + c_m \qquad 4.49$$

$$t(y)-1= \frac{\left[(w_4(1-3_y{}^2+2_y{}^3)+1)(w_3(1-3_y{}^2+2_y{}^2)+1)(1+0.5NU(1-_y{}^2))(t_m-1)\right]}{((1+0.25NU)+(w_3+w_4)(0.3+0.11NU)+w_3w_4(0.17+0.47NU))} \qquad 4.50$$

where $w_3 = \left(\dfrac{NU}{1.2NU+4}\right)^2$; $w_4 = {}^{10}/_3 \beta \Delta c$

It must be noted that although some of the expressions appear complex, in fact, for a specific reactor system, they are constant eg. w_3 .   This tends to radically simplify the expression for the radial temperature profile.

Unlike all other one dimensional models which have been proposed, the above model accounts for the effect of the presence of an exothermic chemical reactor upon the effective Nusselt number, NU'and differentiates between the radial mean reaction rate

and the reaction rate at the radial mean conditions through the distribution factor,Θ. The model has the additional ability to construct the radial profiles of temperature and concentration if required. Indeed, all these features have been made available with minimal addition of complexity to the basically attractive simplicity of the one dimensional model. It must be stressed that the reduced model is generally applicable over the parameter range for which it has been developed and at no stage can it be considered to be an empirical model. The one-dimensional state equations are an exact and direct development from the original two-dimensional model and their reliability is dependent on the accuracy of estimating the pseudo-parameters NU' and Θ. To consider parametric sensitivity would be meaningless as the two models are directly related over a wide range of conditions. The two models are compared in figure 4.04 for the basic data, which can be considered to be a stringent test for the reduced model, as the system is 'finely balanced' which necessitates parallel characteristics of the two model if comparative results are to be produced.

In this chapter, a very simple first order reaction has been considered, which is not at all typical, and in Chapter 7, more typical reaction schemes are considered. Nevertheless, the analysis in this chapter has proved that model reduction is possible, and indicates the direction it might profitably take.
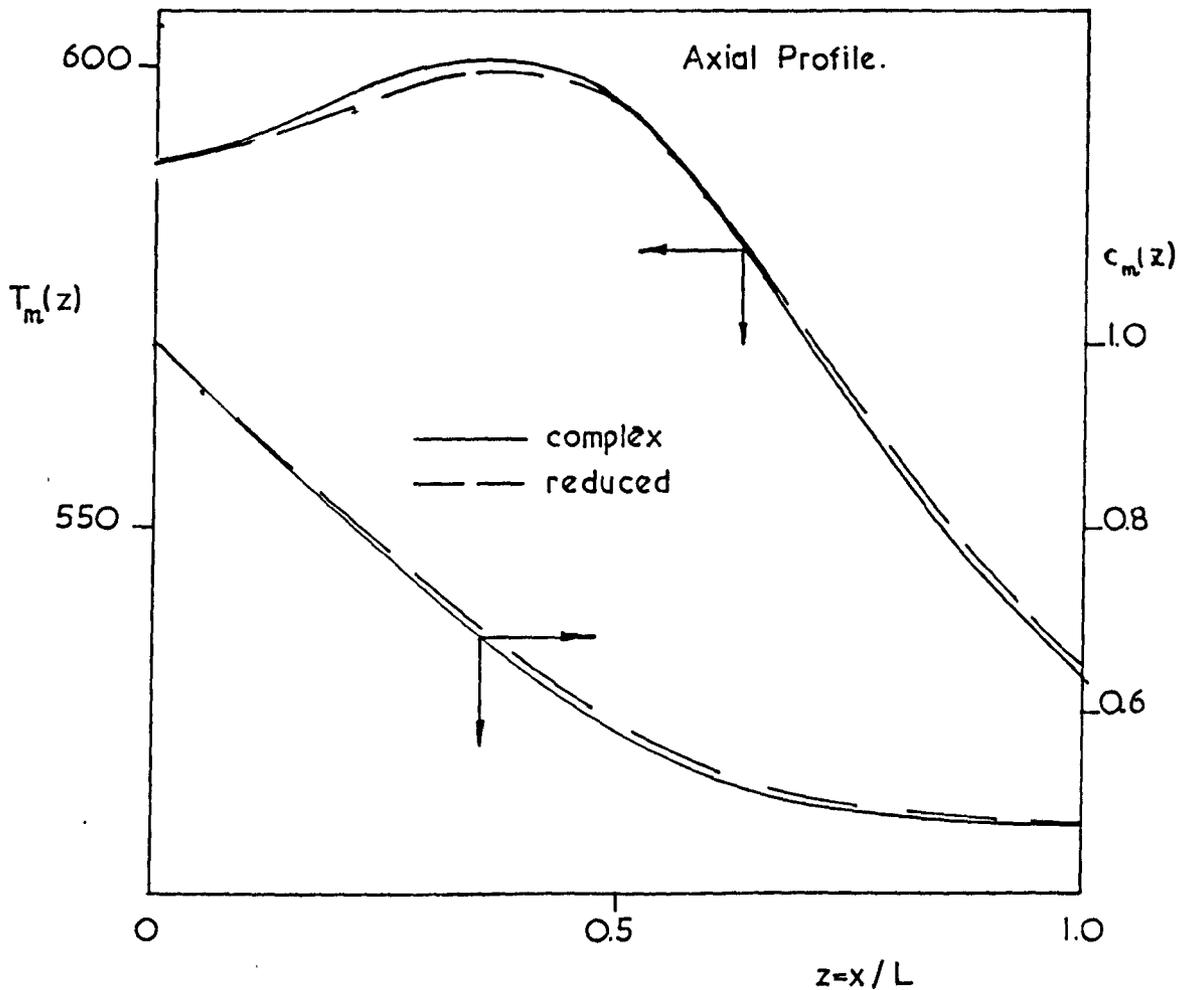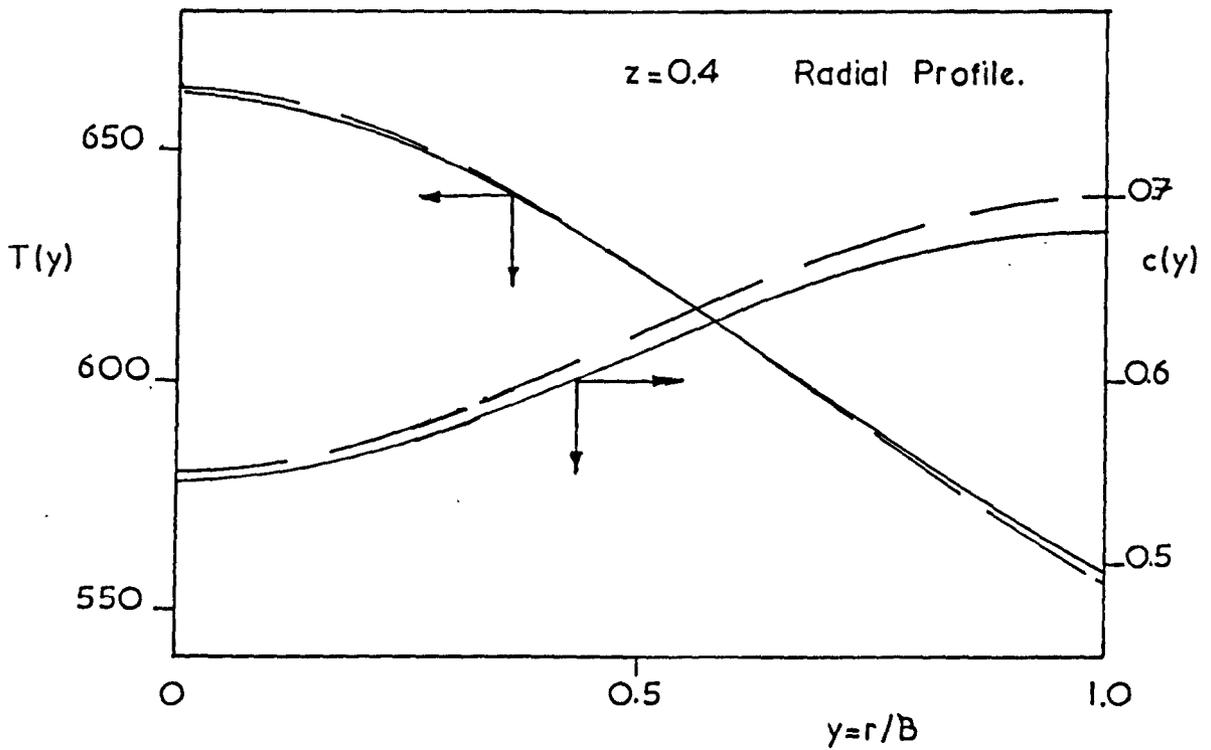
Figure 4.04 . Comparison of the actual and predicted
performance of the fixed bed reactor.

CHAPTER 5

CORRELATION OF THE AXIALLY DEPENDENT PSEUDO PARAMETER

5.1 Discussion.

The overall radial concentration difference, Δc is physically identified as the concentration difference between the tube wall and axis, at any axial position,

$$\Delta c = c(1) - c(0)$$

As the reduced model is solved axially in terms of the radial mean values of the system parameters, i.e. concentration and temperature, the value of Δc is not directly available in terms of the reduced model; but it is required in order to estimate the distribution factor, Θ and the effective Nusselt number, NU' (see the succeeding chapter) and to generate the radial concentration and temperature profiles (see section 4.5). Therefore, an alternative approach is required for the estimation of Δc in conjunction with the formulation and solution of the reduced model.

5.2 Preliminary Analysis.

As no analytical solution exists for the original reactor model, no information as to the functional form of Δc is immediately available. In order to determine the principal parameters or parametric groups on which Δc is dependent, a radically simplified reactor model is considered. Assume that the axial convection terms are negligible compared with the radial diffusion and conduction terms, and that the radial transport is mass transfer limiting. An approximate relation,

$$\Delta c \sim \Phi^2 \left(\eta(0) R^* (c(0), t(0)) - \eta(1) R^* (c(1), t(1)) \right) \qquad 5.01$$

is assumed, which expanding the reaction rate terms gives,

$$\Delta c \sim \Phi^2 \left(c(0)\, k^*(t(0)) - c(1)\, k^*(t(1)) \right) \qquad 5.02$$

Using equation 4.40, the radial concentration profile, $c(0)$ and $c(1)$ are expressed in terms of c_m and Δc, i.e.

$$
\begin{aligned}
c(0) &= c_m - 0.7\,\Delta c \\
c(1) &= c_m + 0.3\,\Delta c
\end{aligned}
\qquad 5.03
$$

which when substituted in equation 5.02, and rearranged gives,

$$\frac{\Delta c}{c_m} \sim \left(\frac{k^*(t(0)) - k^*(t(1))}{0.7\,k^*(t(0)) + 0.3\,k^*(t(1)) + {}^{1}/\Phi^2} \right) \qquad 5.04$$

This expression is clearly a gross approximation and to render it generally applicable a modified solution is proposed which has the same general form, i.e.

$$\frac{\Delta c}{c_m} = \left(\frac{k^*(t_m) - 1}{\nu_1\, k^*(t_m) + \nu_2 + \nu_3 {}^{/}\Phi^2} \right)^n \qquad 5.05$$

where n is an arbitrary power not necessarily an integer and the ν_i are coefficients dependent on the model coefficients which have not yet been considered.

When NU = 0, i.e. the reactor is adiabatic and $\Delta c = 0$; but when NU has a large value but is finite, Δc is independent of NU since the radial transport process is mass transfer limiting. Therefore the expected form of the coefficients, ν_i should be,

$$\nu_i = \left(\frac{F(NU) + 1}{G(NU)} \right)^m \qquad 5.06$$

where m is an arbitrary power and F(NU), G(NU) are functions of NU.

Account must be taken of the general inlet condition where $t_{mo} \neq 1$, from which $k^*(t_{mo}) \neq 1$, so that equation 5.05 does not fulfill the inlet boundary condition for concentration that

$\Delta c \big|_{z=0} = 0$. In this case the function, Δc approaches its
its asymptotic form (given by equation 5.05) from the inlet
($\Delta c = 0$) in a manner described in section 2.5 by equation 2.03,
i.e.,

$$\Delta c = \Delta c \big|_{z=0} \exp\left(-\tfrac{z}{\zeta}\right) + \Delta c_a \left(1 - \exp\left(-\tfrac{z}{\zeta}\right)\right) \qquad 5.07$$

which can be simplified to,

$$\Delta c = \Delta c_a \left(1 - \exp\left(-\tfrac{z}{\zeta}\right)\right) \qquad 5.08$$

where Δc_a is the asymptotic value of Δc and ζ is a pseudo-
parameter.

From the above analysis, numerical experiments may be
designed to verify the form of the proposed solutions and to
determine the constants and pseudo-parameters which have been
introduced.

5.3 The Parametric Analysis.

5.3.1 The Power, n.

The parametric groups, $(k^*(t_m) - 1)$ and $\dfrac{\Delta c}{c_m} = \Delta c^*$ are

correlated for a range of reactor operating conditions, of which
figure 5.01 is typical. For reducing values of $(k^*(t_m) - 1)$ the
gradient (on logarithmic co-ordinates) tends asymtotically to a
value of 2, which is the value of n. For increasing values of
$(k^*(t_m) - 1)$, Δc^* asymptotically approachs a constant value as
predicted by equation 5.05, so that the basic structure of the
predicted solution for Δc is verified.

5.3.2 The General Form of Δc.

Having established the basic structure for the solution
proposed for Δc, the coefficients ν_i are evaluated by plotting
$\left(\dfrac{k^*(t_m) - 1}{\Delta c^{*\frac{1}{2}}}\right)$ and $k^*(t_m)$ for a range of values of Φ^2 and
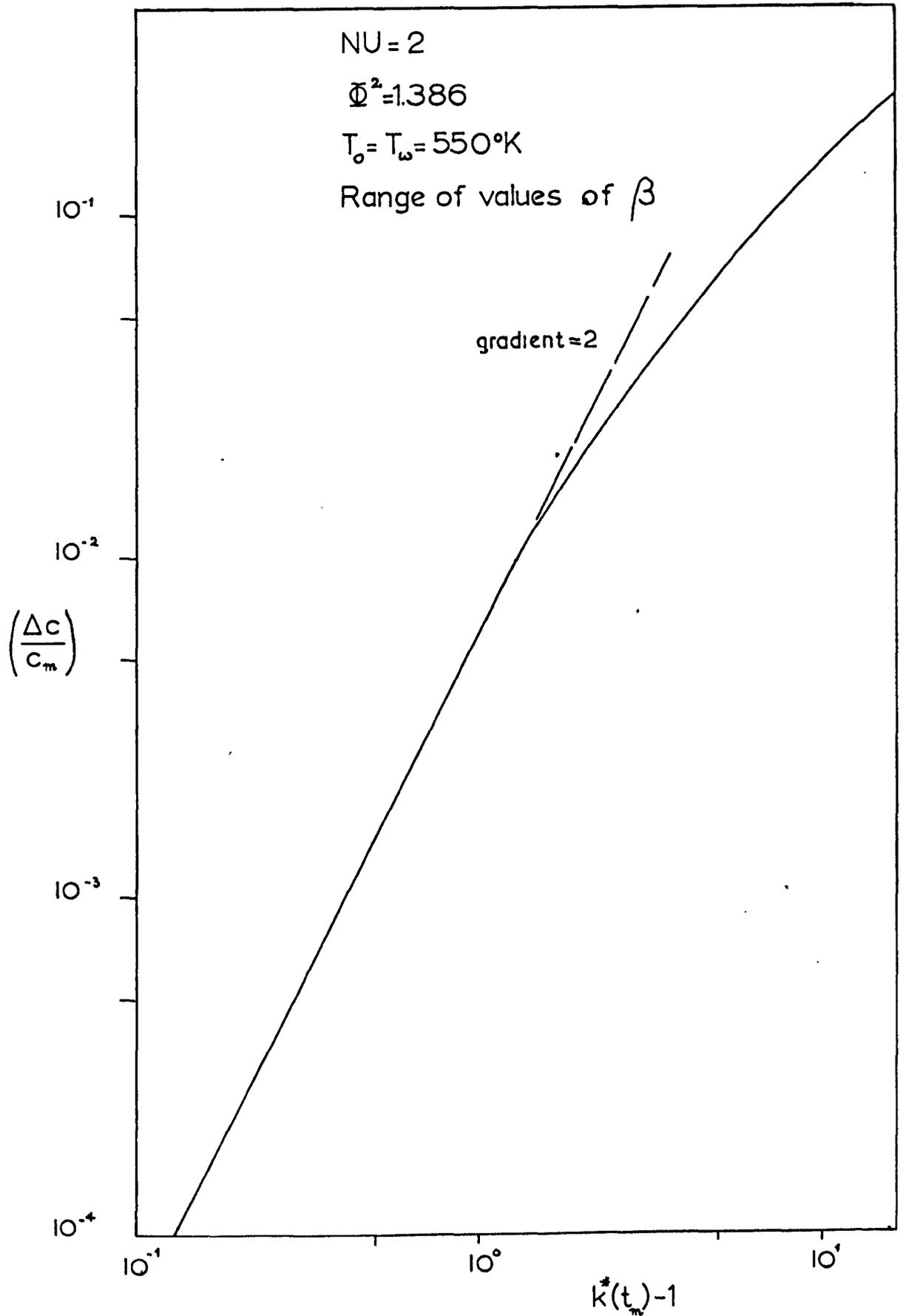
Figure 5.01 . The general form of the pseudo-parameter, Δc.

constant NU. The gradient of the straight line is ν_1 and the intercept (for $k^*(t_m) = 0$) is $(\nu_2 + (\nu_3/\Phi^2))$ as demonstrated in figure 5.02. Physically $k^*(t_m)$ cannot take values below 1, which is the value at the coolant temperature. In the region of $k^*(t_m)$ close to 1, $(k^*(t_m) - 1)$ and $\Delta c^{*\frac{1}{2}}$ are almost zero, and in evaluating the ratio, 'round-off' error is encountered which can distort the results. Therefore in correlating the results care must be taken to ignore the points in this region.

The coefficient ν_1 is constant with respect to Φ^2. In figure 5.03, $(\nu_2 + \nu_3/\Phi^2)$ from figure 5.02 and $1/\Phi^2$ are plotted in order to evaluate ν_2 and ν_3, which are the intercept (for $1/\Phi^2 = 0$) and the gradient of the straight line respectively.

5.3.3 Dependence of Δc on NU.

The coefficients, ν_i, are evaluated by the above method of correlation for a practical range of values of Nusselt number, NU. As discussed in section 5.2 the dependence of ν_i on NU, given by equation 5.06.

The coefficient, ν_2 is found to be constant with respect to NU. By correlating ν_1 and ν_3 with NU on logarithmic co-ordinates, the integer m (from equation 5.06) is the limiting gradient of the curves for decreasing values of NU, which can be seen from figures 5.04, 5. In both cases m = - 1, and ν_3 is inversely proportional to NU, i.e.,

$$\nu_3 = \nu_4 \, NU^{-1} \qquad\qquad 5.09$$

where ν_4 is the constant of proportionality. The coefficients ν_2 and ν_3 may be grouped together as,
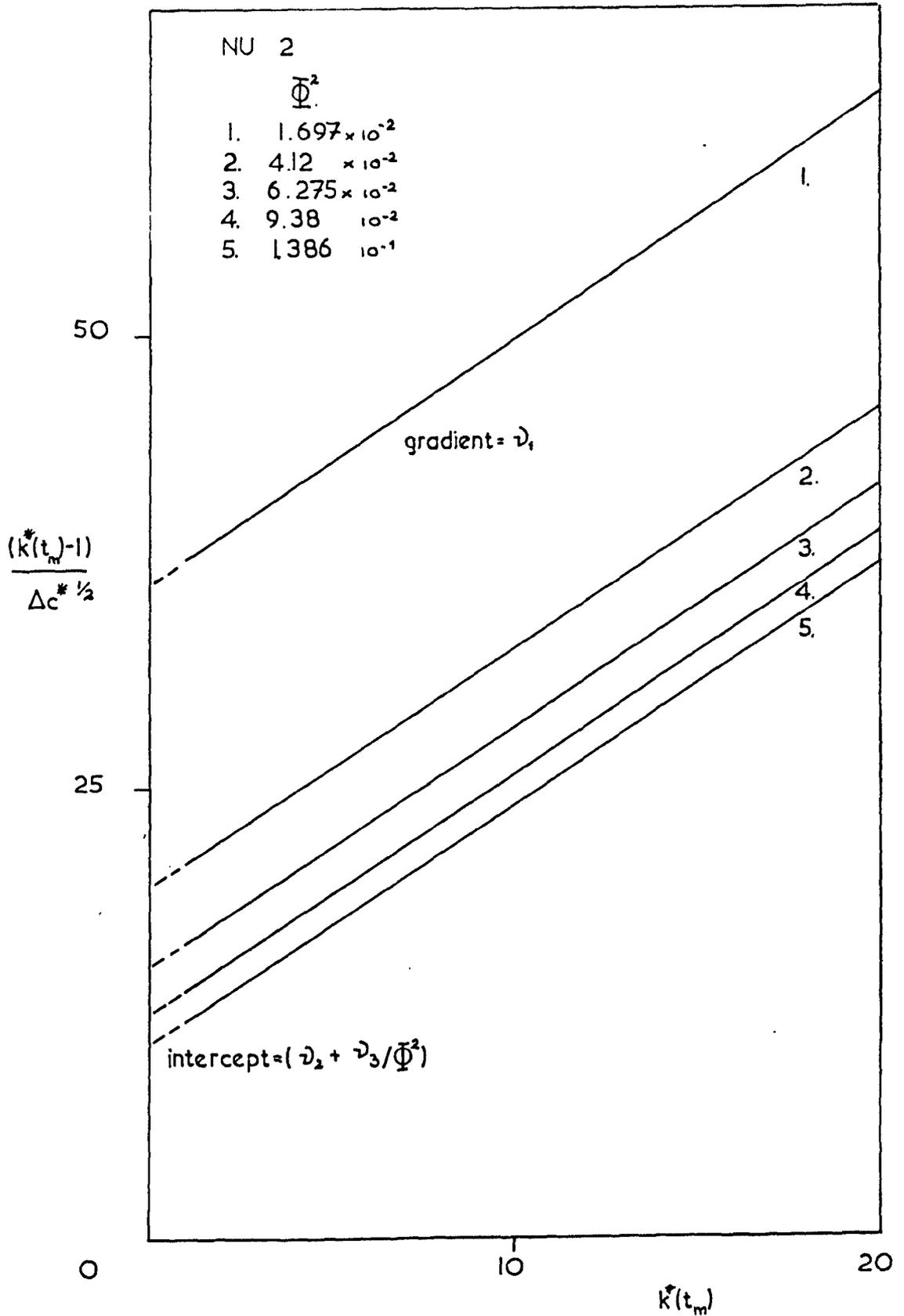
Figure 5.02 . Verification of the general functional
form of the pseudo-parameter, Δc.
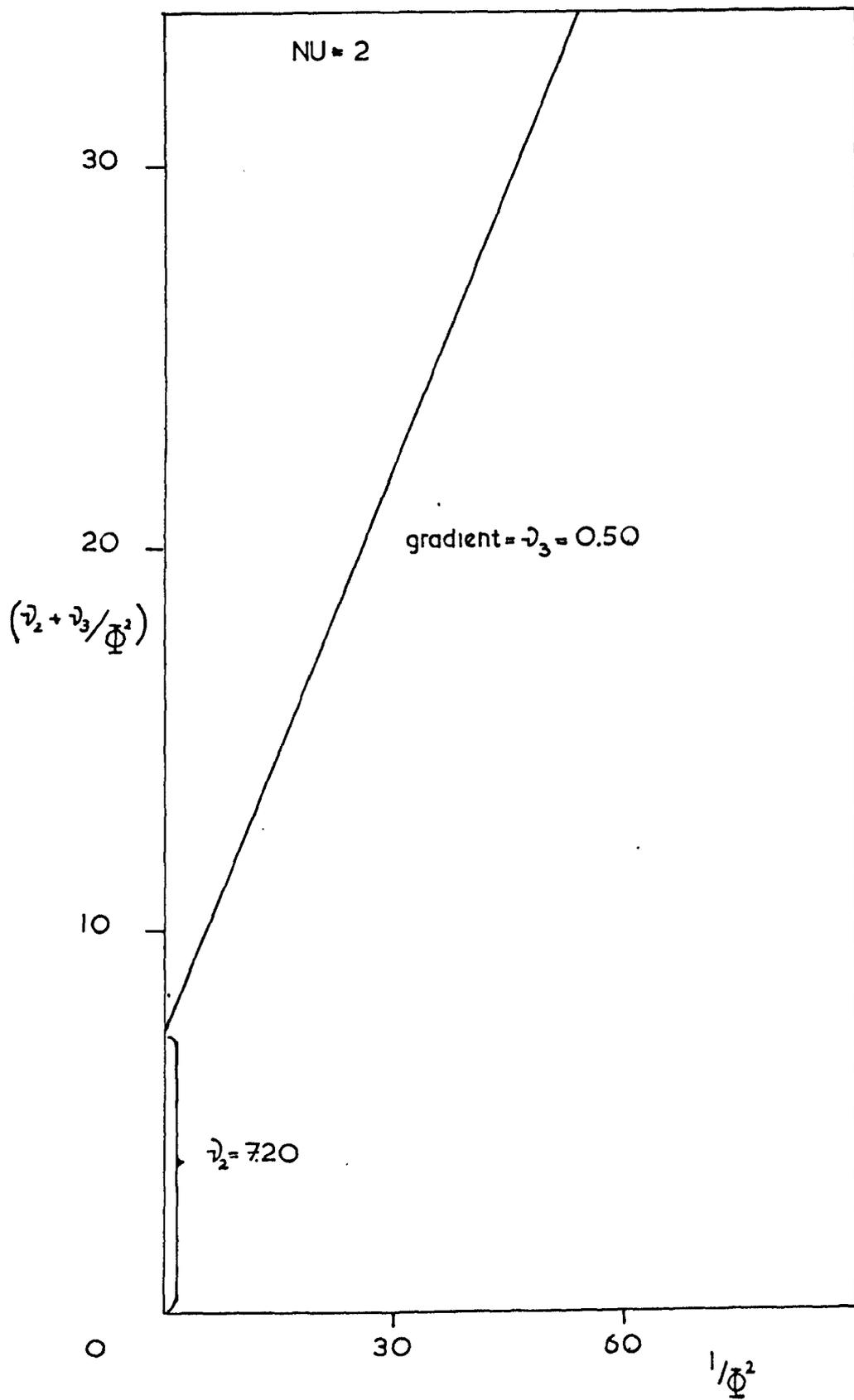
Figure 5.03 . Determination of the coefficients, ν_2 and ν_3.
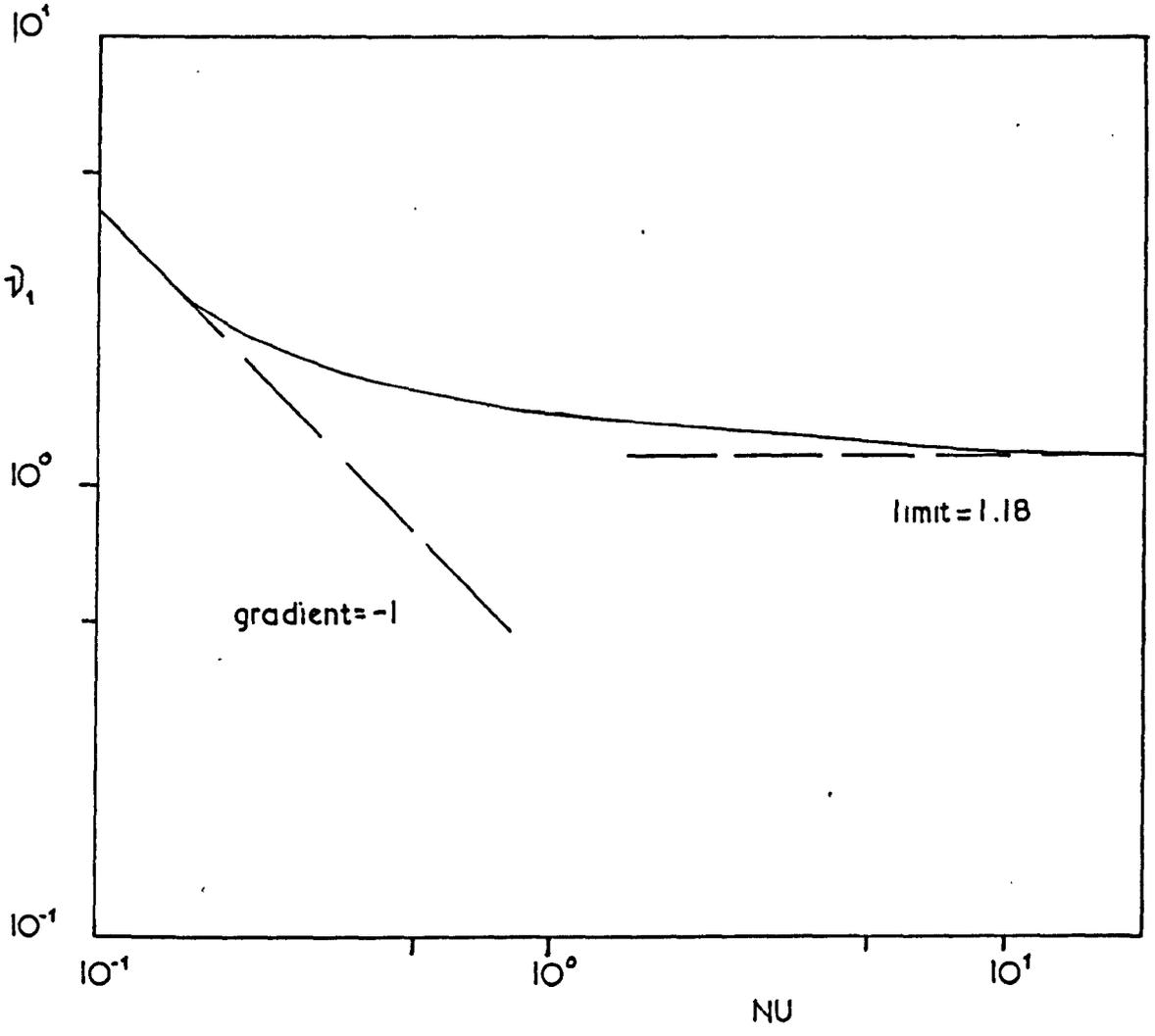
Figure 5.04 . Determination of the general form of
the coefficient, η_1.
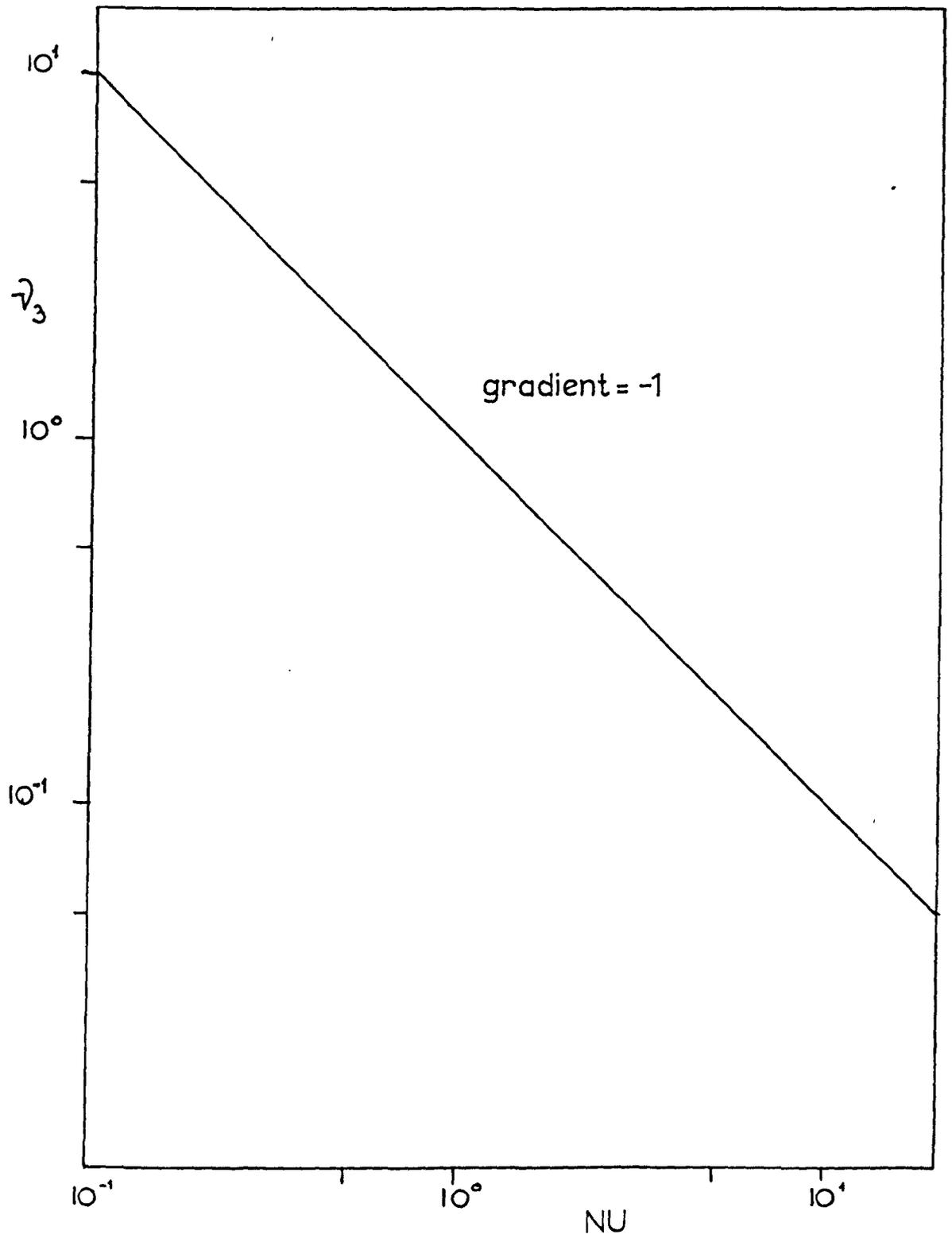
Figure 5.05 . Determination of the coefficient, ν_3.

$$\left(\frac{\nu_2 \ NU \ + \ \nu_4 \ / \ \Phi^2}{NU} \right)$$

which is of the general form given by equation 5.06. If ν_1 is dependent upon NU by the relation,

$$\nu_1 \ = \ \left(\frac{\nu_5 \ NU \ + \ \nu_6}{NU} \right) \hspace{3cm} 5.10$$

then ν_5 and ν_6 are evaluated by plotting ν_1. NU and NU on cartesian co-ordinates, as demonstrated in figure 5.06.

Δc is found to be insensitive to the remaining model coefficients i.e. β, Pe_m and Pe_T, so that the resulting expression for the asymptotic value of Δc may be written as,

$$\frac{\Delta c}{c_m} \ = \ \left(\frac{NU \ (k^* \ (t_m) \ - \ 1)}{1,18 \ k^* \ (t_m) \ (NU \ + \ 0.25) \ + \ 7.2NU \ + \ 1/\Phi^2} \right)^2 \hspace{1cm} 5.11$$

where the value of the constants have been included.

5.4 The Development Function.

As stated in section 5.2, the expression given by equation 5.11 represents the asymptotic form of Δc for the general inlet condition where $k^* \ (t_{mo}) \neq 1$. The type of development function considered for the actual value of Δc from the initial value $\Delta c_i = 0$ to the asymptotic value Δc_a is given by equation 5.08.

$$\Delta c \ = \ \Delta c_a \ (1 \ - \ \exp \ (-\gamma) \ ) \hspace{3cm} 5.12$$

where γ is an axially dependent function which is zero at z = 0. The principal dependent variable of the function γ is the radial mean conversion, $(1 - c_m)$ which has the required initial condition. As may be seen in figure 5.07, which is a graph of $\ln \left(1 - \frac{\Delta c}{\Delta c_a} \right)$
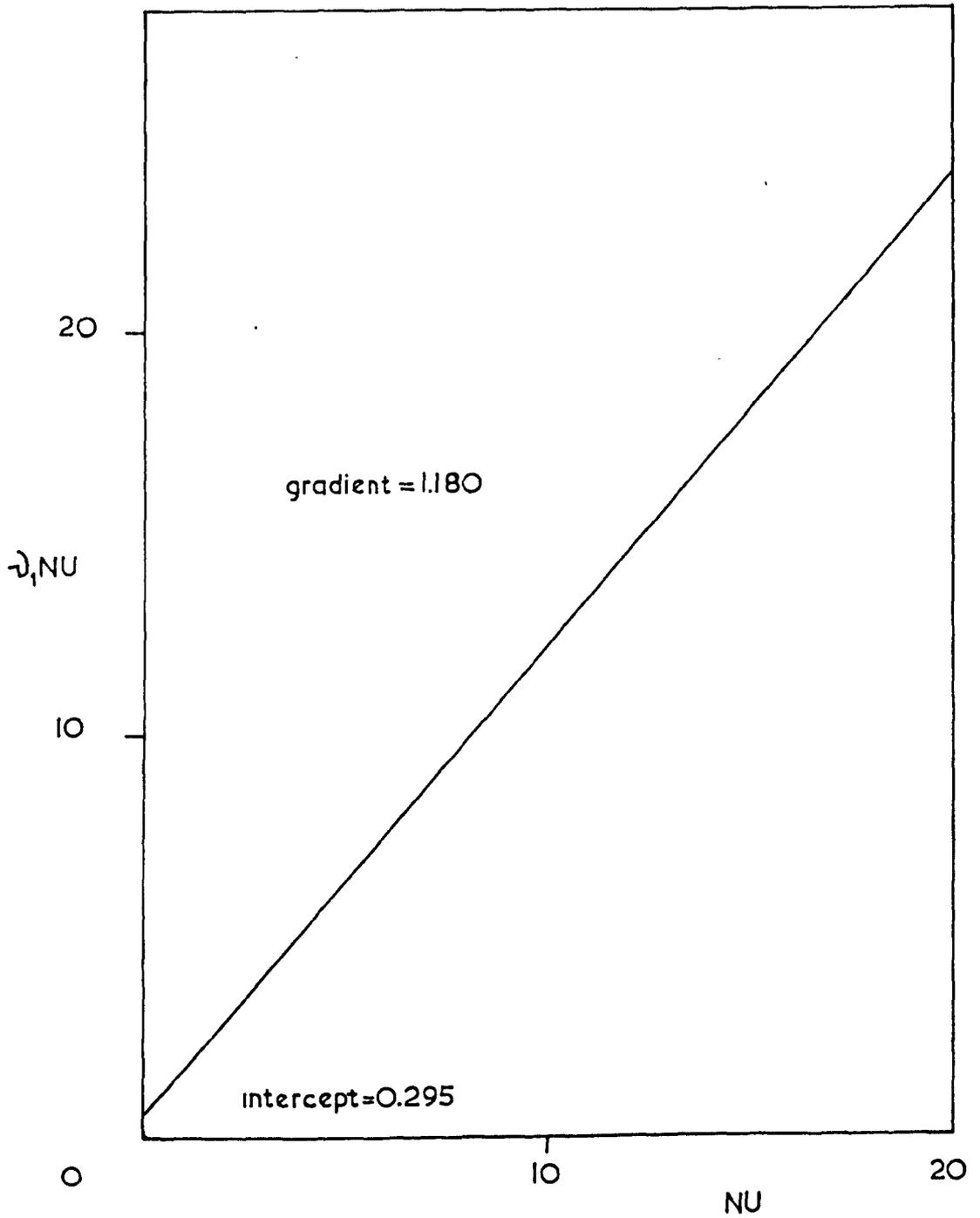
Figure 5.06 . Verification of the functional form
of the coefficient, ν_1.
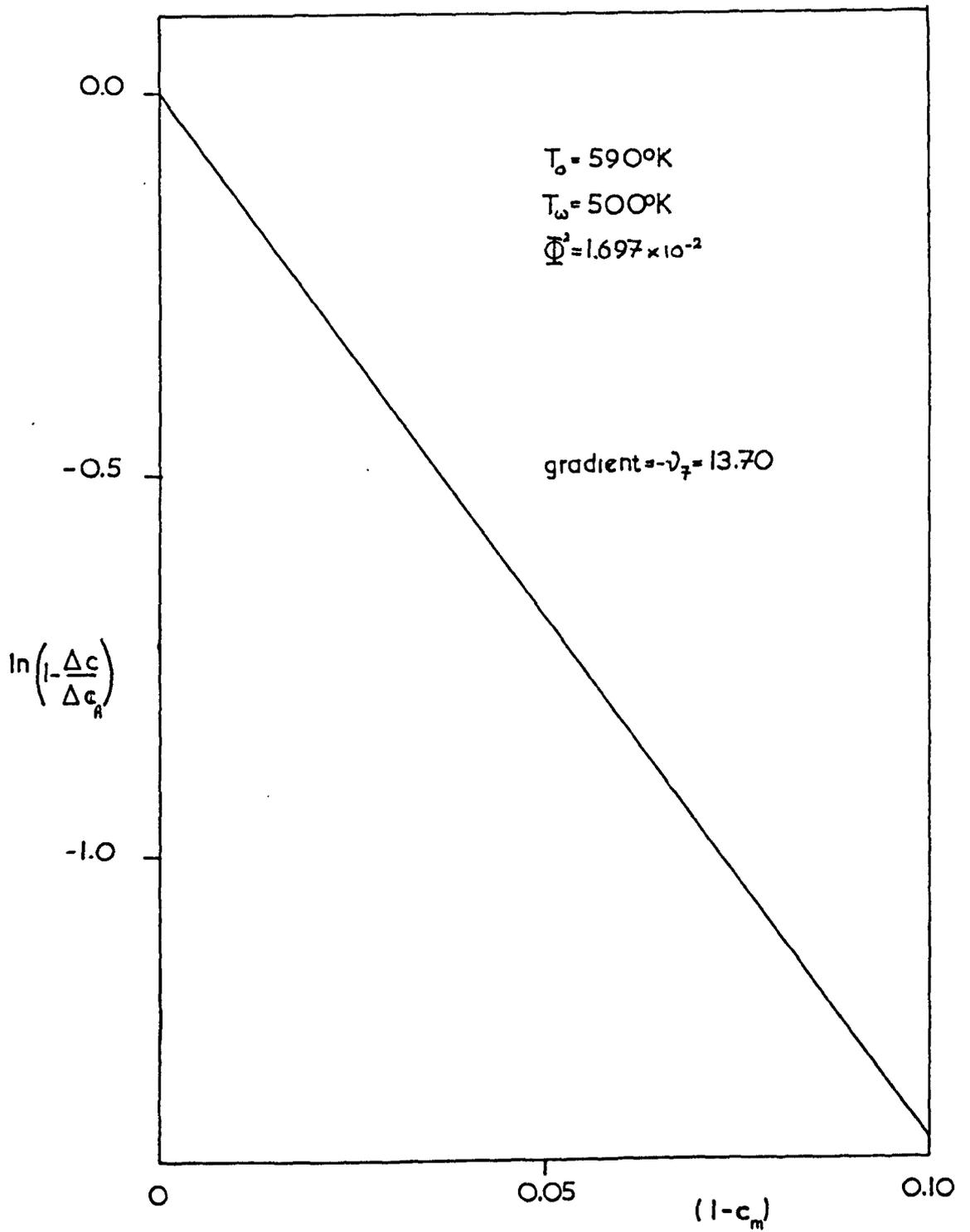
Figure 5.07 . Example of the evaluation of the coefficient, ν_7.

against $(1 - c_m)$, the relationship is linear, i.e.

$$\mathcal{F} = -\mathcal{V}_7 \ (1 - c_m) \qquad\qquad 5.13$$

where $\mathcal{V}_7$ is a coefficient which is dependent upon the model

parameters (as shown below).

5.4.1 Determination of the coefficient, $\mathcal{V}_7$

From figure 5.06, the coefficient, $\mathcal{V}_7$ is constant for any

particular reactor situation when $k^* \ (t_{mo}) = 1$; when $\mathcal{V}_7 = \infty$, as

$\Delta c = \Delta c_a$; and for $k^* \ (t_{mo}) \gg 1$ the process will be mass transfer

limiting, i.e. dependent on Φ^2, so that an expression analogous to

the inverse of Δc is proposed,

$$\mathcal{V}_7 = \left(\frac{\mathcal{V}_8 \ (k^* \ (t_{mo}) - 1) + \mathcal{V}_9 / \Phi^2}{(k^* \ (t_{mo}) - 1)} \right)^n \qquad\qquad 5.14$$

where n is a power and $\mathcal{V}_8$, $\mathcal{V}_9$ are coefficients. In the limit

for decreasing values of $k^* \ (t_{mo}) - 1$, $\mathcal{V}_7 \propto (k^* \ (t_{mo}) - 1)^{-n}$,

so that n may be evaluated by the method described in section

5.31.   The value of the power is found to be 2.   Figure 5.08

verifies the proposed form of $\mathcal{V}_7$ showing that the limiting

conditions are satisfied.   The coefficients $\mathcal{V}_8, \mathcal{V}_9$ are determined

by correlation of $\mathcal{V}_7^{\frac{1}{2}} \ (k^* \ (t_{mo}) - 1)^{-1}$ and $(k^* \ (t_{mo}) - 1)$ as

recounted in section 5.32 and are found to be independent of the

remaining model parameters.   The function $\mathcal{F}$ may now be written,

$$\mathcal{F} = \left(\frac{2.0 \ (k^* \ (t_{mo}) - 1) + 1/\Phi^2}{(k^* \ (t_{mo}) - 1)} \right)^2 (1 - c_m) \qquad\qquad 5.15$$

In comparing this function with the asymptotic functional form of

the overall concentration difference, Δc a similarity can be

seen in that $\mathcal{F}$ is an inverse form of Δc at the reactor inlet

conditions.
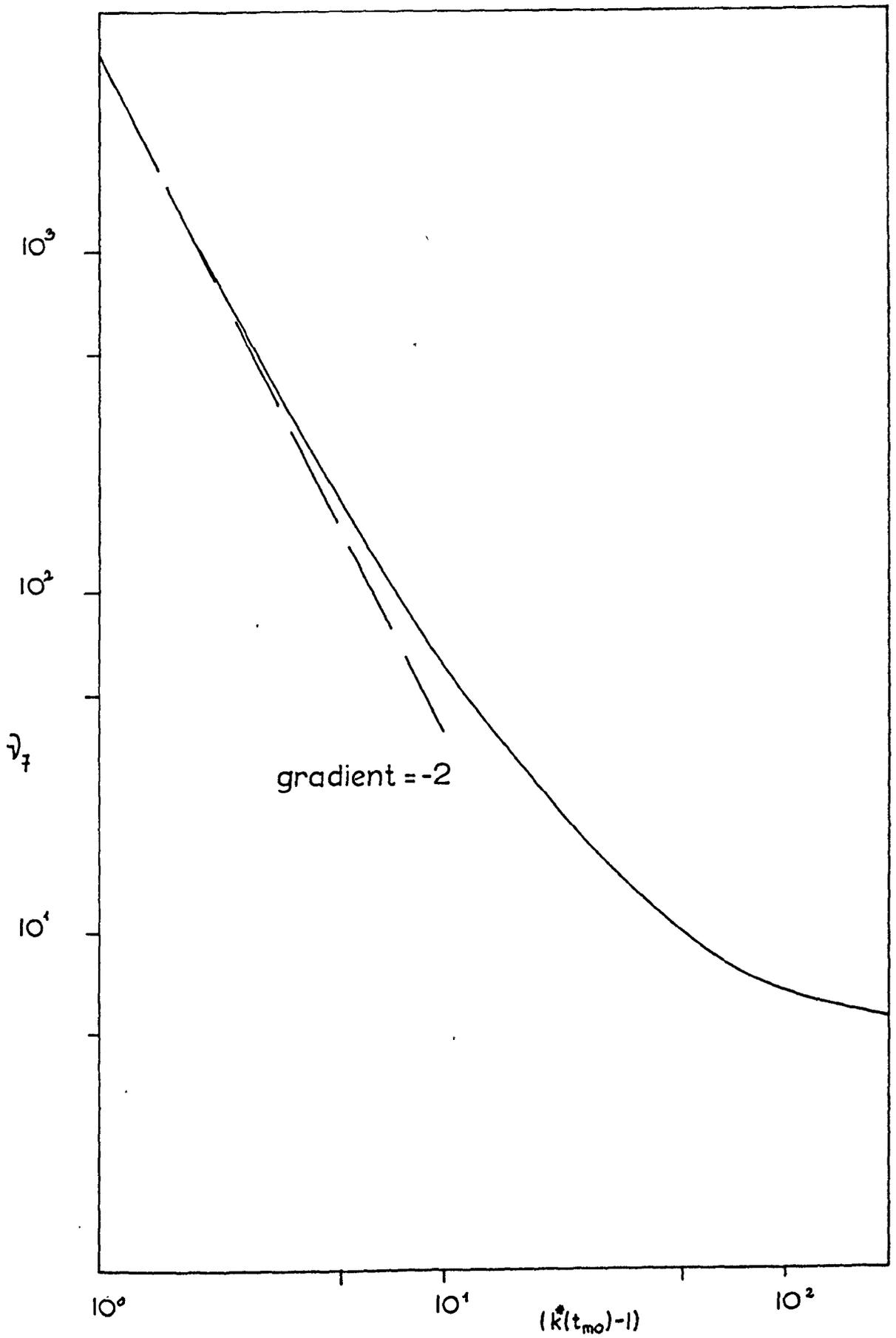
Figure 5.08 . The general functional form of the coefficient, η_7

5.5 Conclusion.

Even though the analysis for the overall concentration difference, Δc is semi-empirical, the resulting expression is generally applicable for any reactor. The basic functional structure is verified by the preliminary theoretical analysis. The expression covers a wide range of conditions; for example over three orders of magnitude of the Nusselt number, NU, (10^{-1} to 10^{1}). The expression is applicable for all conceivable practical values of ϕ^2 as may be seen from figure 5.03 and the fact that when the radial effective diffusivity is infinite, i.e. $\phi^2 = 0$, as would be expected $\Delta c = 0$. When the reactor is adiabatic (NU = 0), Δc is correctly predicted as zero. Although inlet temperature differences of over 100°K have been considered for the analysis of this effect on Δc, practically inlet temperature differences of less than 10°K are usually encountered. Therefore, the expressions derived to predict Δc from the dependent variables of the reduced model, adequately span the possible range of reactor conditions. The only error encountered during the correlations was either statistical i.e. manual errors or manipulative, eg. determining the difference $k^{*} (t_m) - 1$ when $k^{*} (t_m)$ was so close to unity, that round off error became important.

So far Δc has been considered in a physical sense as the overall concentration, but it is used in a more abstract sense with respect to the evaluation of the temperature profile, the effective Nusselt number and the distribution factor. It is considered as reflecting the effect of the presence of an exothermic chemical reaction on the form of the radial profiles.

The functional form of Δc reflects the interdependence on concentration and temperature through the chemical rate expression. Thereafter Δc is therefore no longer considered as a physical quantity, and the semi-empirical expression for Δc can be considered in a new light, i.e. the measure of the interdependence of the concentration and temperature profiles in the presence of an exothermic reaction with respect to the several possible rate limiting processes of heat and mass transfer characterised by Φ^2 and NU.

THE EFFECTIVE NUSSELT NUMBER AND THE DISTRIBUTION FACTOR.

6.1 Introduction.

Both the effective Nusselt number, NU' and the distribution factor, $\mathcal{D}$ were defined in section 4.3 by equations 4.30, 1 which may be rewritten,

$$NU' = NU \left(\frac{t(1) - 1}{t_m - 1} \right) \qquad 6.01$$

and

$$\mathcal{D} = \frac{(\eta \ R^* (c, t))m}{\eta(m) \ R^* (c_m, t_m)} \qquad 6.02$$

The values of these pseudo-parameters must be known in order that the solution of the one-dimensional model equations will be comparable with the two-dimensional model equations, i.e. axial correspondence of the two models.

6.2 The Effective Nusselt Number.

Several workers [16-20] have attempted to derive an expression for the effective Nusselt number, particularly an effective overall heat transfer coefficient, but none have explicitly taken into account the presence of an exothermic chemical reaction or scheme of reactions. In particular it has been assumed in the cases considered that the presence of the exothermic chemical reaction is negligible. In all cases the effective overall heat transfer coefficient has been assumed to be constant with respect to the length of the reactor, whereas if the actual value varies along the reactor length it can be seen that considerable variation can take place as shown in the sketch below (figure 6.01)
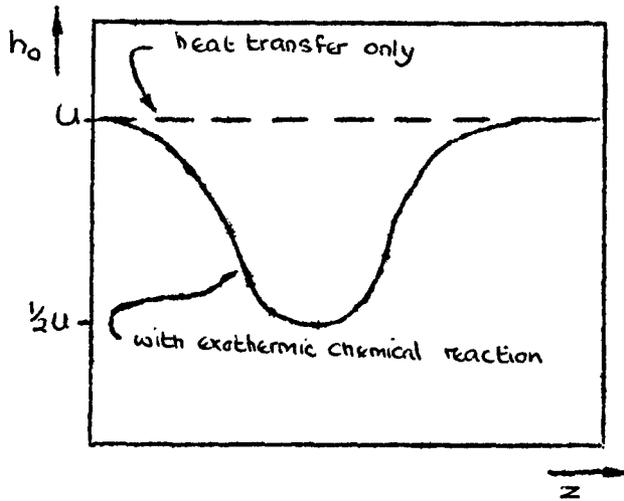
figure 6.01.

The curve shown above is typical for a reactor in which there exists an axial maximum temperature. As the minimum value of the effective overall heat transfer coefficient, h_o generally coincides with the temperature maximum, it is in this region particularly that account must be taken for the axial variation of h_o, and the reason why the gross assumption that $\dot{h}_o$ is constant produces invalid results.

The expression for the effective Nusselt number, NU is derived by making use of the radial temperature profile, which was developed in section 4.43 for the reactor in which an exothermic reaction is taking place, (i.e. equation 4.45).

$$t(y) - 1 = (^{10}/_3 \beta \Delta c \ (1-3y^2 + 2y^3) + 1)\left[\left(\frac{NU}{1.2NU+4}\right)^2 (1-3y^2+2y^3)+ 1\right]$$

$$x \ (\ 1 + 0.5 \ NU \ (1 - y^2) \ ) \ (t(1) - 1)$$

If this relation is substituted in the expression for the radial mean temperature difference,

$$t_m - 1 = 2 \int_0^1 (t(y) - 1) \cdot y \cdot dy$$

and the integral evaluated the radial mean temperature difference and the temperature difference at the tube wall are related by,

$$(t_m - 1) = \left[(1+0.25NU) + \left\{ \left(\frac{NU}{1.2NU+4} \right)^2 + {}^{10}\!/_3 \beta \Delta c \right\} (0.11NU+0.3) \right.$$
$$\left. + {}^{10}\!/_3 \beta \Delta c \left(\frac{NU}{1.2NU+4} \right)^2 (0.47NU+0.17) \right] (t(1)-1) \qquad 6.03$$

When this expression is substituted in equation 6.01 to eliminate $(t_m - 1)$ and $(t(1) - 1)$, the effective Nusselt number is given by,

$$NU' = \left(\frac{NU}{(1+0.25NU)+\left\{ \left(\dfrac{NU}{1.2NU+4} \right)^2 + {}^{10}\!/_3 \beta \Delta c \right\}(0.3+0.11NU)+{}^{10}\!/_3 \beta \Delta c} \times \left(\dfrac{NU}{1.2NU+4} \right)^{(0.17 + 0.47NU)} \right) \qquad 6.04$$

The expression for NU' can thus be generally written as,

$$NU' = \frac{NU}{1 + 0.25NU + P(NU) + Q(NU, \beta \Delta c)} \qquad 6.05$$

where P(NU) is a function of NU only and Q (NU, $\beta \Delta$c) is a function of NU and $\beta \Delta$c and defined by,

$$P(NU) = \left(\frac{NU}{1.2NU+4} \right)^2 (0.30 + 0.11NU) \qquad 6.06$$

$$Q(NU, \beta \Delta c) = \beta \Delta c(0.93 + 0.36NU) + \beta \Delta c \left(\frac{NU}{1.2NU+4} \right)^2 (0.56+1.55NU) \qquad 6.07$$

If P,Q are assumed to be zero or negligible then NU' is the effective Nusselt number for a parabolic temperature profile (or

that predicted by the analytical solution for heat transfer only),
Hence P,Q can be considered to be corrections which allow for the
fact that the temperature profile is not parabolic for the heat
transfer case only and for the presence of an exothermic chemical
reaction which distorts the profile, respectively.   For a
particular value of the Nusselt number, NU, P is constant and Q a
linear function of $\beta \Delta c$.   For a particular set of reactor
conditions, the maximum value of Δc for high values of reaction
rate constant, k^* (t_m) at the mean radial temperature may be
written as,

$$\frac{\Delta c_{max}}{c_m} = \left(\frac{NU}{1.18(NU+0.25)}\right)^2 \qquad\qquad 6.08$$

from equation 5.11.   From this, the maximum value, Q^* of Q may be
expressed as a linear function of βc_m by substitution of Δc_{max} in
equation 6.07.   The term βc_m is the total quantity of heat
available from reaction at the particular axial position. Q^* is
also a function of the Nusselt number NU.   Therefore the maximum
range of values of Q may be determined for a particular reactor
situation expressed as,

$$0 \leqslant Q \ (NU, \beta \Delta c) \leqslant Q^* \ (NU, \beta c_m) \qquad\qquad 6.09$$

where Q^* $(NU, \beta c_m)$ can be determined.   From such an analysis it
can be established whether it is necessary to take account of the
presence of the exothermic chemical reactor in estimating the
effective Nusselt number, NU' for a particular case.   Such a
treatment may enable extra savings in computing time to be made.
In figures 6.01 and 6.02, $(\Delta c_{max} / c_m)$ and $(Q^* / \beta c_m)$ are plotted
against NU.   The function $(Q^* / \beta c_m)$ is approximately linear with
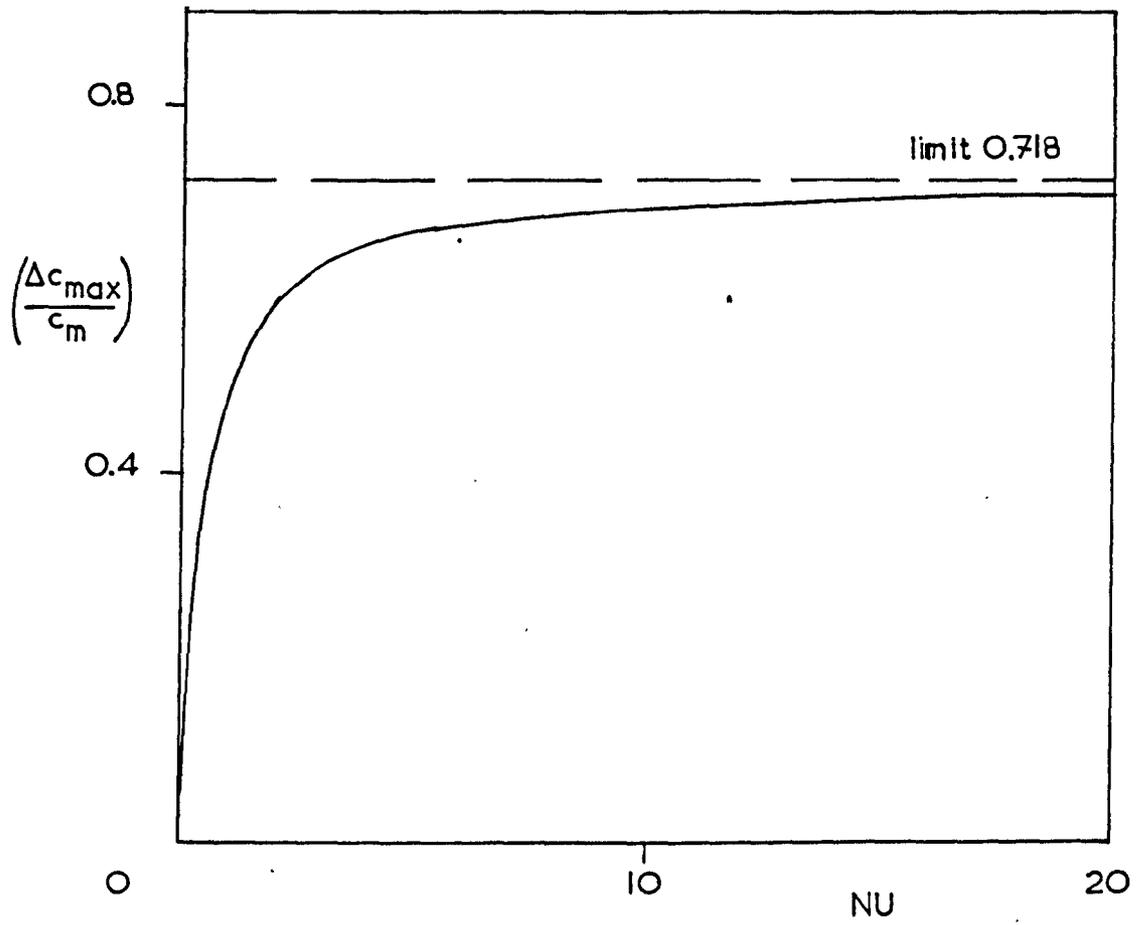
Figure 6.01 . The dependence of Δc_{max} on the
Nusselt number, NU.
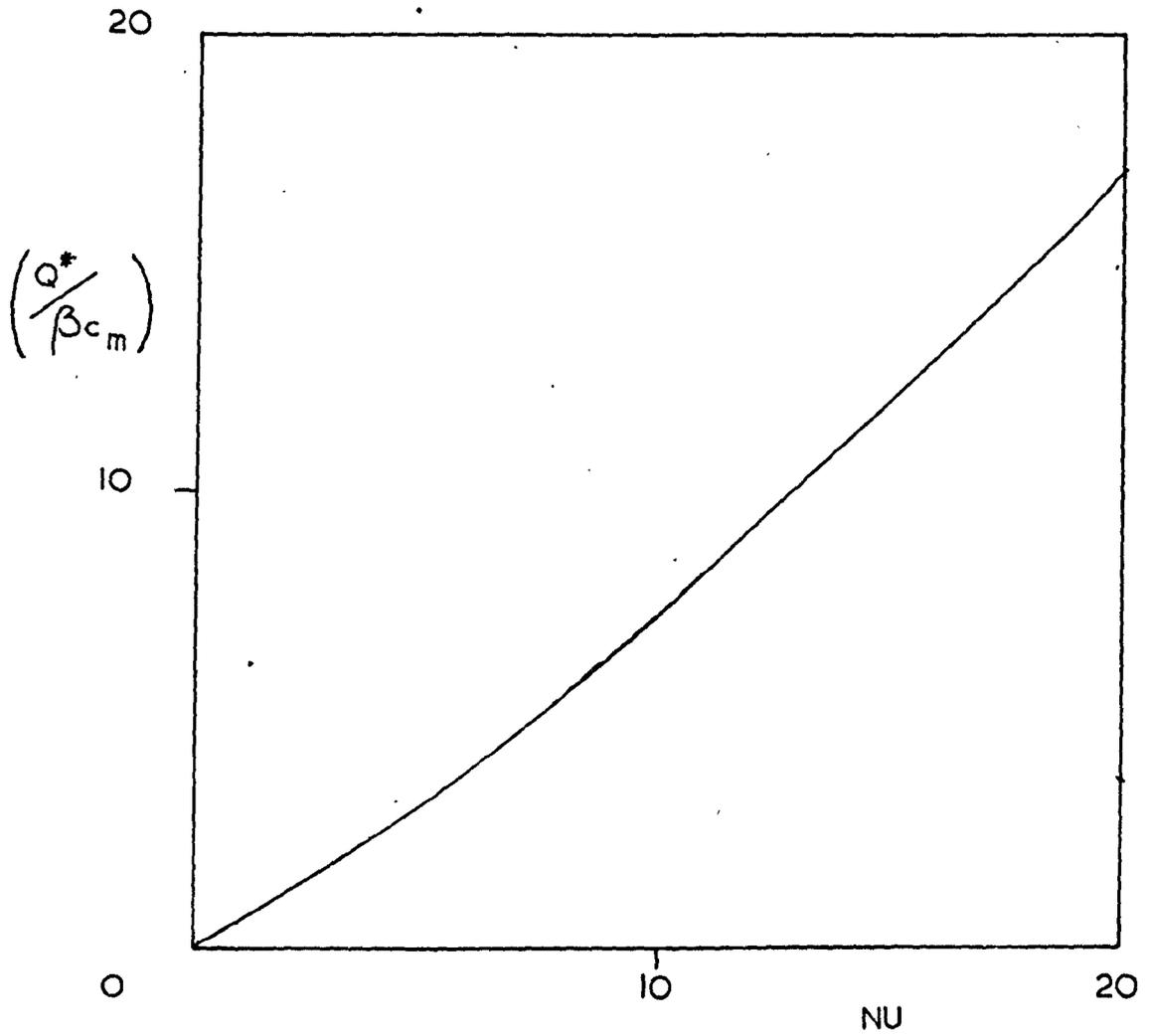
Figure 6.02 . The dependence of the function, Q^* on
the Nusselt number, NU.

respect to NU.

6.3 The Distribution Factor.

The distribution factor, $\mathcal{D}$ is defined in an analogous manner
to the effectiveness factor for the catalyst pellet, i.e. the ratio
of the radial mean reaction rate to the reaction rate at the radial
mean conditions at any axial position. It is a correction factor
for the radial fluid temperature and concentration in the one-
dimensional model. There is no easy method of constructing a
simple algebraic form for it, in terms of the radial mean fluid
values only which complies with the structure of the reduced model.
Indeed, the usually accepted treatment is to assume that the
distribution factor is unity which in some cases is a gross
assumption, as may be seen from figure 6.03 which is a typical plot
of the distribution factor, $\mathcal{D}$, along the reactor length. The
figure also demonstrates the non-linear nature of $\mathcal{D}$ which prevents
a straight-forward prediction of its behaviour.

It is possible to generate the radial reaction rate profile
from the radial temperature and concentration profiles, from which
the radial mean reaction rate can be determined by direct
numerical integration using Simpson's rule. In generating the
reaction rate at each radial node , it is necessary to solve the
pellet equations to determine the effectiveness factor, so that
the reduced model could be said to be degenerating back to a two-
dimensional system. Therefore the number of radial points used
in the radial integration should be kept to a minimum when
evaluating,

$$R_m^* = 2 \int_0^1 R^* (y) \, y \cdot dy. \qquad\qquad 6.10$$
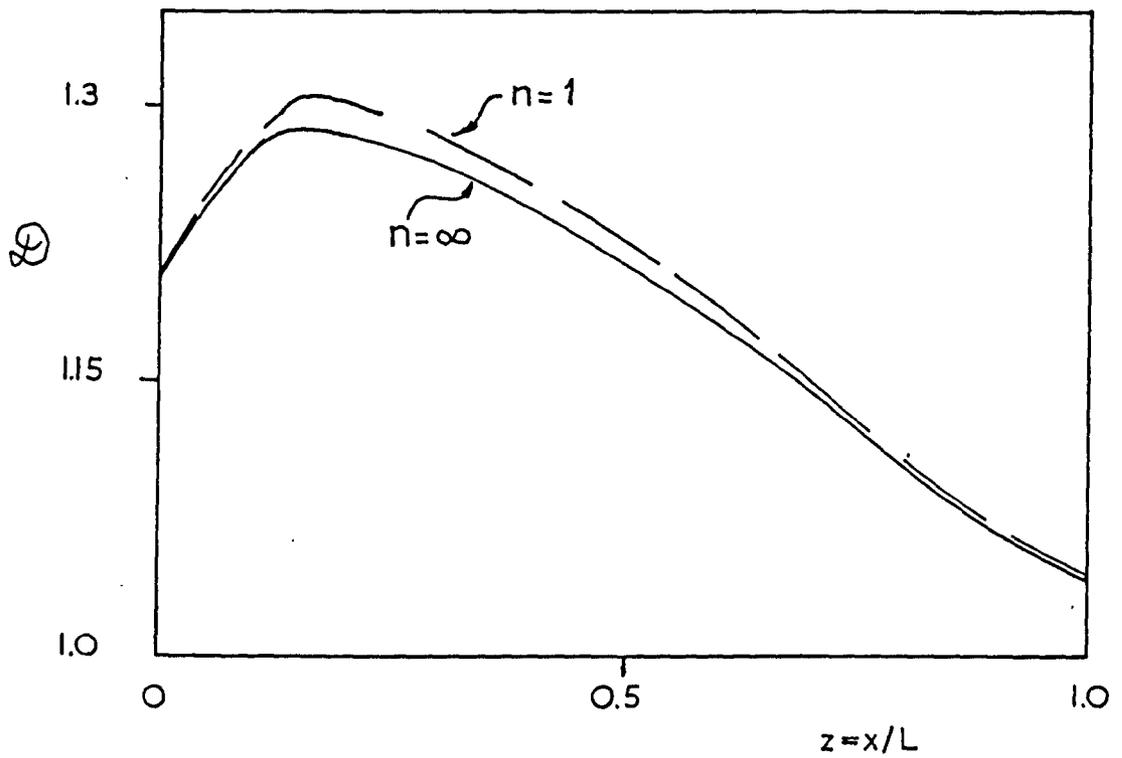
Figure 6.03 . Comparison of the actual and predicted
axial distribution profile.

In the form of Simpson's rule becomes,

$$R_m^* = \frac{1}{12_n^2}\left(2\sum_{i=2}^{2n-2} 4(i-1) R^*\left(\frac{i-1}{2n}\right) + 2_i R^*\left(\frac{i}{2n}\right)\right)$$

where (2n+1) is the number of radial

$$+ \frac{1}{6n}\left(4(2n-1) R^*\left(\frac{2n-1}{2n}\right) + R^*(1)\right) \qquad 6.11$$

positions.

It can be easily seen that it is not necessary to evaluate $R^*(0)$. As Simpson's rule fits the integration curve to a parabola between each three points, and the reaction rate profile can be said to be approximately represented by a parabola, then the value of n, for a reliable result should be small. In fact the difference between $n \approx \infty$ and $n = 1$ is less than 2% for a typical case taken in the region of the temperature maximum. Therefore R_m^* can be adequately predicted from only two values of $R(y)$, using the simplest form of Simpson's integration rule, i.e.

$$R_m^* = \frac{2}{3} R^*\left(\frac{1}{2}\right) + \frac{1}{3} R^*(1) \qquad 6.12$$

and the distribution factor, can be written,

$$\mathscr{D} = \left[\frac{2 R^*\left(\frac{1}{2}\right) + R^*(1)}{3 R^*(m)}\right] \qquad 6.13$$

It is now necessary only to solve the pellet equations at the three radial points at each axial integration step whereas when using the Crank-Nicolson finite difference method to solve the two-dimensional state equations at least 20 radial increments are required for a stable and reliable solution. Figure 6.03 also compares the predicted value from equation 6.13 with the actual

value of the distribution factor along the reactor length. As the reactor data were specifically chosen in order to generate large radial gradients, the situation which has been modelled can be considered to be an extreme case. In the more practical reactor situation, the mean inlet temperature and the coolant temperature are equal or nearly equal, so that the distribution factor is unity at the reactor entrance instead of the relatively high value as shown in the example.

CHAPTER 7

REDUCTION OF THE FIXED BED CATALYTIC REACTOR MODEL

- COMPLEX REACTION SCHEME

$$A \longrightarrow B \longrightarrow C$$
$$\searrow D$$
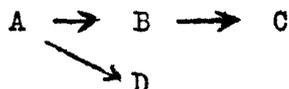
7.1 Introduction.

In Chapter 4, the reaction scheme considered was that for a simple first order irreversible reaction, which in general is not typical of the type of chemical reactions which are normally associated with industrial fixed bed reactors. Nevertheless the analysis was valuable in that it demonstrated that model reduction techniques can be applied to the fixed bed reactor. Considering a more general reaction scheme represented by,

$$A \xrightarrow{1} B \xrightarrow{2} C$$
$$\underset{3}{\searrow} D$$
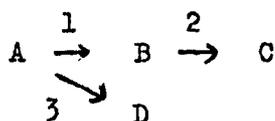
where A is the reactant (in partial oxidation reactions the air is usually in excess and its concentration is effectively constant); B is the desired product for which the process is designed. As catalysts are not generally 100% selective towards the desired product, 'side' reactions occur which for the simplefication of analysis can be lumped into one reaction, where D represents the unwanted products from the side reactions. Finally, B could react further to another set of undesired products, for example by continued reaction with the reactant in excess which could be sequential oxidation, halogenation etc. Then, both competitive and consecutive reactions are occuring.

In this chapter, a reaction scheme of the type described above

is considered, for a first order kinetic system. The techniques, as developed in Chapter 4, for the simple reaction are extended to this system without any increase in the complexity of the reduced model or the functions which describe the radial profiles and the pseudo-parameters.

7.2 The Reactor Model.

The same reactor geometry is considered as in Chapter 4, and the reactor equations are written in the same form except for the introduction of a mass balance for the required product.

Fluid:

$$- G_o \sigma_f \frac{\partial T}{\partial x} + \frac{1}{r} \lambda_f \frac{\partial}{\partial r} \left(r \frac{\partial T}{\partial r} \right) - \frac{3}{b} (1-e) \lambda_p \frac{dTs}{ds} \bigg|_{s=b} = 0 \qquad 7.01$$

$$- \frac{G_o}{\rho_f} \frac{\partial C_A}{\partial x} + D_f \frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial C_A}{\partial r} \right) - \frac{3}{b} (1-e) D_{Ap} \frac{dC_{As}}{ds} \bigg|_{s=b} = 0 \qquad 7.02$$

$$- \frac{G_o}{\rho_f} \frac{\partial C_B}{\partial x} + D_f \frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial C_B}{\partial r} \right) + \frac{3}{b} (1-e) D_{Bp} \frac{dC_{Bs}}{ds} \bigg|_{s=b} = 0 \qquad 7.03$$

Solid:

$$\frac{1}{s^2} \lambda_p \frac{d}{ds} \left(s^2 \frac{dT_s}{ds} \right) + \left(k_1 (-\Delta H_1) + k_3 (-\Delta H_3) \right) C_{As}$$

$$+ k_2 (-\Delta H_2) C_{Bs} = 0 \qquad 7.04$$

$$\frac{1}{s^2} D_{Ap} \frac{d}{ds} \left(s^2 \frac{d C_{As}}{ds} \right) - (k_1 + k_2) C_{As} = 0 \qquad 7.05$$

$$\frac{1}{s^2} D_{Bp} \frac{d}{ds} \left(s^2 \frac{dC_{Bs}}{ds} \right) + k_1 C_{As} - k_2 C_{Bs} = 0 \qquad 7.06$$

where the boundary conditions are,

$$\left. \begin{array}{rcl} T &=& T_{ht}\,(r) \\[4pt] C_A &=& C_{AO} \\[4pt] C_B &=& 0 \end{array} \right\} \quad x = 0, \ 0 \leq r \leq B \qquad\qquad 7.07$$

$$\frac{\partial T}{\partial r} = \frac{\partial C_A}{\partial r} = \frac{\partial C_B}{\partial r} = 0 \quad r = 0, \ 0 \leq x \leq L \qquad\qquad 7.08$$

$$\frac{\partial C_A}{\partial r} = \frac{\partial C_B}{\partial r} = 0 \qquad\quad r = B, \ 0 \leq x \leq L \qquad\qquad 7.09$$

$$-\lambda_f \frac{\partial T}{\partial r} = U\,(T - T_c) \qquad r = B, \ 0 \leq x \leq L \qquad\qquad 7.10$$

$$\left. \begin{array}{l} \dfrac{dT_s}{ds} = \dfrac{dC_{As}}{ds} = \dfrac{dC_{Bs}}{ds} = 0 \qquad\qquad s = 0 \\[14pt] \left. \begin{array}{l} - D_{Ap}\,\dfrac{dC_{As}}{ds} = k_{Ag}\,(C_{As} - C_A) \\[12pt] - D_{Bp}\,\dfrac{dC_{Bs}}{ds} = k_{Bg}\,(C_{Bs} - C_B) \\[12pt] -\lambda_p\,\dfrac{dT_s}{ds} = h_f\,(T_s - T) \end{array} \right\} \ s = b \end{array} \right\} \begin{array}{l} 0 \leq x \leq L \\[4pt] 0 \leq r \leq B \end{array} \quad 7.11$$

where $k_i = k_{oi}\,\exp\left(-E_i/RT_s\right)$

As for the case of the simple first order reaction, McGreavy and Thornton [15] have shown that the catalyst pellet is essentially isothermal with a relatively large temperature rise across the fluid film. Under such conditions it is possible to solve equations 7.05 and 7.06 in terms of the unknown pellet temperature, T_s.

The resulting non-linear algebraic equation is solved to complete the solution. An effectiveness factor, η is defined by the expression,

$$\eta = \frac{4\pi b^2 k_{Ag} (c_A - c_{As=b})}{4/3 \pi b^3 (k_{01} \exp(-E_1/RT) + k_{03} \exp(-E_3/RT)) c_A} \qquad 7.12$$

and for a desired product, B the selectivity, ψ is defined by,

$$\psi = \frac{k_{Bg} (c_{Bs=b} - c_B)}{k_{Ag} (c_A - c_{As=b})} \qquad 7.13$$

The model equations are now rewritten in dimensionless form, incorporating the effectiveness factor and selectivity.

Fluid:

$$- Pe_T \frac{\partial t}{\partial z} + \frac{1}{y} \frac{\partial}{\partial y} \left(y \frac{\partial t}{\partial y} \right) + NU_s (t_s - t)|_{v=1} = 0 \qquad 7.14$$

$$- Pe_m \frac{\partial c_A}{\partial z} + \frac{1}{y} \frac{\partial}{\partial y} \left(y \frac{\partial c_A}{\partial y} \right) - \eta (\phi_1^2 k_1^* + \phi_3^2 k_3^*) c_A = 0 \qquad 7.15$$

$$- Pe_m \frac{\partial c_B}{\partial z} + \frac{1}{y} \frac{\partial}{\partial y} \left(y \frac{\partial c_B}{\partial y} \right) + \eta \psi (\phi_1^2 k_1^* + \phi_3^2 k_3^*) c_A = 0 \qquad 7.16$$

where the boundary conditions are,

$$\left. \begin{array}{l} t = t_{ht} (y) \\[2mm] c_A = 1 \\[2mm] c_B = 0 \end{array} \right\} \quad z = 0, \quad 0 \le y \le 1 \qquad 7.17$$

$$\frac{\partial t}{\partial y} = \frac{\partial c_A}{\partial y} = \frac{\partial c_B}{\partial y} = 0 \quad y = 0, \quad 0 \le z \le 1 \qquad 7.18$$

$$\frac{\partial c_A}{\partial y} = \frac{\partial c_B}{\partial y} = 0 \qquad y = 1, \quad 0 \leq z \leq 1 \qquad\qquad 7.19$$

$$-\frac{\partial t}{\partial y} = NU (t - 1) \qquad y = 1, \quad 0 \leq z \leq 1 \qquad\qquad 7.20$$

At this stage the analysis is concentrated on the fluid field so that the pellet equations 7.04, 7.05 and 7.06 have not been rewritten. The dimensionless model parameters are consistent with the previous definitions. The model is solved as before using the Crank-Nicolson finite difference scheme (see Appendix 2).

7.3 Generalised Reduction of the Reactor Model.

The generalised model reduction is carried out as before by integrating the reactor state equations 7.14, 7.15 and 7.16 with respect to 2.y. dy to eliminate the radial transport terms to give,

$$- Pe_T \frac{dt_m}{dz} - 2 NU (t (1) - 1) + NU_s \left[(t_s - t)\big|_{y=1} \right]_m = 0 \qquad 7.21$$

$$- Pe_m \frac{dc_{Am}}{dz} - \left[\eta (\Phi_1^2 k_1^* + \Phi_3^2 k_3^*) c_A \right]_m = 0 \qquad\qquad 7.22$$

$$- Pe_m \frac{dc_{Bm}}{dz} + \left[\eta \blacktriangledown (\Phi_1^2 k_1^* + \Phi_3^2 k_3^*) c_A \right]_m = 0 \qquad\qquad 7.23$$

where the boundary conditions are,

$$\left. \begin{array}{rcl} t_m &=& t_{mo} \\[2mm] c_{Am} &=& I \\[2mm] c_{Bm} &=& 0 \end{array} \right\} \quad z = 0$$

In order that the reduced model is expressed in terms of radial mean concentration and temperature only, pseudo-parameters are

defined.

The effective Nusselt number, $NU' = NU \left(\dfrac{t(1) - 1}{t_m - 1} \right)$ 7.24

Three distribution factors,

$$\mathcal{D}_T = \frac{\left[(t_s - t)\big|_{v=1} \right]_m}{(t_{sm} - t_m)\big|_{v=1}}$$ 7.25

$$\mathcal{D}_{R1} = \frac{\left[\eta (\Phi_1^2 k_1^* + \Phi_3^2 k_3^*) c_A \right]_m}{\eta(m) \left[\Phi_1^2 k_1^*(m) + \Phi_3^2 k_3^*(m) \right] c_{Am}}$$ 7.26

$$\mathcal{D}_{R2} = \frac{\left[\eta \psi (\Phi_1^2 k_1^* + \Phi_3^2 k_3^*) c_A \right]_m}{\left[\eta(m) \psi(m) (\Phi_1^2 k_1^*(m) + \Phi_3^2 k_3^*(m)) c_{Am} \right]}$$ 7.27

The estimation of the pseudo-parameters is discussed later in this chapter, in section 7.5. The reduced state equations may now be rewritten as,

$$-Pe_T \frac{dt_m}{dz} - 2NU'(t_m - 1) + \mathcal{D}_T NU_s (t_{sm} - t_m)\big|_{v=1} = 0 \quad 7.28$$

$$-Pe_M \frac{dc_{Am}}{dz} - \mathcal{D}_{R1} \eta(m) (\Phi_1^2 k_1^*(m) + \Phi_3^2 k_3^*(m)) c_{Am} = 0 \quad 7.29$$

$$-Pe_M \frac{dc_{Bm}}{dz} - \mathcal{D}_{R2} \eta(m) \psi(m) (\Phi_1^2 k_1^*(m) + \Phi_3^2 k_3^*(m)) c_{Bm} = 0 \quad 7.30$$

(where $k_i^*(m)$ is evaluated at t_m).

The result is a set of non-linear first order ordinary differential equation, and in order to solve them it is necessary to have some knowledge of the radial concentration and temperature profiles.

7.4 Regeneration of Description.

To simplify the analysis, the complex reaction scheme is initially considered decoupled into (1) a competitive and (2) a consecutive reaction scheme, i.e.

(1) $A \xrightarrow{1} B$ (2) $A \xrightarrow{1} B \xrightarrow{2} C$

$ {}_{3}\searrow D$
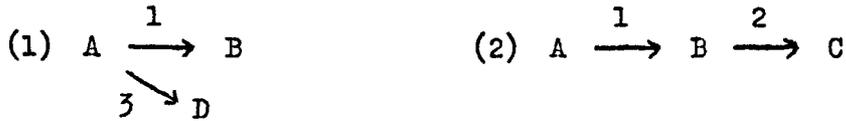
The systems are then combined for the final analysis. The bases for the analysis are the profiles which have been developed for the simple reaction scheme.

7.4.1 The Radial Concentration Profile for the Competitive Reaction Scheme.

The concentration profile for the reactant, A is of the same form as for the simple reaction as would generally be expected and can be written,

$$c_A (y) = \Delta c_A (3y^2 - 2y^3 - 0.7) + c_{Am} \qquad 7.31$$

where Δc_A, the overall radial concentration difference is considered as the composite of the two possible reaction routes, i.e.

$$\Delta c_A = \Delta c_{A1} + \Delta c_{A3} \qquad 7.32$$

Effectively, two simple reactions are being considered which may be summed so that Δc_{A1} and Δc_{A3} are treated as being derived from two different species. This approach is also used later in deriving the functional form of Δc_A. In figure 7.01 a typical comparison is given of the actual radial concentration profile with the profile derived from the expression given in equation 7.31. As can be seen the difference between the two profiles is small.
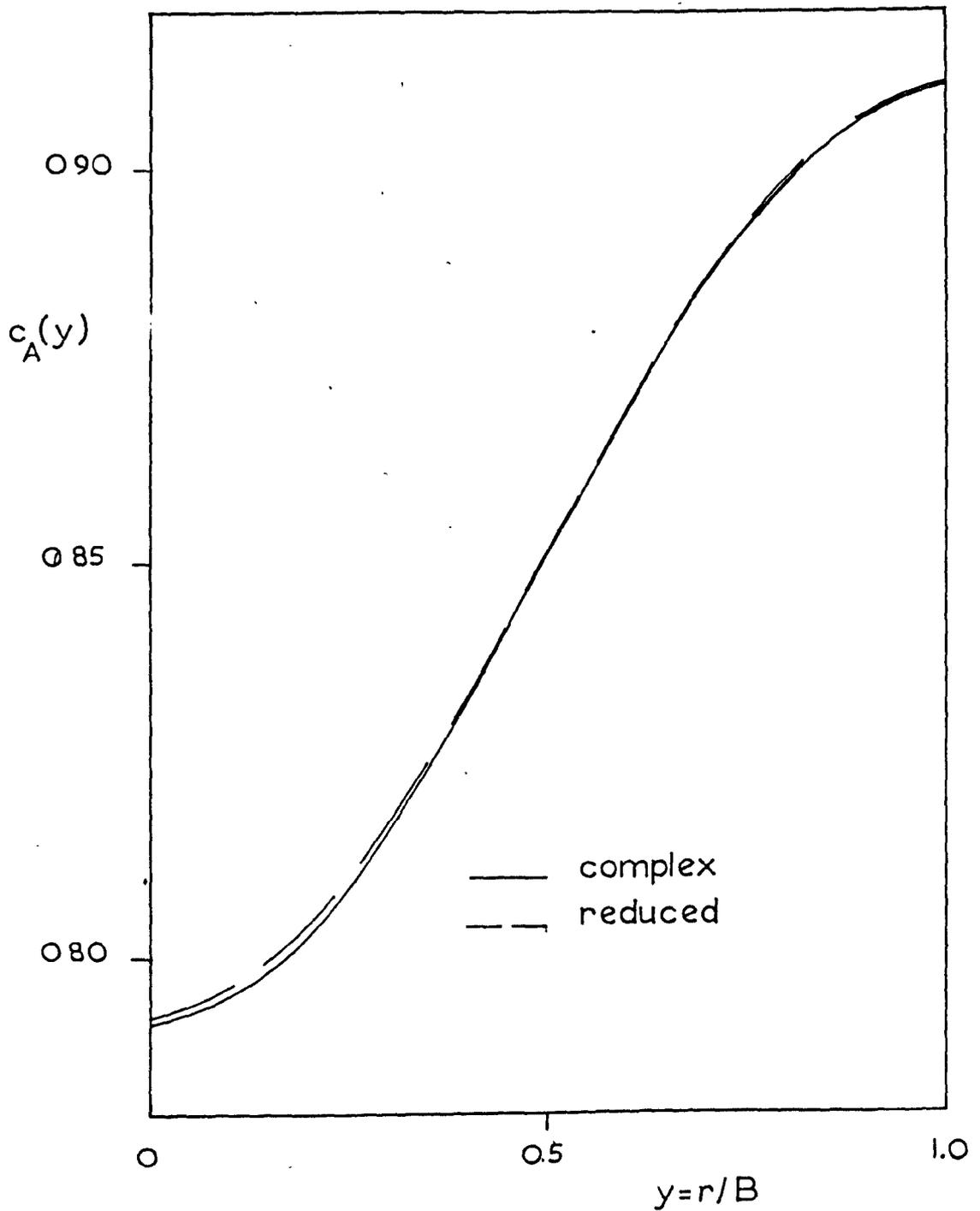
Figure 7.01 . Comparison of the actual and predicted
radial concentration profiles of the
reactant, A.

As stated above, Δc_{A1} and Δc_{A3} are considered as being derived from two separate reactions and by inspection of Δc_B and Δc_D, which correspond to the above values respectively, under various reactor conditions for a differing range of kinetic data, the general expression for Δc_{A1} and Δc_{A3} may be derived by carrying out the analysis described in Chapter 5 on both Δc_B and Δc_D,

$$\frac{\Delta c_{A1}}{c_{Am}} = \left(\frac{NU \left(k_i^* (t_m) - 1 \right)}{1.18 \, k_i^* (t_m) (NU + 0.25) + 7.2 \, NU + 1/\Phi_i^2} \right)^2 \qquad 7.33$$

together with the analogous expression accounting for the entrance effects. This result is reasonable as the following equation shows,

$$\Delta c_A = \Delta c_{A1} + \Delta c_{A3} \sim \eta(o) \left(R_1^* (0) - R_1^* (1) \right) \Phi_1^2 + \eta(o) \left(R_3^*(0) - R_3^*(1) \right) \Phi_3^2 \qquad 7.34$$

which is analogous to equation 5.01 in Chapter 5.

7.4.2 The Radial Concentration Profile for the Consecutive Reaction Scheme

Consider the reaction scheme,

$$A \xrightarrow{\ 1\ } B \xrightarrow{\ 2\ } C$$
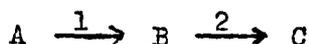
the concentration profile of the reactant, A will obviously be that for the simple reaction considered in Chapter 4. If reaction 2 in the scheme did not take place then the concentration profile of the desired product, B would be the mirror image of that of the reactant A. At the stage when reaction 1 becomes less than reaction 2, then the radial concentration profile of the product, B will approach the form of the reactant A. Therefore, it would

be expected that the radial concentration profile of the desired product B will be in the form of a cubic function, but the value of the overall concentration difference could possibly change sign at around the stage where the overall concentration of B is a maximum. In fact from observation of actual profiles the functional form of the concentration profile behaves as expected, except near the region where the overall concentration difference changes sign, but as it approaches zero then the error is negligible. Then the functional form of the radial concentration profile of B may be written,

$$c_B (y) = \Delta c_B (3y^2 - 2y^3 - 0.7) + c_{Bm} \qquad 7.35$$

This profile is compared with the actual profiles for various stages of the reaction in figure 7.02.

It is now necessary to formulate a general expression for the overall radial concentration difference of the desired product B, Δc_B. A simple relationship is considered as before, i.e.

$$\Delta c_B \sim - \Phi_1^2 (R_1^* (0) - R_1^* (1)) + \Phi_2^2 (R_2^* (0) - R_2^* (1)) \qquad 7.36$$

and using the selectivity ψ ,

$$\Delta c_B \sim - \Phi_1^2 (\psi(0) R_1^* (0) - \psi(1) R_1^* (1)) \qquad 7.37$$

This is now assumed to take the more convenient form,

$$\Delta c_B \sim - \psi (m) \Phi_1^2 (R_1^* (0) - R_1^* (1)) \qquad 7.38$$

which may be rewritten,

$$\Delta c_B \simeq - \psi (m) \Delta c_A \qquad 7.39$$
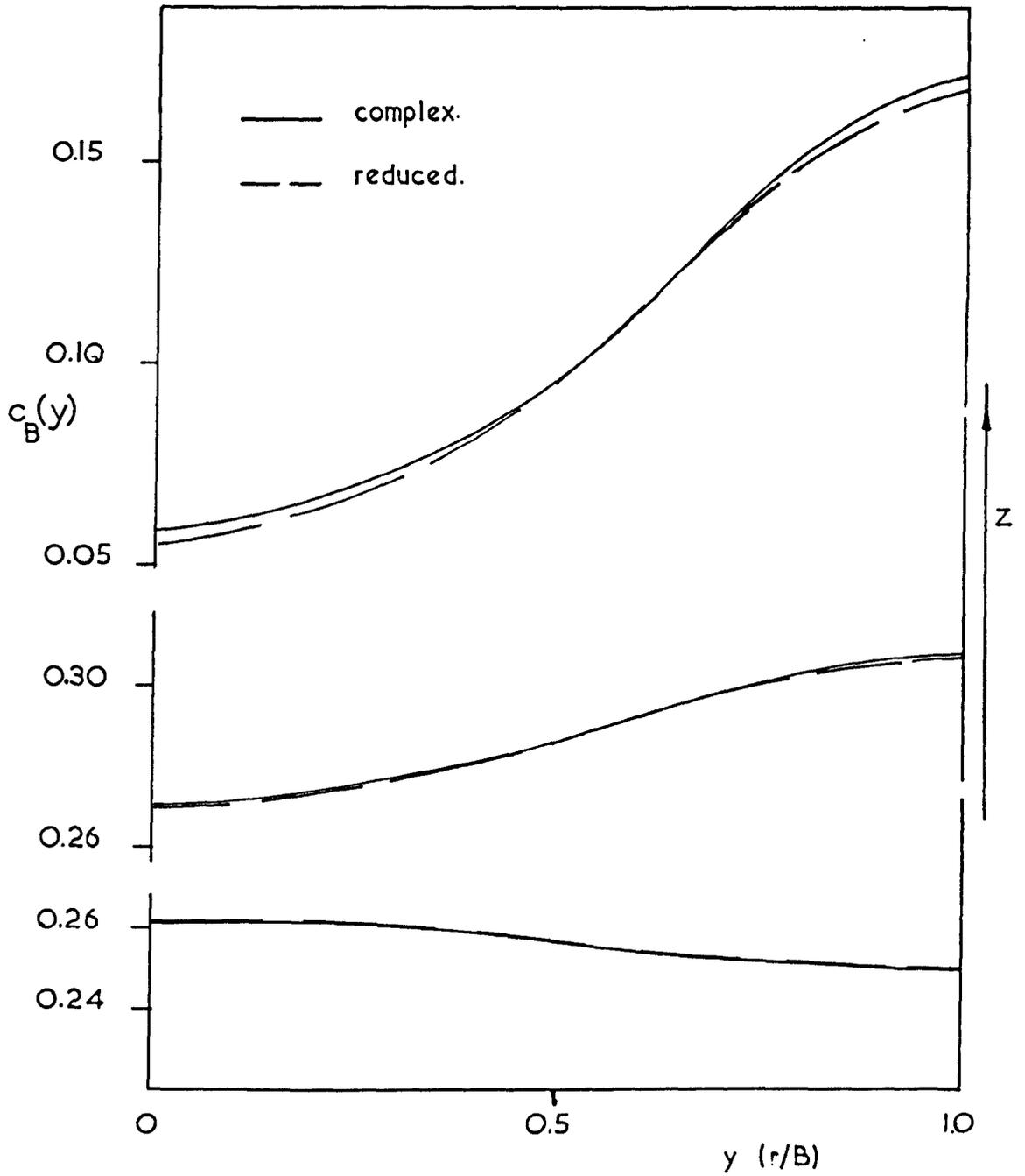
Figure 7.02 . Comparison of the actual and predicted
radial concentration profiles of the
desired product, B.

where $\psi(m)$ is evaluated at the radial mean conditions. This relationship is tested in figure 7.03. The maximum deviation from this relationship occurs where $\psi(m) = 0$, which is also the region in which the predicted profile deviates most from the actual profile; but the expression given in equation 7.39 provides an adequate and simply formulated prediction for Δc_B which is in terms of the reduced model parameters. Indeed when the complete reaction scheme is considered, this relationship still holds.

7.4.3 The Radial Concentration Profile for the Combined Reaction Scheme.

The analysis of sections 7.4.1 and 7.4.2 are now conjoined in order to consider the complete complex reaction scheme. Then, the concentration profiles for the reaction scheme, $A \xrightarrow{1} B \xrightarrow{2} C$, $\xrightarrow{3} D$

may be represented by,

$$c_A (y) = \Delta c_A (3y^2 - 2y^3 - 0.7) + c_{Am} \qquad 7.40$$

where $\Delta c_A = \Delta c_{A1} + \Delta c_{A3}$ and both Δc_{A1} and Δc_{A3} are estimated from equation 7.33.

$$c_B (y) = \Delta c_B (3y^2 - 2y^3 - 0.7) + c_{Bm} \qquad 7.41$$

where $\Delta c_B = - \psi(m) \Delta c_A \qquad 7.42$

These are essentially the results from the previous two sections.

7.4.4 Comments on the Radial Concentration Profiles.

Although it is not a constraint of the complex reactor model that it should provide a description of the radial concentration profile, i.e. it is only necessary to know the mean radial value for any function of the model, an extensive analysis of the profiles
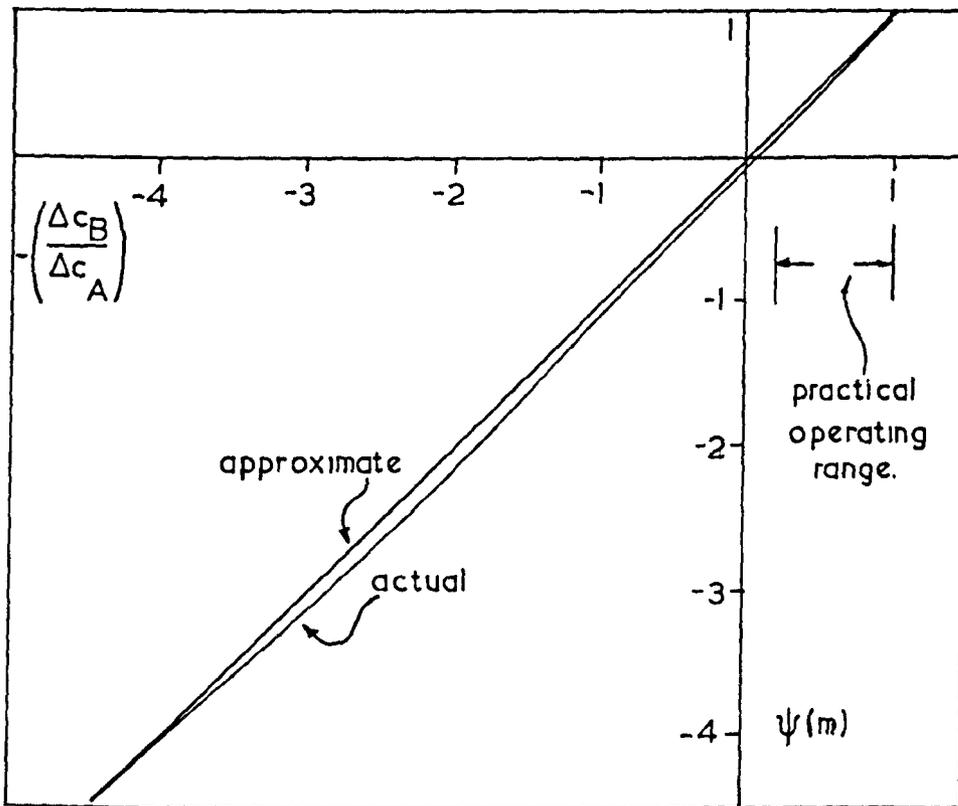
Figure 7.03 . Prediction of the pseudo-parameter,Δc_B.

has been made in the previous sections which must be justified.
As the values of the distribution factors are estimated
numerically by integration of the radial reaction rate profile
with respect to 2.y. dy, which has previously been constructed
from the concentration and temperature profiles for a
predetermined set of radial points, it becomes obvious why it has
been necessary to produce functional representations of the radial
concentration profiles. As the reduced model is not extremely
sensitive to the accuracy of the estimations of the distribution
factor, (the effective Nusselt number is the most important term),
then it is unnecessary to go to extreme lengths to predict a very
accurate value of the radial concentration, when the only
requirements are that the profiles should exhibit all the essential
characteristics to a reasonable degree of accuracy.

The values of the overall radial concentration difference
play an important role in predicting the radial temperature profile,
hence it is necessary to provide a reliable estimate of their
values, as the effective Nusselt number is directly related to the
temperature profile. Therefore the prediction of the radial
concentration difference in its abstract sense, (i.e. the effect
of the presence of an exothermic reaction) is biassed towards its
role in the generation of the temperature profile rather than the
concentration profile.

7.4.5 The Radial Temperature Profile for the Competitive
       Reaction Scheme.

If the heat balance for the reactor is considered for the
general reaction scheme, i.e. equation 7.14, a total amount of
heat is considered to be gained from the exothermic chemical

reactions through heat transfer at each radial position. So that, effectively with respect to the fluid, only one reaction is occuring which will affect the form of the radial temperature profile. Consequently in the particular case for the competitive reaction scheme, the two forward reactions could perhaps be considered as a ~~simple~~ single heat source.

A correction function, f_3 (y) is defined in a similar manner to that of f_2 (y) in section 4.4.3, i.e.

$$f_3 \ (y) \ = \ \left[\left(\frac{t(y) - 1}{t(y)_{ht} - 1} \right) - 1 \right] \qquad 7.43$$

where $t(y)$ is the radial temperature profile for the competitive reaction scheme. The function f_3 will have the same boundary conditions as f_2, written as,

$$f_{3cm} \ (1) \ = \ 0$$
$$f'_{3cm} \ (0) \ = \ f'_{3cm} \ (1) \ = 0 \qquad 7.44$$

where again $t(1)$ is the reference temperature. As would be expected f_3 has the same functional form as f_2,

$$f_3 \ (y)_{cm} \ = \ w_5 \ (1 - 3_y{}^2 \ + \ 2_y{}^3) \qquad 7.45$$

and w_5 is the axially dependent coefficient. For the limiting cases where reactions one and three are zero, then from the analysis in section 4.4.3 w_5 will take the values,

$$w_5 = {}^{10}/3 \beta_3 \ \Delta c_3 \qquad , \qquad \text{reaction 1 = 0}$$
$$w_5 = {}^{10}/3 \beta_1 \ \Delta c_1 \qquad , \qquad \text{reaction 3 = 0} \qquad 7.46$$

The simplest combination for the case is,

$$w_{5cm} = {}^{10}/3 \, (\beta_1 \Delta c_1 + \beta_3 \, \Delta c_3) \qquad\qquad 7.47$$

This relationship is simply tested by a plot of

w_{5cm} and ${}^{10}/3 \, (\beta_1 \Delta c_1 + \beta_3 \, \Delta c_3)$ for various values of

β_1, β_3 (see figure 7.04), the gradient being unity, and the line

passes through the origin.

As mentioned earlier in this chapter, reaction three is

considered to represent the several possible side reactions which

have been lumped into one for the sake of simplifying the analysis.

The form of equation 7.47 lends itself to this approach so that the

reaction three term could be written,

$$\beta_3 \Delta c_3 = \sum_{i=1}^{n} \beta_i \Delta c_i \qquad\qquad 7.48$$

where n is the number of side reactions, and the reaction term in

the heat balance state equation has an equivalent form,

$$\beta_3 \, R_3 \,(c,t) = \sum_{i=1}^{n} \beta_i \, R_i \,(c,t). \qquad\qquad 7.49$$

It may be seen that these expressions are analogous, so that it is

possible to predict the form of the coefficient, w_{5cm} by inspection

of the heat generation term in the heat balance and replacing the

rate term $R_i \,(c, t)$. by Δc_i.

7.4.6 The Radial Temperature Profile for the Consecutive Reaction Scheme.

As in section 7.4.2, the effect of the first reaction of the

consecutive scheme is that of the simple reaction on the

temperature profile as described in section 4.43, so that if the

exothermicity, β_2 of the second reaction is zero, the correction
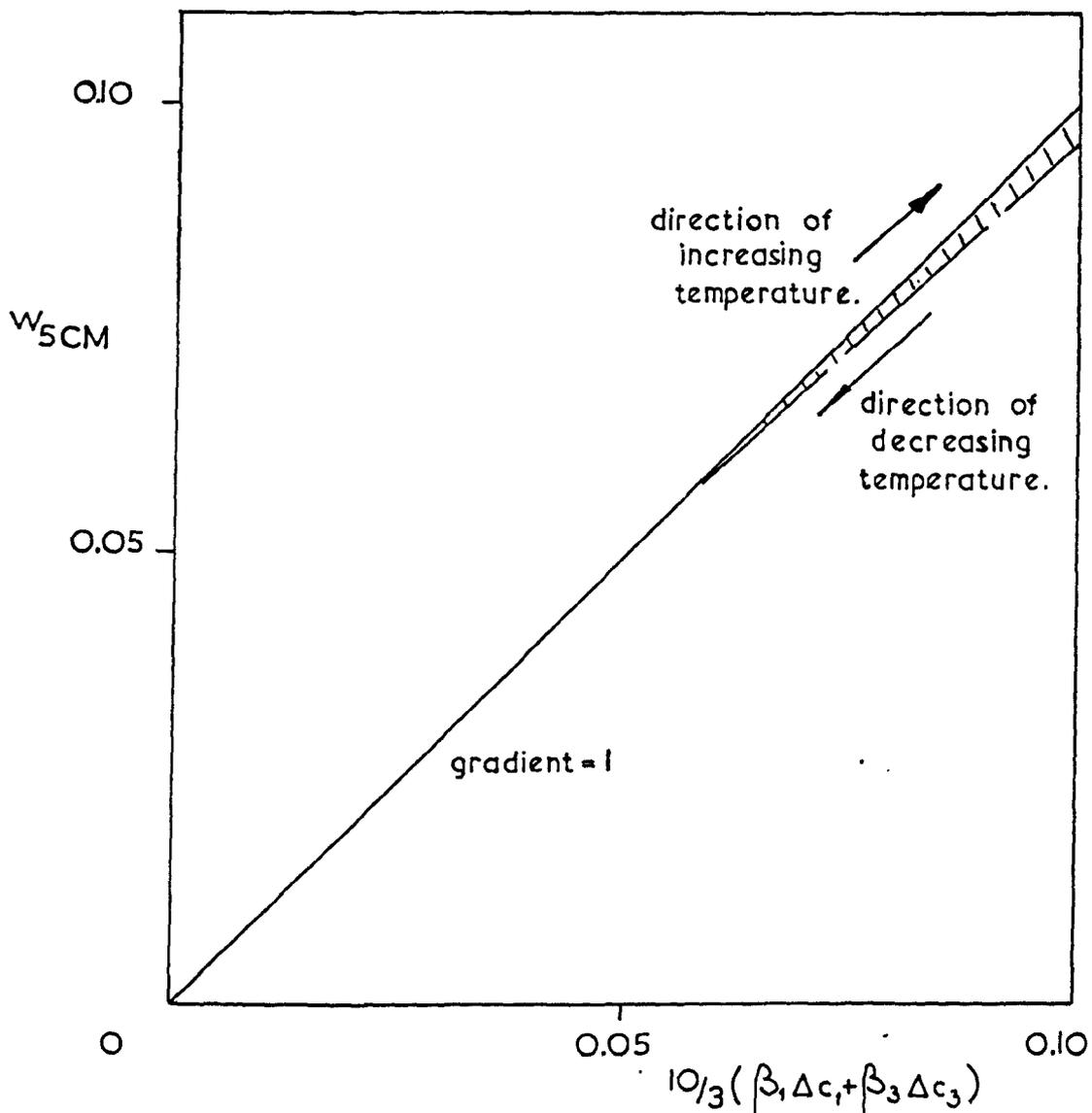
Figure 7.04 . Prediction of the coefficient w_5 for
a competitive reaction scheme.

function f_3 will be,

$$f_3 (y) = {}^{10}/3 \beta_1 \Delta c_A (1 - 3_y{}^2 + 2y^3) \qquad 7.50$$

The major interest of this section is the effect of the second reaction on the form of the temperature profile when $\beta_2 \neq 0$. It would be expected from the previous analysis the term $(\beta_2 \Delta c_B)$ in some form will represent the effect of the second reaction on the functional form of the correction function, f_3. The behaviour of f_3 and w_5 is observed for a case where $\beta_1 = \beta_2$, so that each reaction stage has a comparable and measurable effect and the value of Δc_B changes sign over the reactor length. By observation, when $(\beta_2 \Delta c_B)$ is negative, (i.e. when Δc_B is negative), the effect of reaction two is additive to that of reaction one on the coefficient, w_5; the converse is also true, when $\beta_2 \Delta c_B$ is positive. Consider figure 7.05 (a & b), which diagramatically shows the two above cases, from which it is possible to physically explain the above observations. When Δc_B is negative (figure 7.05 (a)), the rate of heat generation of the second reaction will be greater at the tube axis than at the tube wall, and hence will add to the distortion of the temperature profile. Conversely when Δc_B is positive this would expect the effect of the second reaction to be negative. It must be noted here that in order for Δc_B to change sign the heats of reaction must be very high and the reaction allowed to go towards completion (i.e. the product goes through its maximum value), so that this region is of more academic than practical interest. Δc_B changes sign as the rate of loss of c_B exceeds the rate of production of c_B.
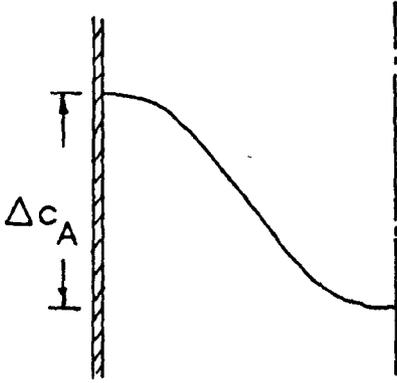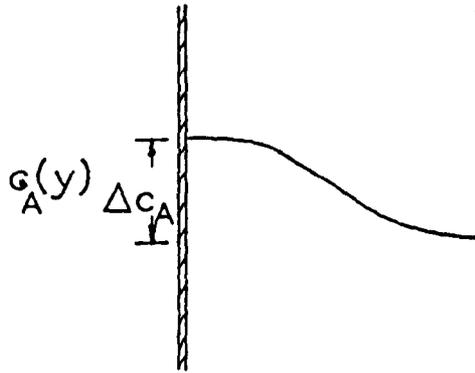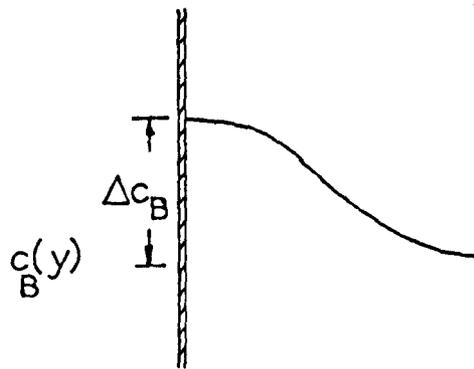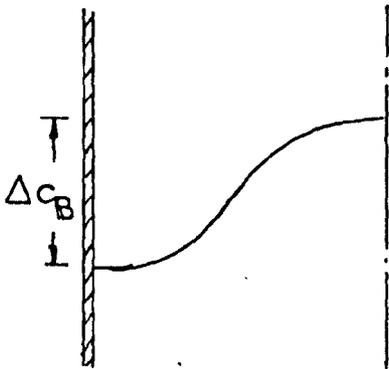
Figure 7.05 . Diagramatic representation of the limiting effects the consecutive reaction scheme.

The functional form of f_3 still closely approximates to the cubic form, and as would be expected, the greatest deviation occurs when w_5 changes sign, although at this stage the absolute value of w_5 is close to zero (see fig. 7.06). The simplest form which could be expected for w_5 would be,

$$w_{5_{CN}} = {}^{10}/3 \left(\beta_1 + \beta_2 \psi(m) \right) \Delta c_A \qquad 7.51$$

(where $\Delta c_B = - \psi(m) \Delta c_A$) so that $w_{5_{CN}}$ and ${}^{10}/3 \left(\beta_1 + \beta_2 \psi(m) \right) \times \Delta c_A$ are correlated for various values of β_1 and β_2 to test the relationship. As in the last section the line should have unity gradient and pass through the origin (see fig. 7.07).

Summarising, the correction function, f_3 retains the same functional form with respect to the radial dimension, y, and w_5 maintains a simple algebraic relation to Δc_A and Δc_B, i.e.,

$$f_3(y)_{CN} = {}^{10}/3 \left(\beta_1 \Delta c_A - \beta_2 \psi(m) \Delta c_A \right) (1 - 3y^2 + 2y^3) \qquad 7.52$$

7.4.7 The Radial Temperature Profile for the Combined Reaction Scheme.

The reaction schemes of the two previous sections are now combined for the general reaction schemes. As shown in section 7.4.5, the effects of all primary reactions (i.e. the first stages of each sequential reaction scheme), it would be expected that the effects of the competitive and consecutive reaction on the correction function, f_3 are merely additive with respect to the coefficient, w_5, and also the functional form of f_3 is the same in all cases with respect to the radial coordinate, y. Therefore for the reaction scheme,

$$A \longrightarrow B \longrightarrow C$$
$$\searrow D$$
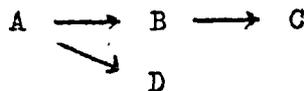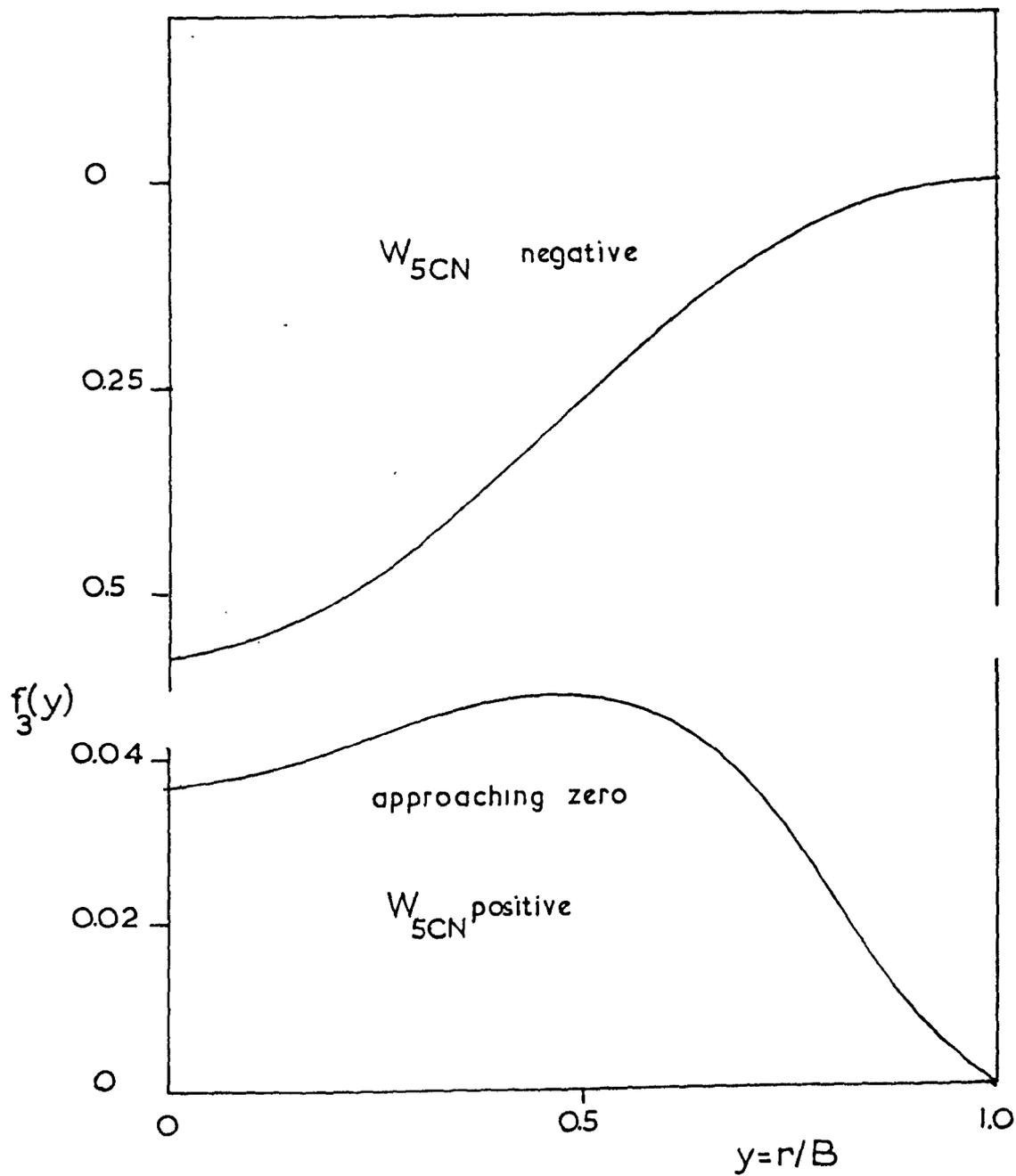
Figure 7.06 . The functional form of the correction

function, f_3 in the region in which W_5

changes sign.
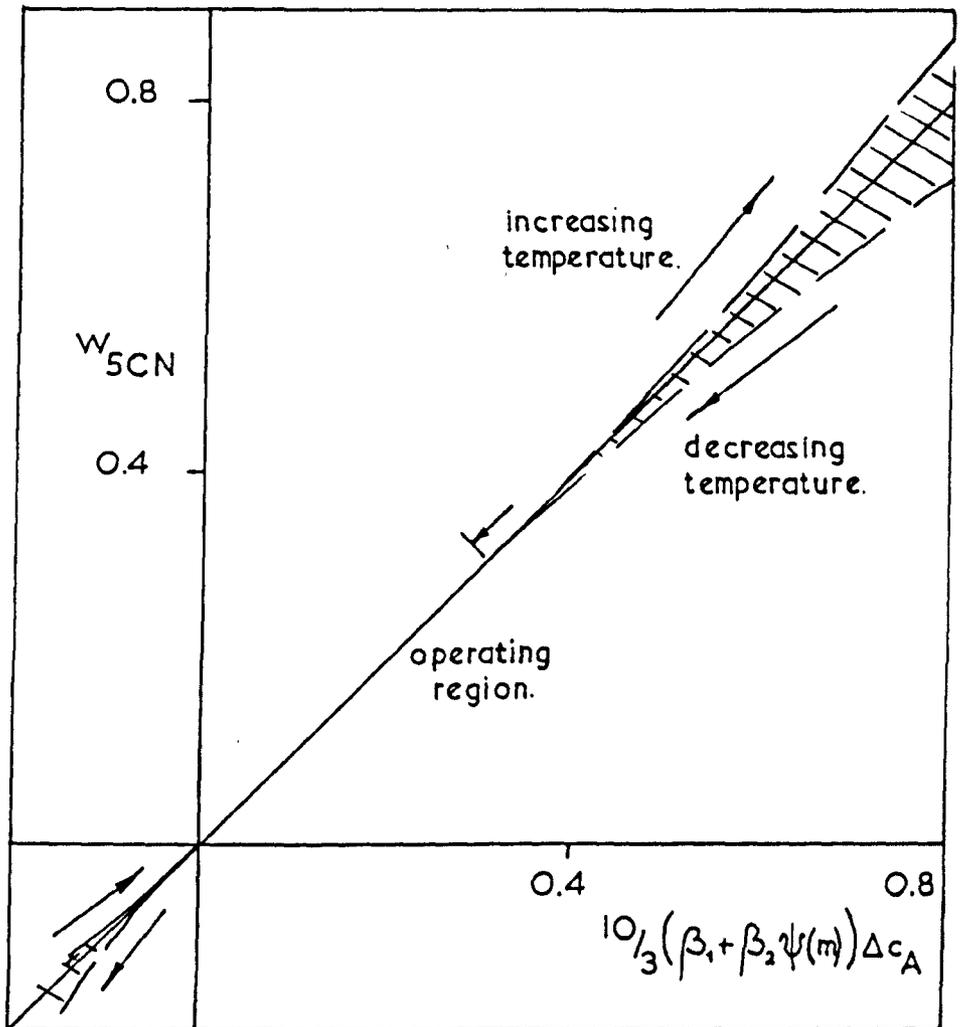
Figure 7.07 . Prediction of the coeffient w_5

for a consecutive reaction scheme.

the correction function, f_3 to the heat transfer temperature profile, t_{ht} (y) may be written,

$$f_3(y) = {}^{10}/3 \left[\beta_1 \Delta o_{A1} + \beta_3 \Delta o_{A3} - \beta_2 \Delta o_B \right] (1 - 3y^2 + 2y^3) \qquad 7.53$$

but as $\Delta o_A = \Delta o_{A1} + \Delta o_{A3}$ and $\Delta o_B = - \psi(m) \Delta o_A$ then

$$f_3(y) = {}^{10}/3 \left[\beta_1 \Delta o_{A1} + \beta_3 \Delta o_{A3} + \beta_2 \psi(m) \Delta o_A \right] (1 - 3y^2 + 2y^3) \qquad 7.54$$

This relationship has been tested and found to be true, (see fig. 7.08).

The temperature profile which has been developed for the complex reaction scheme has retained the simplicity of form with respect to y of the simple reaction scheme. The only increase in complexity has been isolated in the coefficient, w_5, which involves more terms in order to account for each exothermic reaction step. No increase in complexity of the functional representation of the radial temperature profile has been incurred in the extension to the complex reaction scheme.

7.4.8 Comments.

As may be seen throughout section 7.4, extension to a complex reaction scheme has been shown to be possible and made with a minimal increase in complexity, while all the required information about the radial profiles has been presented. Although it is not claimed that the final expressions are exact, they are valid over the practical operational range of the reactor to an accuracy comparable with that of estimating the physical parameters used in the model. It must be emphasised that the expressions are general, although approximate, solutions of the radial profiles
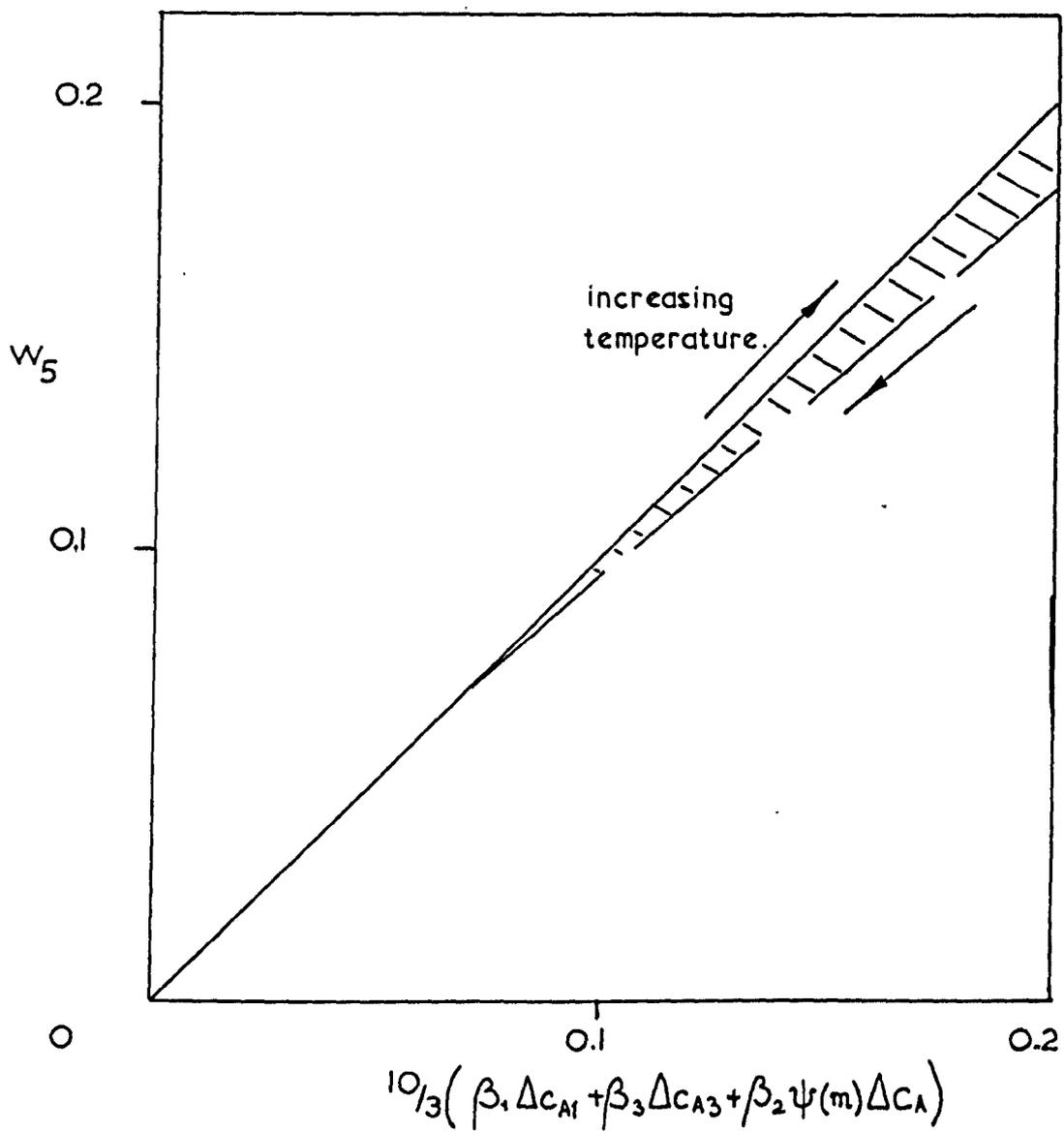
Figure 7.08 . Prediction of the coefficient w_5 for
the complex reaction scheme.

for both temperature and concentration.

It is important to note that the overall concentration difference, Δc is not used in terms of its physical sense when used in the radial temperature profile, but rather as the effect of the presence of an exothermic chemical reaction. This still indicates the complex 'coupled' nature of the original model.

It is now necessary to derive the pseudo-parameters defined in section 7.3 from the radial profiles which have been developed above, in order to complete the analysis.

7.5 The Pseudo-parameters.

7.5.1 The Effective Nusselt Number, NU'.

As the effective Nusselt number maintains its original definition, i.e.

$$NU' = NU \left(\frac{t(1) - 1}{t_m - 1} \right)$$

and the functional form of the radial temperature profile has changed only in the expression for the coefficient, w_5 from that for the simple reaction, the same expression for NU' (derived in section 6.2) can be written down, replacing w_4 by w_5.

$$NU' = \left[\frac{NU}{(1+0.25NU)+\left[\left(\frac{NU}{1.2NU+4}\right)^2 + w_5\right](0.3+0.11NU)+w_5\left(\frac{NU}{1.2NU+4}\right)^2 (0.17+0.47NU)} \right]$$

7.55

This expression is rewritten to collect the terms in w_5, so that,

$$NU' = \frac{NU}{(1+0.25NU) + P(NU) + Q(w_5, NU)}$$

7.56

-75-

where,

$$P(NU) = \left(\frac{NU}{1.2NU+4}\right)^2 (0.3 + 0.11NU)$$

$$Q(w_5,NU) = w_5 \left[(0.3+0.11NU)+\left(\frac{NU}{1.2NU+4}\right)^2 (0.17+0.47NU)\right]$$

$$\left.\begin{array}{c} \\ \\ \\ \\ \\ \end{array}\right\} \quad 7.57$$

For a particular reactor situation, the Nusselt number, NU is constant, so that $P(NU)$ is constant, and $Q(w_5,NU)$ is a direct linear function of w_5, and NU' is inversely related to w_5, as discussed in section 6.2. Consider the coefficient w_5 in more detail,

$$w_5 = 3^{1/3} \left(\beta_1 \Delta_{c_{A1}} + \beta_3 \Delta_{c_{A3}} + \beta_2 \psi(m) (\Delta_{c_{A1}} + \Delta_{c_{A3}})\right) \quad 7.58$$

The terms P and Q are considered as corrections to the effective Nusselt number derived from a purely parabolic temperature profile which assumes the overall heat transfer coefficient to be constant. The constant term, P corrects NU' to that for a purely heat transfer situation, which was carried out in the early stages of this work. The separate effects of the three exothermic reactions are considered in the term, Q. In fact both reactions one and three have the same type of effect in that they produce a positive contribution to the value of w_5 and hence Q, so that their overall effect is to always reduce the value of the effective Nusselt number. Considering the second reaction, although its overall term is positive, the mean selectivity, $\psi(m)$ can take negative values. In most practical cases $\psi(m)$ will be generally always positive, (between approximately 0.2 and 1.0) it is unlikely that the reaction would be allowed to go so far to completion, unless of course if either the product of the second

reaction is desired or the reactor is out of control, so the two
limiting cases will at first be discussed separately. At the
entrance of the reactor when the reaction is initiated, the
selectivity is at its maximum value of one, as the reactions
proceed this value will decrease, but as the product, B reaches
its maximum, the value of ψ (m) is still positive, although
approaching zero. Therefore, in such a reactor situation, the
second reaction will always make a positive contribution to the
value of the coefficient, w_5 and the value of the effective
Nusselt number will be reduced from its value for the case of heat
transfer only. As the reaction proceeds further, ψ (m)
continues to decrease until it becomes negative and a situation
can be reached where,

$$\left| \beta_2 \psi(m) \, (\Delta_{c_{A1}} + \Delta_{c_{A3}}) \right| \geqslant (\beta_1 \Delta_{c_{A1}} + \beta_3 \Delta_{c_{A3}})$$

(especially for the case where reaction three does not take place,
or $\beta_3 = 0$), so that w_5 takes on negative values and $(P + Q) \leqslant 0$.
This usually occurs in the region of the axial temperature maximum,
and means that the radial temperature profile is very nearly
parabolic. If the inlet temperature to the reactor and coolant
temperature are equal or nearly equal, then in the inlet region
of the reactor even though the assumption that the radial
temperature profile was purely parabolic would perhaps produce
large relative errors, (of approximately 25 - 30%) the absolute
errors would be small as $(t(y) - 1)$ would be close to zero.
Therefore in some region of reactor operation it would be quite
reasonable to assume a purely parabolic temperature profile,
where the effective Nusselt number is given by,

$$NU' = \frac{NU}{1 + 0.25 \, NU}$$

In conclusion, although the above case could exist, in the normal region of reactor operation $\psi(m)$ and hence w_5 will always be positive (as is easily seen from figure 7.09), so that no major simplifications can be made.

7.5.2 <u>The Distribution Factors</u>

No detailed discussion need be made on the method of evaluation of the distribution factor as this has already been amply covered in section 6.3, and the same expression is used for their estimation which may be summarised as,

if $\quad \mathcal{D} = 2 \dfrac{\int_0^1 R(y). \, y. \, dy}{R(m)}$

then $\mathcal{D}$ is estimated by $\mathcal{D} = \left(\dfrac{2 \, R\left(\frac{1}{2}\right) + R(1)}{3 \, R(m)} \right)$

7.6 <u>Conclusion.</u>

In this chapter the techniques of model reduction have been applied to a more general reaction scheme. This has been successfully achieved with minimal increase in complexity of the reduced model, which was in fact the major point of interest of this section of the work. Because the techniques of model reduction could be applied to reactor in which a simple reaction was taking place, it did not necessarily follow that the same techniques could be applied to a reactor in which a more complex scheme of reactions was occuring. In addition the question was asked, if model reduction was successfully achieved, was the resulting model tractable as far as optimisation studies etc., are
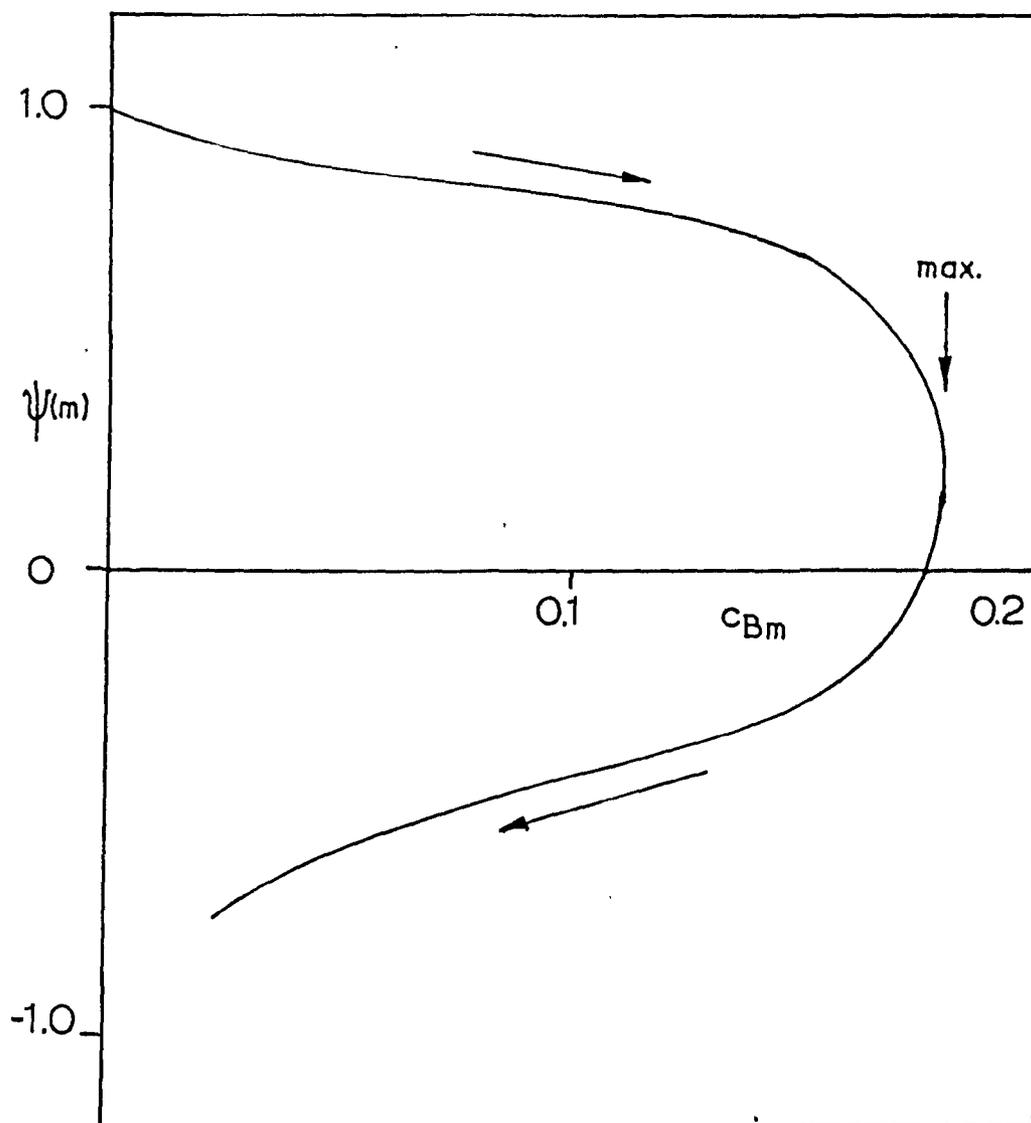
Figure 7.09 . Variation of the selectivity at the radial
mean conditions with to the radial mean
concentration of the desired product along
the reactor length.

concerned, as it is pointless producing a reduced model which is more complex than the original model. In fact the reduced model produced in this chapter is marginally more complex than that for the simple reaction, but is still very satisfactory.

The general forms of the radial profiles and the related pseudo-parameters are summarised in table 7.01, and the general form of the reduced state equations are,

$$- Pe_T \frac{dt_m}{dz} - 2NU' (t_m - 1) + \partial_T NU_S (t_{sm} - t_m)\big|_{v=1} = 0$$

$$- Pe_M \frac{dc_A}{dz} - \partial_{R1} \eta (m) (\bar{\phi}_1^2 k_1^* (m) + \bar{\phi}_3^2 k_3^* (m)) c_{Am} = 0$$

$$- Pe_M \frac{dc_B}{dz} - \partial_{R2} \eta (m) \psi (m) (\bar{\phi}_1^2 k_1^* (m) + \bar{\phi}_3^2 k_3^* (m)) c_{Am} = 0$$

and

$$NU' = \frac{NU}{(1+0.25NU)+\left[\left(\frac{NU}{1.2NU+4}\right)^2 + w_5\right](0.3+0.11NU)+w_5\left(\frac{NU^2}{1.2NU+4}\right)(0.17+0.47NU)}$$

and the general form of the distribution factor is,

$$\partial = \left(\frac{2 R (\tfrac{1}{2}) + R (1)}{3 R (m)}\right)$$

Reductions of computing time of 20 : 1 are possible, but when the reduced model is programmed to produce exactly to same amount of information as the two-dimensionless model reductions of 10 : 1 are achieved.

Table 7.01.

Reaction scheme	Form of w_5
Simple $A \xrightarrow{1} B$	$^{10}/3 \, \beta_1 \Delta c_A$
Competitive $A \xrightarrow{1} B$ $\xrightarrow{3} D$	$^{10}/3 \, (\beta_1 \Delta c_{A1} + \beta_3 \Delta c_{A3})$
Consecutive $A \xrightarrow{1} B \xrightarrow{2} C$	$^{10}/3 \, (\beta_1 + \psi(m)\beta_2) \Delta c_A$
Mixed $A \xrightarrow{1} B \xrightarrow{2} C$ $\xrightarrow{3} D$	$^{10}/3 (\beta_1 \Delta c_{A1} + \beta_3 \Delta c_{A3}) + \beta_2 \psi(m) \Delta c_A$

$\Delta c_B = -\psi(m) \Delta c_A$ (where $\Delta c_A = \Delta c_{A1} + \Delta c_{A3}$) for all the above cases.

General forms of the radial profiles.

Temperature:

$$(t(y) - 1) = \left[w_5 (1-3y^2+2y^3) + 1 \right] \left[\left(\frac{NU}{1.2NU+4} \right)^2 (1-3y^2+2y^3) + 1 \right]$$

$$x \left[1 + 0.5NU (1 - y^2) \right] (t(1) - 1)$$

where w_5 is defined above.

Concentration:

$$c_i(y) = \Delta c_i (3y^2 - 2y^3 - 0.7) + c_{i_m}$$

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CHAPTER 8

METHOD OF SOLUTION OF THE REDUCED MODEL

The reduced model comprises a set of simultaneous ordinary differential equations coupled with a set of algebraic equations representing the radial profiles and the pseudo-parameters, which have the general form,

$$\Theta'_{mi} (z) = g_i (\Theta_{m1}, \Theta_{m2}, \Theta_{m3}, Sj)$$ 8.01

$$\Theta_i (y, z) = h_i (\Theta_{m1}, \Theta_{m2}, \Theta_{m3}, Sj, y)$$ 8.02

$$Sj = Sj (\Theta_{m1}, \Theta_{m2}, \Theta_{m3})$$ 8.03

where $\Theta_{mi} = 2 \int_0^1 \Theta_i \cdot y \cdot dy$

and $i = 1, \ldots, I$, $j = 1, \ldots, J$, where I and J are the number of dependent variable and pseudo-parameters respectively. The Θ_{mi} and Θ_i are the mean radial values and the values of the dependent variables, i.e. t, c_A and c_B, and the functions g_i and h_i represent the right hand sides of the ordinary differential equation and the algebraic expressions for the radial profiles respectively (see equations 4.47, 4.48, 4.49 and 4.50 for typical examples). The S_i are the pseudo-parameters (eg Δc_A, Δc_B, NU' etc.). Equations 8.01, 8.02 and 8.03 are considered simultaneously. The ordinary differential equations are solved by the Runge-Kutta-Merson method as described in appendix 3. It is necessary to evaluate the functions g_i at each internal axial step of the integration procedure, and a separate algorithm is required to calculate them.

The algorithm is entered with the values of the dependent

variables, Θ_{mi}, from which the pseudo-parameters and subsequently the functions g_i are evaluated. This, in fact, is the basic reason for developing the expressions for the pseudo-parameters in terms of the radial mean fluid values. It ensures that they can be evaluated directly from variables which are readily available. Hence, the overall integration procedure is only a little more complex than that for the simplified one-dimensional model which has been found so attractive because of the small computational effort required for solution. For example, in order to evaluate the chemical rate term, the effectiveness factor, the concentration and the kinetic rate constant are required which are the only variables necessary to determine the overall concentration difference, Δc. This in turn is the only term required for the calculation of the effective Nusselt number, NU'.

Consider a specific example of the use of the above-mentioned algorithm for the simple reaction scheme, using the standard test data (see table 4.01). This data was specifically designed to represent a physical system which exhibited large radial gradients, as discussed in section 4.1. The right hand sides of the ordinary differential equations are written, for the case under consideration, as

$$g_1 = \frac{dt_m}{dz} = -2NU' \, (t_m - 1) + \beta \Phi^2 \mathcal{D} \, \eta \, (m) \, R^* \, (c_m, \, t_m) \qquad 8.04$$

$$g_2 = \frac{dc_m}{dz} = -\Phi^2 \, \mathcal{D} \, \eta \, (\bar{m}) \, R^* \, (c_m, \, t_m) \qquad 8.05$$

or, rewritten with the numerical values of the constants,

$$g_1 = \frac{dt_m}{dz} = -2NU'(t_m - 1) + 1.124 \times 10^{-2} \,\mathcal{D}\, \eta(m) \, R^*(c_m, t_m) \qquad 8.06$$

$$g_2 = \frac{dc_m}{dz} = -1.697 \times 10^{-2} \,\mathcal{D}\, \eta(m) \, R^*(c_m, t_m) \qquad 8.07$$

On entering the algorithm the values of c_m and t_m are known. The pellet equations are solved iteratively to determine the effectiveness factor $\eta(m)$. The rate constant $k^*(t_m)$ is computed from,

$$k^*(t_m) = \eta(m) \exp(23.18 \,(t_m - 1) \,/\, t_m) \qquad 8.08$$

For first order kinetics,

$$\eta(m) \, R^*(c_m, t_m) = c_m \, k^*(t_m) \qquad 8.09$$

The overall concentration difference can be simply written as,

$$\Delta c = \left(\frac{k^*(t_m) - 1}{1.35 \, k^*(t_m) + 36.65} \right)^2 c_m \qquad 8.10$$

when the relevant values of the constants in equation 5.11 are substituted.

(Foot note: For non-optimising compilers where exponentiation is used for evaluating integer exponent, it may be avoided in the computational procedure by evaluating Δc in the following manner,

$$\Delta c' = \frac{k^*(t_m) - 1}{1.35 \, k^*(t_m) + 36.65} \quad \text{and} \quad \Delta c = \Delta c' \times \Delta c' \times c_m$$

which consequently requires less computational effort)

Since $t_{mo} \neq 1$, the above expression for Δc gives the asymptotic value, and the corrected value of Δc is given by,

$$\Delta c \quad = \quad \Delta c_a \ (1 - \exp \ (\ - 13.7 \ (1 - c_m) \ ) \ ) \qquad 8.11$$

from equation 5.12. The axial profiles of Δc and Δc_a are compared in figure 8.01, from which it can be seen that Δc_a rapidly approaches Δc. The exponentional term monatonically approaches zero at a rate dependent on the constant, i.e. 13.7 in this case. As the evaluation of an exponential term is relatively time consuming, its elimination from the computational procedure would help to minimise the overall computing time. This can be achieved when the exponential has fallen below a preprescribed value, dependent on the required accuracy, e.g. by using a conditional statement such as the 'if' statement in Algol.

Once Δc is known, the effective Nusselt number, NU' can be easily calculated from,

$$NU' \ = \ \frac{1}{(0.776 + 0.736 \ (5) \ \Delta c)} \qquad 8.12$$

It will be noted that this expression is far simpler than the general form of NU' as given by equation 6.04, as will always be the case when numerical values for a specific system are used.

It now only remains to calculate the distribution factor, from the expression,

$$\mathcal{D} \ = \ \frac{2 \ \eta \ (\tfrac{1}{2}) \ R^* \ (\tfrac{1}{2}) + \eta \ (1) \ R^* \ (1)}{3 \ \eta \ (m) \ R^* \ (m)} \qquad 8.13$$

This requires the solution of the pellet equations for the effectiveness factor at $y = \tfrac{1}{2}$ and $y = 1$. The value of the dependent variables are given by,
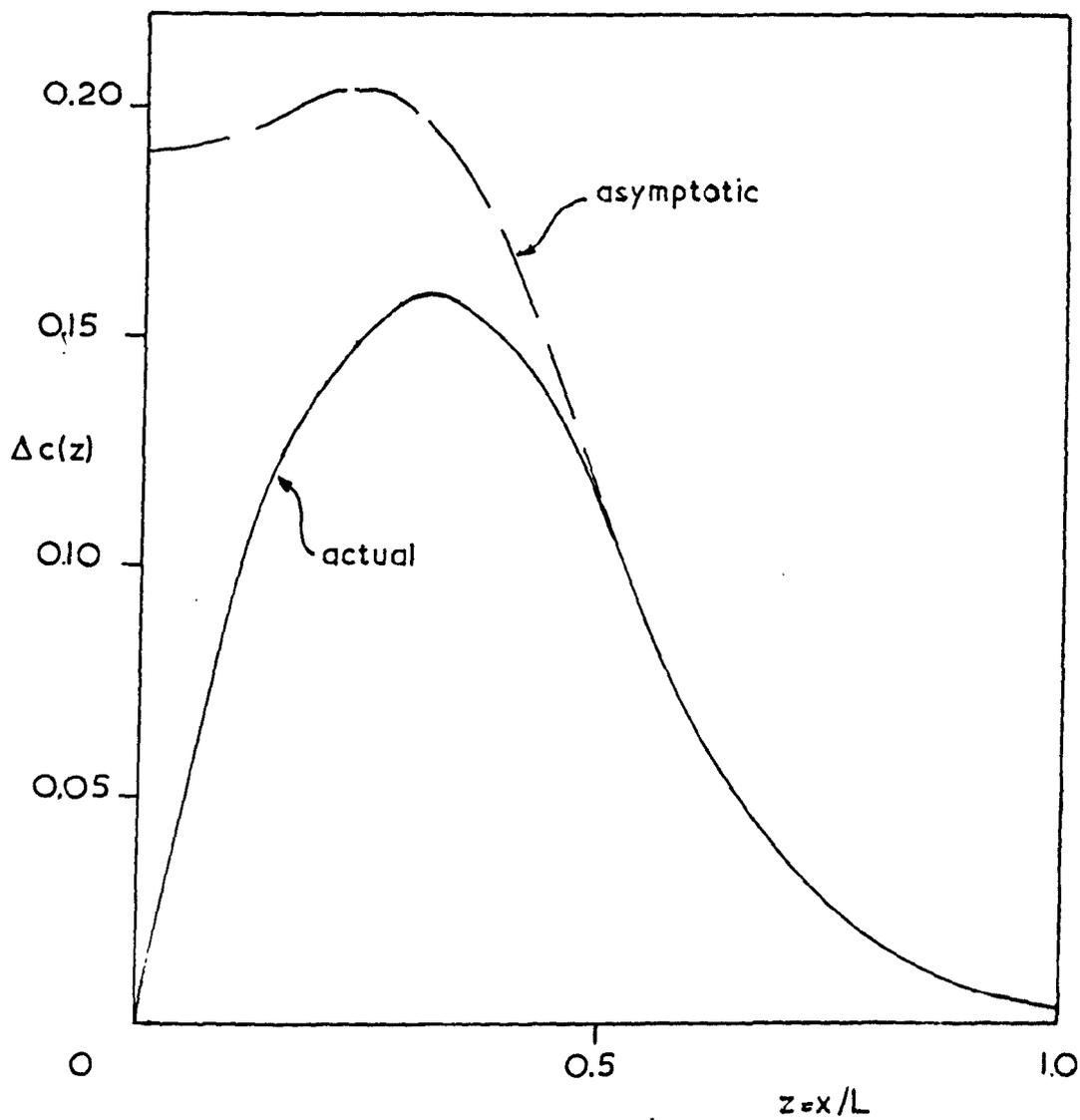
Figure 8.01 . Comparison of the actual and asymptotic
axial profiles of Δc.

$$t(1) = \frac{NU'}{2}(t_m - 1) + 1 \quad, \quad c(1) = c_m + 0.3\,\Delta c \qquad . \qquad 8.14$$

$$t(\tfrac{1}{2}) = (2.027\,\Delta c + 1.836)\,(t(1)-1) + 1, \quad c(\tfrac{1}{2}) = c_m - 0.2\,\Delta c \qquad 8.15$$

Subsequently the reaction rate terms can be calculated. The axial profiles of the distribution factor, $\mathcal{D}$ as derived from the above approximation and from the exact integration procedure for this particular set of data are compared in figure 6.03, where it is seen that the agreement is very good. If equations 8.06 and 8.07 are examined the overall rate term which is required is $\mathcal{D}\,\eta(m)\,R^*(m)$, which if equation 8.13 is rearranged, is given by,

$$\mathcal{D}\,\eta(m)\,R^*(m) = \tfrac{1}{3}\,(2\eta(\tfrac{1}{2})\,R^*(\tfrac{1}{2}) + \eta(1)\,R^*(1)\,) \qquad 8.16$$

Therefore it is not necessary to calculate the reaction rate at the mean conditions. Finally the right hand sides of the differential equations are evaluated.

A block diagram of the procedure is shown in figure 8.02. It can be seen that there is an efficient flow of information throughout the algorithm and there is no redundant information produced, which helps to maintain a low computational load. The only significant increase in required effort is that the solid equations have to be solved three times as opposed to once for the simple case. The extra computation is due to the fact that the reaction rates at $y = \tfrac{1}{2}$ and $y = 1$ are required in order to calculate the distribution factor.

At this stage the integration process is complete and the remaining computation depends on the nature and the use of the reaction model. For example, if the model is being used in an
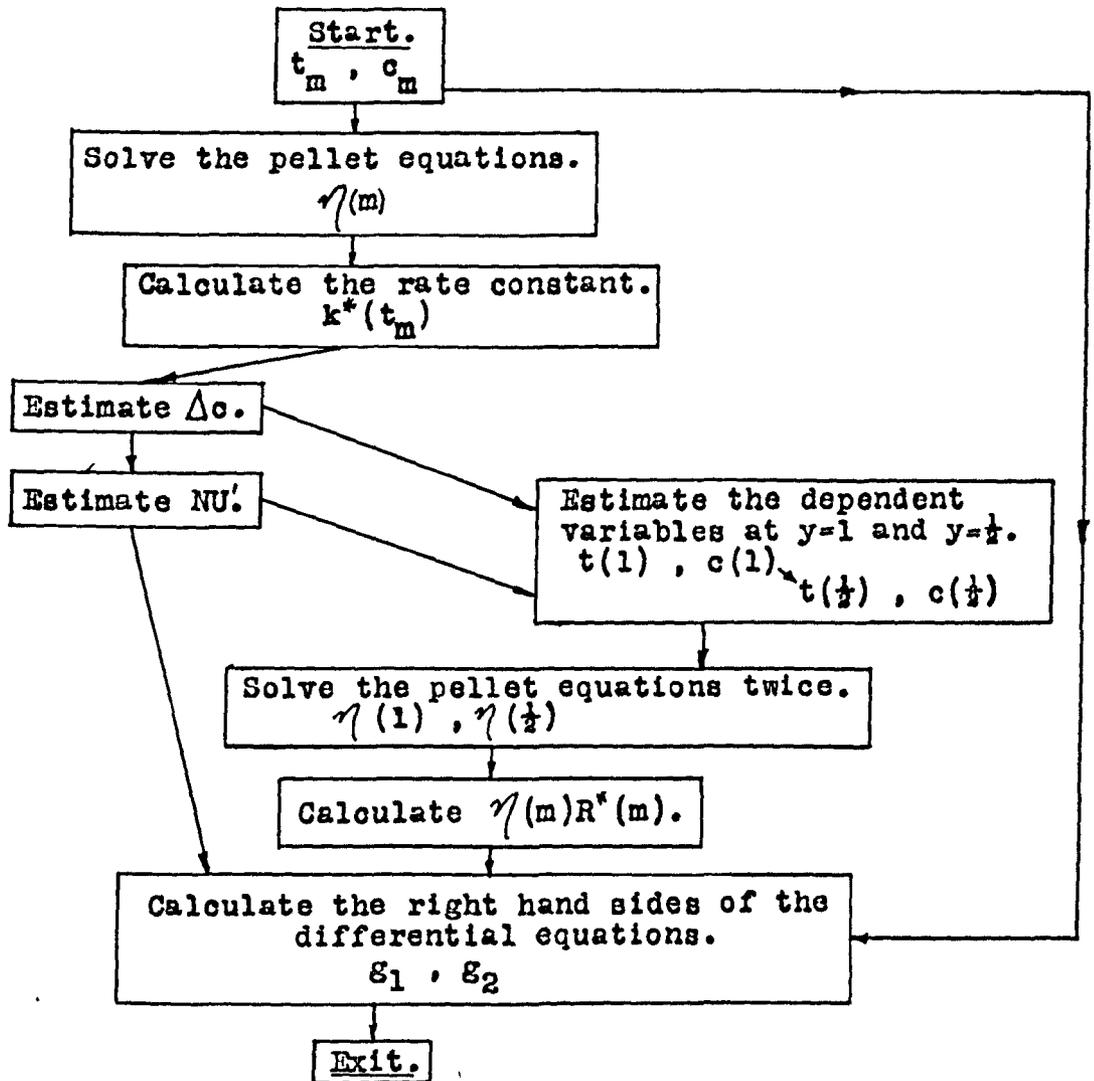
Figure 8.02 . Block diagram of the method of evaluating the right hand sides of the ordinary differential equations of the reduced model.

optimisation algorithm, then the axis temperature need only be calculated from,

$$t(0) = (4.840 \, \Delta c + 2.195) \, (t(1) - 1) + 1 \qquad 8.17$$

as it is the only constraint associated with the radial profiles. In addition it will be only necessary to calculate the axis temperature in the region of the maximum temperature. On the other hand, if the model is used in conjunction with catalyst decay problem, then the full extent of the radial temperature profile is required for updating the catalyst profiles. But, as generally, catalyst decay is a relatively slow process, then it may only be necessary to carry out such a procedure at infrequent intervals.

APPENDIX 1

DETERMINATION OF THE SECOND ORDER
CORRECTION FUNCTION, Ω_{II}

The function, Ω_{II} is defined by,

$$\Omega_{II}(y, NU) = \left[\frac{f_i(y, NU)}{\left(\frac{NU}{1.2NU+4}\right)^2 (1 - 3y^2 + 2y^3)} \right] - 1 \qquad A1.01$$

and represents the deviation of the function, f_1 from a simple

cubic functional form. In figure A1.01, Ω_{II} is plotted against

Nusselt number, NU at various radial positions. As may be seen

from the figure,

when $NU \longrightarrow 0$, $\Omega_{II} \longrightarrow$ constant value$_1$

and $NU \longrightarrow \infty$, $\Omega_{II} \longrightarrow$ constant value$_2$

from which a possible form for Ω_{II} at constant y may be proposed,

$$\Omega_{II} = \left(\frac{Y_1 \ NU + Y_2}{Y_3 \ NU + 1} \right) \qquad A1.02$$

where Y_i are functions of the radial coordinate, y, only.

The limits of Ω_{II} may now be written,

$$\lim_{NU \to 0} \Omega_{II} = Y_2 \quad , \quad \lim_{NU \to \infty} \Omega = (Y_1/Y_3) \qquad A1.03$$

The Y_i are determined at the various values of y, by setting

up three simultaneous equation in Y_i after substituting for

at three different values of NU. The remaining values of

$\Omega_{II}(NU)$ are used to check the results, which are tabulated

below.
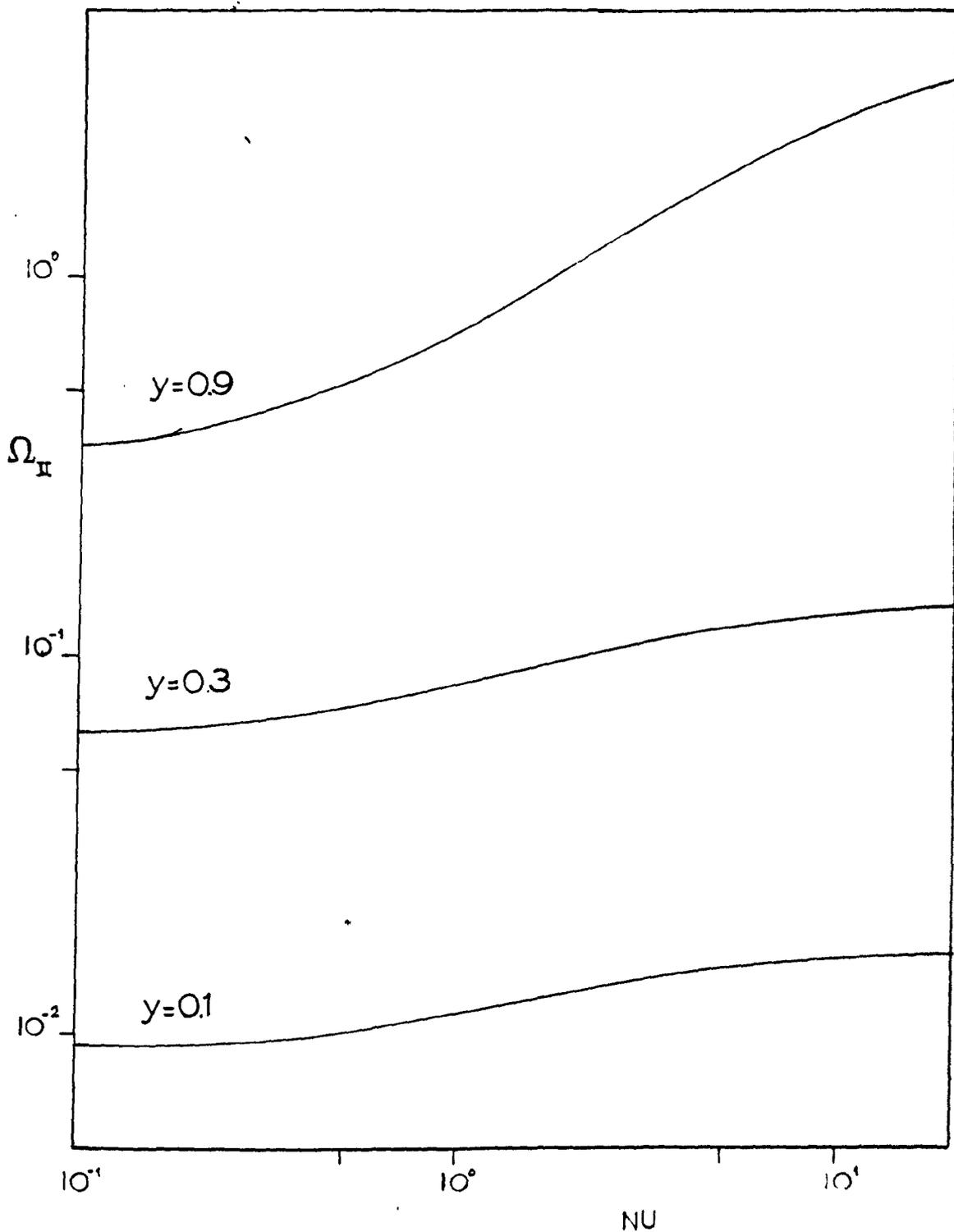
Figure A1.01 . The variation of the secondary correction
function, Ω_{II} with respect NU , for various
values of the radial coordinate.

Table A1.01.

y	Y_1	Y_2	Y_3
0.9	0.478	0.320	0.099
0.7	0.313	0.215	0.255
0.5	0.174	0.126(5)	0.375
0.3	0.070	0.056	0.455
0.1	0.011	0.010	0.495

In figure A1.02, Y_3 , $\left[\left(Y_1/Y_2\right) - 1\right]$ and Y_2 are plotted along the radius. The function $\left[\left(Y_1/Y_2\right) - 1\right]$ is the mirror image of Y_3. In fact, the function Y_3 is a simple algebraic function represented by,

$$Y_3 \approx 0.5 \left(1 - y^2\right) \tag{A1.04}$$

so that,

$$\left(Y_1/Y_2\right) = 1 + 0.5y \left(2 - y^2\right) \tag{A1.05}$$

Unfortunately Y_2 is non-integer order with respect to y, but is nevertheless of the simple form,

$$Y_2 = 0.4 \, y^{1.6} \tag{A1.06}$$

Since Ω_{II} only represents a second order effect Y_2 is adequately approximated by,

$$Y_2 = 0.4 \, y^2 \tag{A1.07}$$

to simplify the analysis.

The complete function Ω_{II} may now be summarised by the form,

$$\Omega_{II} = 0.4y^2 \left[\frac{\left\{1 + 0.5y \left(2 - y\right)\right\} NU + 1}{1 + 0.5 \left(1 - y^2\right)}\right] \tag{A1.08}$$
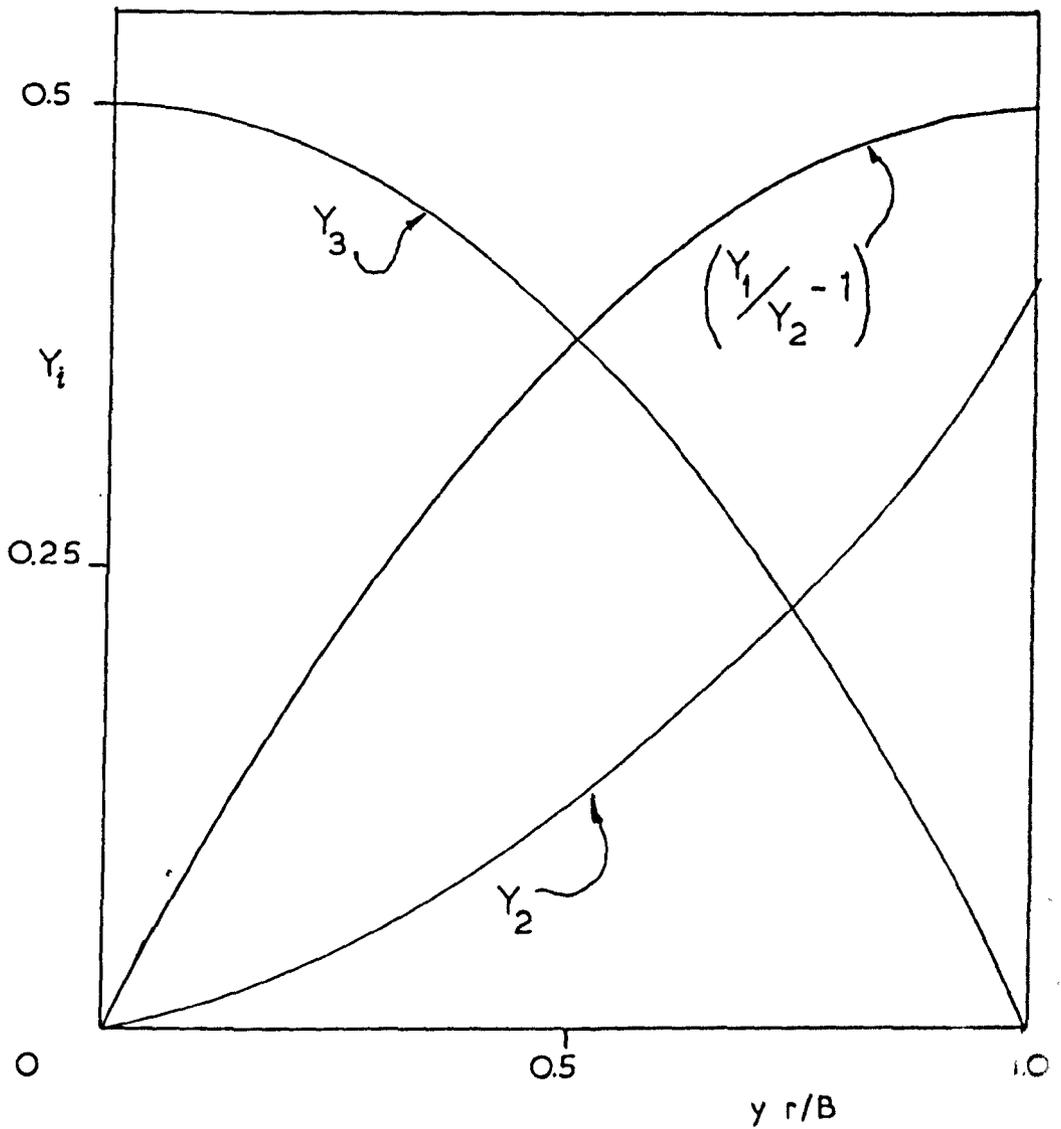
Figure A1.02 . The radially dependent coefficients, Y_i of the secondary correction function, Ω_{II}.

THE FINITE DIFFERENCE SOLUTION OF THE TWO-DIMENSIONAL REACTOR MODEL

The state equations for the general two-dimensional model are of a general form, and may be written as,

$$-Pe_i \frac{\partial \theta}{\partial z} + \frac{1}{y} \frac{\partial}{\partial y}\left(y \cdot \frac{\partial \theta}{\partial y}\right) + F_1 \theta + F_2 = 0 \qquad \text{A2.01}$$

with the boundary conditions,

$$\theta = \theta_0 \qquad z = 0$$

$$\frac{\partial \theta}{\partial y} = 0 \qquad y = 0, \quad 0 \leq z \leq 1 \qquad \text{A2.02}$$

$$-\frac{\partial \theta}{\partial y} = F_3 + F_3 F_4 \qquad y = 1, \quad 0 \leq z \leq 1$$

The parameters θ, Pe_i and F_i are listed below in table A2.01.

Table A2.01

θ	Pe_i	F_1	F_2	F_3	F_4
t	Pe_T	$-NU_s$	$NU_s t_s$	NU	-1
c_A	Pe_M	$-\eta(\Phi_1^2 k_1^* - \Phi_3^2 k_3^*)$	0	0	0
c_B	Pe_M	0	$-\eta\psi(\Phi_1^2 k_1^* - \Phi_3^2 k_3^*)$	0	0

NOTE. (1) For the simple reaction scheme let $k_2^* = k_3^* = 0$

(2) For the fixed bed heat exchanger $k_1^* = k_2^* = k_3^* = 0$

Equations A2.01 and A2.02 are solved by using the Crank-Nicolson[33] finite difference analogue, for which gradients in the radial direction are represented by the central difference approximation and in the axial direction by a first order finite difference

approximation, which may be expressed as,

$$\frac{\partial^2 \Theta}{\partial y^2} = \frac{1}{2h^2} \left[(\Theta_{n+1, m+1} - 2\Theta_{n, m+1} + \Theta_{n-1, m+1}) + (\Theta_{n+1, m} - 2\Theta_{n, m} + \Theta_{n-1, m}) \right] \qquad A2.03$$

$$\frac{1}{y} \frac{\partial \Theta}{\partial y} = \frac{1}{4nh^2} \left[(\Theta_{n+1, m+1} - \Theta_{n-1, m+1}) + (\Theta_{n+1, m} - \Theta_{n-1, m}) \right] \qquad A2.04$$

$$\frac{\partial \Theta}{\partial z} = \frac{1}{k} (\Theta_{n, m+1} - \Theta_{n, m}) \qquad A2.05$$

$$F_1 \Theta = \frac{1}{2} \left(F_{1\ n, m+1}\ \Theta_{n, m+1} + F_{1\ n, m}\ \Theta_{n, m} \right) \qquad A2.06$$

$$F_2 = \frac{1}{2} \left(F_{2\ n, m+1} + F_{2\ n, m} \right) \qquad A2.07$$

The subscripts n and m represent the radial and axial positions respectively. If the number of radial and axial steps are N and M, then the radial and axial increment are given by

$$h = (\,^1/N\,) \text{ and } k = (\,^1/M\,) \text{ respectively.}$$

As the problem is initial valued in the axial direction so that all the values at the 'm position' are known quantities.

The finite difference expressions of equations A2.03-7 are substituted into equation A2.01 to give,

$$A_n \Theta_{n+1,\ m+1} + B_n \Theta_{n,\ m+1} + C_n \Theta_{n-1, m+1} = D_n \qquad A2.08$$

where

$$A_n = \frac{N^2}{2} (1 + \,^1/2n) \qquad A2.09$$

$$B_n = -N^2 + Pe_i M + 0.5 F_{1\ n,\ m+1} \qquad \text{A2.10}$$

$$C_n = \frac{N^2}{2} (1 - 1/2n) \qquad \text{A2.11}$$

$$D_n = -\frac{N^2}{2}(1 + 1/2n)\Theta_{n+1,m} + (N^2 + Pe_i M - 0.5 F_{1\ n,m})\Theta_{n,m}$$

$$\qquad \text{A2.12}$$

$$-\frac{N^2}{2}(1 - 1/2n)\Theta_{n-1,m} - 0.5 (R_{2\ n,m+1} + R_{2\ n,m})$$

This expression is valid for $1 \leqslant n \leqslant N-1$, where N and O represent the positions of the finite difference nodes at the tube wall and axis respectively.

At the tube axis, $\dfrac{\partial \Theta}{\partial y} = 0$, hence $\dfrac{1}{y}\dfrac{\partial \Theta}{\partial y}$ is indeterminate.

Applying l'Hopital's Rule, equation A2.01 becomes

$$-Pe_i \frac{\partial \Theta}{\partial z} + 2 \frac{\partial^2 \Theta}{\partial y^2} + F_1 \Theta + F_2 = 0$$

Because of the symmetry of the problem, $f_{-1} = f_1$ the finite difference equation can be written,

$$A_o \Theta_{1,m+1} + B_o \Theta_{o,m+1} = D_o \qquad \text{A2.13}$$

where

$$A_o = 2N^2 \qquad \text{A2.14}$$

$$B_o = -2N^2 + Pe_i M + 0.5 F_{1\ o,m+1} \qquad \text{A2.15}$$

$$D_o = -2N^2 \Theta_{1,m} + (2N^2 - Pe_i M - F_{1\ o,m})\Theta_{o,m}$$

$$\qquad \text{A2.16}$$

$$-0.5 (F_{2\ o,\ m+1} + F_{2\ o,m})$$

At the tube wall, the boundary condition is written in finite difference form.

$$0.25N \ (\Theta_{N+1,m+1} - \Theta_{N-1,m+1}) + (\Theta_{N+1,m} + \Theta_{N-1,m})$$

$$+ \ 0.5 \ F_3 \ (\Theta_{N,m+1} + \Theta_{N,m}) \ + \ F_3 \ F_4 \ = \ 0 \qquad \text{A2.17}$$

Equation A2.17 is substituted in equation A2.08 in order to eliminate the hypothetical function values, $f_{N+1, \ m+1}$ and $f_{N+1,m}$ to give,

$$B_N \Theta_{N, \ m+1} \ + \ C_N \Theta_{N-1, \ m+1} \ = \ D_N \qquad \text{A2.18}$$

where

$$B_N \ = \ - \ N^2 + Pe_i \ M + 0.5 \ F_{1 \ N, \ m+1} - F_3 \ (N+1) \qquad \text{A2.19}$$

$$C_N \ = \ N^2 \ . \qquad \text{A2.20}$$

$$D_N \ = \ (N^2 + Pe_i M - 0.5 \ F_{1 \ N,m} + F_3 \ (N+1) \ ) \Theta_{N,m}$$

$$- \ N^2 \Theta_{N-1, \ m} - 0.5 \ (F_{2 \ N, \ m+1} + F_{2 \ N,m}) + F_3 \ F_4 \ (2N+1) \qquad \text{A2.21}$$

Equations A2.08, A2.13 and A2.18 represent a system of simultaneous algebraic equations,

$$\underline{E} \ \underline{\Theta} \ = \ \underline{D} \qquad \text{A2.22}$$

where,

$$\underline{E} \ = \ \begin{bmatrix} B_0 & A_0 & 0 & 0 & 0 \\ C_1 & B_1 & A_1 & 0 & \\ & C_n & B_n & A_n & \\ 0 & 0 & C_N & B_N \end{bmatrix}$$

Equation A2.22 is solved by using the Thomas [34] method described below*. It is necessary to solve the pellet equations at each node of the finite difference scheme, for which method

are well described by Cresswell [27] and Thornton [35].

*The Thomas Method.

The unknowns are eliminated by letting,

$$w_0 = B_0 \qquad\qquad\qquad\qquad \text{A2.23}$$

$$W_n = B_n - C_n q_{n-1} \qquad n = 1, 2, \ldots, N \qquad \text{A2.24}$$

$$q_{n-1} = \frac{A_{n-1}}{w_{n-1}} \qquad\qquad\qquad \text{A2.25}$$

$$g_0 = D_0 \qquad\qquad\qquad\qquad \text{A2.26}$$

$$g_n = \frac{D_n - C_n\, g_{n-1}}{w_n} \qquad n = 1, 2, \ldots, N \qquad \text{A2.27}$$

These equations transform to,

$$\Theta_N = g_N \qquad\qquad\qquad\qquad \text{A2.28}$$

$$\Theta_n = g_n - q_n \Theta_{n+1} \qquad n = N-1, N-2, \ldots, 0. \qquad \text{A2.29}$$

APPENDIX 3

THE 4° RUNGE KUTTA MERSON METHOD FOR THE SOLUTION
OF A SET OF SIMULTANEOUS ORDINARY DIFFERENTIAL EQUATIONS

The Runge Kutta Merson method [32] is a slight modification
of the fourth order Runge Kutta technique, which gives an automatic
and rapid method for determining the maximum interval to be used
for a preprescribed accuracy.   The formulae for the integration
of,

$$\theta' (x) = g (x, \theta) \qquad\qquad\qquad\qquad \text{A3.01}$$

may be written,

$$\theta_{n+1} = \theta_n + \tfrac{1}{2} (k_1 + 4 k_4 + k_5) + 0 (h^5) \qquad\qquad \text{A3.02}$$

where,

$$k_1 = \tfrac{1}{3} h \; g (x_n, \theta_n) \qquad\qquad\qquad\qquad \text{A3.03}$$

$$k_2 = \tfrac{1}{3} h \; g (x_n + \tfrac{1}{3} h, \theta_n + k_1) \qquad\qquad\qquad \text{A3.04}$$

$$k_3 = \tfrac{1}{3} h \; g (x_n + \tfrac{1}{3} h, \theta_n + \tfrac{1}{2} k_1 + \tfrac{1}{2} k_2) \qquad\qquad \text{A3.05}$$

$$k_4 = \tfrac{1}{3} h \; g (x_n + \tfrac{1}{2} h, \theta_n + \tfrac{3}{8} k_1 + \tfrac{9}{8} k_3) \qquad\qquad \text{A3.06}$$

$$k_5 = \tfrac{1}{3} h \; g (x_n + h, \theta_n + \tfrac{3}{2} k_1 - \tfrac{9}{3} k_3 + 6 k_4) \qquad \text{A3.07}$$

The advantage of this method is that an estimation of the truncation
error, ε can be made.

$$5 \varepsilon = k_1 - \tfrac{9}{2} k_3 + 4 k_4 - \tfrac{1}{2} k_5 \qquad\qquad\qquad \text{A.308}$$

The interval changing criteria is the following, if the right hand
side of equation A3.08 is greater than 5 times the preassigned
accuracy, the interval, h is halved and the computation for the
step is begun again.   But if the right hand side of equation
A3.08 is less than $^5/_{32}$ of the preassigned accuracy, then the
interval may be doubled and the calculation for the step repeated.

This method is 20% faster and more reliable than the standard fixed interval procedure.

It may be noted that the computation time increases with specification of greater prescribed accuracy. If the method is to be used for solution of the reduced model in an optimisation algorithm, during the preliminary approach to the optimum low accuracy could be prescribed to minimise the overall computation time, with a higher accuracy used in the region of the optimum for the final stages of computation.

APPENDIX 4

METHOD OF ORTHOGONAL COLLOCATION

The orthogonal collocation method was developed by Villadsen and Stewart [30] who give complete details of its implementation. The basic procedure is as follows. Consider an unknown function $f(y)$ which satisfies the linear or non-linear differential equation,

$$L^V(f) = 0 \quad \text{in} \quad V \qquad\qquad A4.01$$

and the linear or non-linear boundary condition

$$L^S(y) = 0 \quad \text{on} \quad S \qquad\qquad A4.02$$

where y is a position vector and S is a boundary adjoining the volume V. The dependent variable f is approximated by a series expansion $f^{(n)}$ containing n undetermined parameters; the parameters are then determined by applying equations A4.01 or A4.02 at each of n selected points. Interior collocation requires that the function $f^{(n)}$ satisfies the boundary condition identically.

Consider the fixed bed reactor which has the generalised boundary conditions,

$$\left. \frac{\partial f}{\partial y} \right|_{y=0} = 0 \quad \text{or} \quad f = f(y^2) \qquad\qquad A4.03$$

$$a\frac{\partial f}{\partial y} + bf = c, \quad y = 1 \qquad\qquad A4.04$$

where a, b and c are constants.

The solution is expanded in the form,

$$f(y,z) = f(1,2) + (1 - y^2) \sum_{i=1}^{M} a_i(t) P_{i-1}(y^2) \qquad\qquad A4.05$$

where $P_{i-1}(y^2)$ is a polynomial of degree i-1 in y^2 and is defined by the relation,

$$\int_0^1 w(y^2) \, P_i(y^2) \, P_j(y^2) \, y^{a-1} = C_i \delta_{ij} \quad i,j=1,\ldots,n \qquad \text{A4.06}$$

where $w = 1-y^2$ gives a form of Jacobi polynomials, and $w=1$ gives Legendre polynomials. The constant, $a = 1, 2, 3$ for planar, cylindrical and spherical geometry. This form automatically satisfies the first boundary condition (equation A4.03). The exact form of the polynomials is not needed however. The collocation points are the roots to

$$P_n(y^2) = 0 \quad \text{for } y^2 = y_j^2 \quad j=1,\ldots,n \qquad \text{A4.07}$$

The roots are tabulated below for Legendre polynomials and spherical geometry.

n = 1	0.70711	1.0		
n = 2	0.45970	0.88807	1.0	
n = 3	0.33571	0.70711	0.941965	1.0

The complete results are tabulated by Villadsen and Stewart[30].
To apply collocation to

$$\frac{\partial f}{\partial z} = \tau_1 \nabla^2 f + \tau_2 \left(\frac{\partial^2 f}{\partial y^2} \right)^2 + F(f) \qquad \text{A4.08}$$

$$-\frac{\partial f}{\partial y} = \tau_3 (f - f_c) \, , \; y = 1 \qquad \text{A4.09}$$

the terms are evaluated at the collocation points y_j.

$$\frac{df}{dz} = \tau_1 \sum_{j=1}^{n+1} B_{ji} f_i + \tau_2 \left(\sum_{j=1}^{n+1} A_{ji} f_i \right)^2 + F(f_i), \; j=1,\ldots,n. \qquad \text{A4.10}$$

$$-\sum_{i=1}^{n+1} A_{n+1,i} f_i = \tau_3 (f_{n+1} - f_c) \qquad \text{A4.11}$$

Equations A4.10 and A4.11 give n+1 equations for the n+1 unknowns at the collocation points and the boundary condition.

The set of ordinary differential equations are solved by a
standard scheme, i.e. Runge Kutta, and the coefficients C_i, $B_{j,i}$
and $A_{j,i}$ can be computed from algorithms found in Villadsen and
Stewart.

NOMENCLATURE.

$\left. \begin{array}{c} a_i^{(m)} \\ b_i^{(m)} \end{array} \right\}$ arbitrary coeffient.

b pellet radius.

B tube radius.

$\left. \begin{array}{c} c, \; c_A, \; c_B \\ c_s, \; c_{As}, \; c_{Bs} \end{array} \right\}$ dimensionless fluid and solid concentration.

c_m radial mean concentration.

$\left. \begin{array}{c} C, \; C_A, \; C_B \\ C_s, \; C_{As}, \; C_{Bs} \end{array} \right\}$ fluid and solid concentration.

C_0 inlet fluid concentration.

D_f effective fluid diffusivity.

D_p pellet diffusivity.

$\mathcal{D}$ distribution factor.

e bed voidage.

E activation energy.

$f_i(y)$ correction function.

$F(NU), \; G(NU)$ arbitrary functions of Nusselt number.

F_i generalised state equation coeffient.

g_i right hand side of the ordinary differential equations.

$g_n(z)$ dini series polynomial for mass transfer

h_f solid/fluid heat transfer coefficient.

h_i right hand side of radial profile.

h_o overall heat transfer coefficient.

h_w inside film wall heat transfer coefficient.

$h_n(z)$ dini series polynomial for heat transfer.

$J_o'(\lambda_n)$ Bessel function.

k_g	gas/solid mass transfer coefficient.
$k_i(t)$	rate constant.
$k_i^*(t)$	reduced rate constant.
k_o	pre-exponential constant.
L	reactor length.
m	axial increment of finite difference matrix.
M	number of axial increments.
n	radial increment of finite difference matrix.
N	number of radial increments.
NU	Nusselt number.
NU'	effective Nusselt number.
NU_s	effective pellet Nusselt number.
Pe_i	effective Peclet number.
Pe_M	effective Peclet number for mass transfer.
Pe_T	effective Peclet number for heat transfer.
$P(NU)$, $Q(NU, \beta \Delta c)$	corrections functions to approximate effective Nusselt number.
r	radial distance.
$R(c, t)$	reaction rate.
$R^*(c, t)$	reduced reaction rate.
R_g	Gas constant.
s	reduced pellet radial distance.
S_j	pseudo-parameter.
Sh'	effective Sherwood number.
SH_s	effective reactor Sherwood number.
t, t_m, t_s	dimensionless fluid, radial mean fluid and solid temperature.
$t(y)_{ht}$	radial temperature for heat transfer only.

$t(y)_p$	parabolic approximate temperature profile.
T, T_s	fluid and solid temperature.
T_{mo}	radial mean inlet temperature.
T_w	constant coolant temperature.
u_i	constant.
U	wall heat coefficient.
v	pellet radial distance.
w_i	temperature profile coefficient.
x	axial distance.
y	reduced radial distance.
Y_i	radially dependent coeffients.
z	reduced axial distance.

Greek.

β_i	thermicity group.
γ	activation energy group.
$\Delta c_{A,B}$	overall radial concentration difference for the reactant and product.
ΔH_i	heat of reaction.
ε_i	coefficient in radial concentration profile.
ζ	axially dependent coefficient.
η	effectiveness factor.
Θ	dependent variable.
$\Theta^{(m)}$	m^{th} approximation to Θ.
λ_f	effective radial thermal conductivity.
λ_s	solid conductivity.
ν_i	coefficient in the expression for Δc.
$\xi_n^e(y)$	dini series polynomial for heat transfer.
ρ_f	fluid density.

σ_f fluid specific heat.

ϕ a fluid reaction modulus.

ϕ_s a solid reaction modulus.

Φ_i^2 effective reactor reaction modulus.

ψ selectivity.

$\Psi_n(y)$ dini series polynomial for mass transfer.

Ω_i trial function.

Ω_{II} second order correction function.

REFERENCES

1. Froment, G.F., C.E.S., (1962) $\underline{17}$ 849.

2. Damköhler, G.D., Chem. Ing., (1937) $\underline{3}$ 430.

3. Thiele, E.W., I.E.C., (1939) $\underline{31}$ 916.

4. Wheeler, A., Advances in Catalysis. Vol. 3 p. 249, Academic Press (1951)

5. Weisz, P.B., C.E.P. (Symp. Series), (1959) $\underline{55}$ 29.

6. Carberry, J.J., A.I.Ch.E.J., (1961) $\underline{7}$ 350.

7. Beek, J., ibid, 337.

8. Tinkler, J.D., Mezner, A.B., I.E.C., (1961) $\underline{53}$ 663.

9. Schillson, R.E., Amundson, N.R., C.E.S., (1961) $\underline{13}$ 226.

10. Weisz, P.B., Hicks, J.S., C.E.S., (1962) $\underline{17}$ 265.

11. Petersen, E.E., ibid, 383.

12. Butt, J.B., C.E.S., (1966) $\underline{21}$ 275.

13. Gunn, D.J., ibid, 383.

14. McGreavy, C., Cresswell, D.L., Can.J.C.E. (1969) $\underline{47}$ 583.

15. McGreavy, C., Thornton, J.M., C.E.S., (1970) $\underline{25}$ 303.

16. Froment, G.F., I.E.C., (1967) $\underline{59}$ 18.

17. Beek, T., Advance in Catalysis. Vol. 3 p. 222, Academic Press (1951).

18. Colburn, A.P., I.E.C., (1951) $\underline{23}$ 190.

19. Leva, M., I.E.C. (1948) $\underline{40}$ 747.

20. Maguire, M., Lapidus, L., G.I.Ch.E.J., (1965) $\underline{11}$ 85.

21. Shah, M.J., A.I.Ch.E. - I. Chem. E. Symp. Series, (1965) $\underline{4}$ 47.

22. McGreavy, C., Turner, K., Can. J.C.E. (1970) $\underline{48}$ 200.

23. Amundson, N.R., I.E.C., (1956) $\underline{48}$ 26.

24. Schlichting, , Boundary Layer Theory, McGraw-Hill, (1960).

25. Yagi, S., Wakao, N., A.I.Ch.E.J. (1959) $\underline{5}$ 79.

26. Carslaw, M.S. Jaeger, J.C., Conduction of Heat in Solids, (2nd. Ed.), Oxford Univ. Press, (1960).

27. Cresswell, D.L., Ph. D. Dissertation, University of Leeds (1969)

28. Bernard, R.A., Wilhelm, R.H., C.E.P. (1950) $\underline{46}$ 233.

29. Latinen, G.A., Dissertation, Princeton Univ., Princeton, New Jersey (1951)

30. Villadsen, J., Stewart, W.E., C.E.S., (1967) $\underline{22}$ 1483.

31. Villadsen, J., Sørensen, J.P., C.E.S., (1969) $\underline{24}$ 1337.

32. Lance, G.N., Numerical Methods for High Speed Computers, p.56 ILIFFE (1960)

33.   Crank, J., Nicolson, P., Proc. Camb. Phil. Soc. (1947) 43 50.

34.   Lapidus, L., Digital Computation for Chemical Engineers, McGraw-Hill (1962).

35.   Thornton, J.M., Ph.D. Dissertation, University of Leeds (1970)

36.   Ahlberg, J.H., Nilson, E.N., Walsh, J.L., The Theory of Cubic Splines and their Applications, Academic Press, (1967).