

OPTIMAL DESIGN OF
REACTORS FOR SINGLE EXOTHERMIC
REVERSIBLE REACTIONS

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by

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ABSTRACT

The problem of selection of the best flow reactor for the production of a substance by means of a reversible exothermic reaction is treated by solving for a large number of different reactors the classical problem of minimizing the volume for given feed flow-rates and compositions and (parametricly) varying outlet conversions, and comparing the resulting minima and their corresponding controls.

The reaction rate expression used in numerical examples is linear in conversion, the forward and reverse reaction rate "constants" having Arrhenius temperature dependence although the theory is developed for an arbitrary reaction rate function.

The reactors considered include those with internal heat exchange of the U-tube and regenerative types for which an iterative gradient minimization method is used in conjunction with a perturbation method for determining the gradient, and an N stage adiabatic cascade with "cold shot" or indirect intercooling for which a powerful new algorithm involving a $2N-1$ to 1 dimensional reduction is used. The variational problem arising

when $N \rightarrow \infty$ is reduced to that of evaluating a few elementary line integrals in the conversion enthalpy plane. A connection is established with the MT reactor of Cholette *et al.*, and the degeneracy occurring when the "cold shot" is unreasonably hot is elucidated.

The sensitivity of the minima to variables which are adjustable only in the design stage is also investigated, and numerical procedures discussed.

In the development of algorithms for computing the optimal adiabatic cascades and the corresponding variational problems no special thermochemical properties are assumed for the reaction mixture, although in numerical examples the adiabatic temperature rise coefficient is assumed to be a constant.

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Notation.

This work comprises ^{Many} ~~may~~ self-contained arguments: in order to avoid the proliferation of symbols the same symbols are used from time to time with different meanings. The symbols are defined in the text, usually adjacent to the expressions in which they appear. Symbols used to identify odd points in figures may or may not have any connection with the symbols appearing below in a list showing the location of the definitions of the main symbols used. Equations are shown bracketed.

- a See (4.20), (4.25b), (5.31), (5.32), also text after (6.20). a_1 see (5.31). a_i see (2.20)
- b constant see (4.19). b_0 , see (6.6, 7, 8, 9). b_1 see (5.33, 6.6, 7, 8, 9). $\hat{b}_0$, $\hat{b}_1$ values of b_0 and b_1 corresponding to minimum F (Chapter VI). b_i see (2.20).
- c. c_1 see (5.33).
- d. Differential operator.
- e. $\bar{e}$, e' , e'' error criteria: text following (5.33).
- f. f_i flowrate of ith. species (2.2). function (3.10).
function (6.17).

- g. See (6.19).
- h. used only as enthalpy/mole basic reference substance. h_i for stage i ; h_m for subsidiary feed, etc.
- $\bar{k}$. steplength for forward integration Chapter VI.
- m. volume or mass of catalyst. m_f total volume or mass of catalyst. m^* minimum m . m' see (4.20).
- n. maximum number of steps allowed for forward integration Chapter VI.
- p. see (4.26). p' see (A5.20). p_i see (6.25, 6.27)
- q. q'_j see (A5.20). q_j see (6.38).
- r. A'/A , see (3.12). Reaction rate, see (4.28). See (A5.20)
- t. see (2.12). see (6.4). t_f see (3.2). t_f^* see (3.1). t_i see (5.13). t'_i see (5.14).
- u. u_{ij} see (6.24), (6.26).
- v. Reaction rate: see text above (2.7).
- w. Basic molal flowrate. w_0 at entry. w_f at exit. w' see (4.20). w_s along singular control, Chapter IV. w_i in stage i Chapter V.
- x. See (2.9). x' see (4.21). x_1, x_2 , see text above 4.28. x_i see (6.18).

- y. Conversion. y_o inlet conversion. y_f exit conversion. $y_f^* = \max y_f$. y_m subsidiary feed conversion. y_{a_i} , y_{e_i} ith stage inlet and outlet conversions. y' equilibrium conversion (Chapter V). y_o see Chapter II Pt.1g. $\tilde{y}$ see (5.58). y_h, y_T see (5.34). y_o see (6.5). y_1, y_2 see Fig. 6.1, equation (6.9). y_i see (6.17, 18, 19, 20).
- z_i see (6.20).
- A. A, A' see text after (1.1). $\bar{A}$ see (6.10).
- B. See (4.14). B' see (4.20). $\bar{B}$ see (5.52).
- C. Specific heat at constant pressure per mole basic reference substance.
- E. see (5.56).
- F. F_i see (5.23). F_i conversion see (5.65). Final value of t see (6.10).
- G. G_{ki} adjoint variables, see (6.31).
- H. H, H' see text after (1.1). $\bar{H}_i$ see text above (2.18). H Hamiltonian see (4.37).
- J. Adiabatic temperature rise coefficient.
- K. Suffix Chapter V. Function Chapter V. Part IV. Constant (5.40). Ratio of sectional area of right

hand to left hand tube in Fig. 6.1.

- L. L_i see (5.64). L'_i see (A5.2b). L_{ji} see (6.39-41).
- M. M_i chemical formula of ith. species Chapter II.
M objective function (3.13). See (5.1).
- N. Number of stages, Chapter II and V.
- P. Bound on p: see text around (4.27). P_{iK} matrix
see (5.50).
- Q. See Chapter II Part II.
- R. Reaction cost: Text following (3.13).
- S. Separation cost: text following (3.13). Singular
locus, (4.42). Sets of variables Chapter V. S'_i
Lagrange parameter (A5.20).
- T. Temperature. T^* optimum temperature. T_{a_i} , T_{e_i}
ith stage inlet and exit temperatures (Chapter V).
 T_i trajectory type i in Chapter IV.
- U. See (2.29)
- V. See (2.28)
- W. W_i adjoint variables (6.36, 37).
- X. X' see (4.23).
- Z. Lagrange function (A5.20).
- α . α_i see text above (2.2)
- δ . small increment operator. $\delta_{ij} = 1$ for $i = j$
otherwise 0.

θ . see (2.23).

λ . λ_i adjoint variables (4.33).

ν . ν_i stoichiometric coefficient of i th. species.

Chapter II.

ϕ . see (5.52a).

Φ . see (5.52a).

χ . see (5.59).

ψ . see (5.50).

CHAPTER I

Introduction. Synopsis and Review of Previous Work

INTRODUCTION:

The Chemical Engineer is often required to specify what type of reactor should be used in a given processing step, and what its operating conditions should be; a full-scale evaluation of alternatives would in general be undesirable, of course, so indirect criteria must be used.

We are concerned with flow reactors for single reversible exothermic reactions (such as the water-gas shift reaction): we can predict the performance of such a reactor if we know the reaction rate per unit volume as a function of composition, temperature and pressure, the thermochemistry of the system and the heat and mass transfer processes taking place in the reactor. For design purposes we need not know the details of the transfer processes or the microkinetics; good approximations can often be achieved with simple models (See for example References 2, 10, 47, 56, 57).

Let us suppose that the reactor we need to specify is to be part of a proposed plant which is to be designed

and operated in such a way as to maximize profit. The reactor type may be considered an adjustable design variable which may take on the value 1 for the first reactor to be considered, 2 for the next, and so on, in a mathematical model of the plant.

Suppose this model is a good one, and that we could find for what values of the design and operating variables the profit is maximum; we might then choose as best the (in general unique) reactor corresponding to the maximum profit, but it would be prudent to take into account other factors. The sensitivity of the maximum to variables which are adjustable only at the design stage, to variables which are difficult to control, etc. should be investigated and unreasonably sensitive reactors rejected; besides, it is usually difficult to formulate such an optimization problem which is both realistic and tractable so that some factors may have been omitted from (or crudely represented by) the objective function and/or the restraint relations, and these factors¹ will have to be considered at the end.

The (formal) problem of finding the maximum profit may be tackled by first finding the attainable region²

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1. For examples of social factors see Refs. 2 and ~~67~~.
 2. See Chapter III and Ref. 63. Other decomposition procedures may be used. See e.g. Ref. ~~68~~.

for the reactor (in the space of the variables common to the reactor and its environment), next finding a point $\underline{X}$ of the attainable region which corresponds to the minimum of the objective function, and then finding a reactor control which will realise $\underline{X}$. In problems of special interest in reactor theory, $\underline{X}$ will lie on the border of the attainable region for the reactor, and we will be considering, for the most part, methods for finding this border.

The reactor may be connected to its environment in a complex manner, giving rise to an attainable region of high dimensionality whose border is to be found only at considerable expense. Much useful information about the relative merits of the various alternative reactors can be obtained however by formulating and solving (for each proposed reactor) certain simpler optimization problems¹: with the solutions to these problems (together with a knowledge of their limitations) to hand one may carry out a preliminary screening. Besides, as a result of this screening, for the reaction system as a whole general priorities will be established - e.g. under what conditions backmixing is desirable,

1. See e.g. Refs. 22, 25, 30, 31.

whether heat economy is important, etc. With this sort of information available the designer may be able to see some fundamental reason underlying the superiority of certain reactors and develop a novel alternative with unique advantages.

A large class of the above simplified optimization problems reduce to the basic problem: for given inlet and outlet flowrates and conversions, minimize the reactor volume or mass of catalyst. Solving this problem is in fact equivalent to finding a point on the border of the attainable region for the reactor when its space is spanned by the variables: flowrate, inlet and outlet conversions, and volume (or mass of catalyst).

PRINCIPAL OBJECTIVES OF THIS WORK:

Our first objective was to develop methods for treating the basic problem efficiently for several different types of reactors, especially where the outlet conversion is to be varied parametricly.

Our second objective was to compare many different types of reactors, using the solution to the basic problem as the main criterion; in this study the reaction was assumed to proceed (in each reactor) at a

rate $v(y,T)$ moles reference substance/unit time, volume (or mass of catalyst) given by:

$$v(y,T) = H(1-y)\exp(-A/T) - H'y \exp(-A'/T) \quad (1.1)$$

(y conversion¹, T temperature °K).

A constant adiabatic temperature rise coefficient J of 158.5 °K was used; cold shot temperatures of 300°K and 600°K were used; the inlet conversion was almost always zero and the outlet conversion varied parametricly from about 0.1 to about 0.99. The three sets of reaction rate function (1.1) parameters shown in Table 1.1. were used: the parameters have the following properties:

- 1) The differences $A'-A$, and the ratios H/H' are constant - i.e. the equilibrium line in the yT plane is the same for each set, and
- 2) The activation energy ratios A'/A are respectively 1.5, 2, and 3.

SYNOPSIS OF CONTENTS: PREVIOUS WORK:

In Chapter II heat and material balance equations are derived for use in later chapters and some impor-

1. More precisely in Chapter II.

tant properties of the function $v(y,T)$ - equation (1.1) are discussed. Only the presentation of this material is new. Some useful changes of variable are discussed, for example the use of enthalpy instead of temperature which allows many problems for reaction systems of complex thermochemistry to be treated almost as easily as those for which the adiabatic temperature rise coefficient is constant.

Also in Chapter II it is shown that many important reactors belong to the class: distributed feed reactors, and sub-classifications are made to facilitate subsequent development.

In Chapter III the basic optimization problems which are treated later for various reactors are stated precisely; a proof of equivalence is given and the well known¹ problem of the optimum indirect control of a tubular reactor is discussed from a new² standpoint³ (based on an idea of F. Horn's). The connection between the basic problem and the recycle problem is also discussed: (See also Ref. (24)). An asymptotic expression is given which forms the basis of

1. References 13 to 34.

2. An outline of the proof is given in Reference (2).

3. For tubular reactor, tank reactor etc. read ideal tubular reactor, etc. Precise definitions are given in Chapter II.

a transformation useful in representing optimal conversion-volume relations graphically.

Chapter IV contains new problems and new results. By an extension of the method used in Chapter III the problem of perfect mixed control of an ideal feed bypass reactor is shown to degenerate (for non-autocatalytic systems) to the indirect control problem for a tubular reactor.

The problem of perfect direct control is solved for the ideal distributed feed reactor and a corresponding problem for a tank reactor is discussed. Some important degenerate solutions of the former problem are discussed. These are the adiabatic tank-tube (MT reactor - Refs. 32 and 33) and the adiabatic tube. The condition that the latter should be optimal (subsidiary feed too hot) is shown to be in general identical with the condition that no cold shot be used in an optimal N stage adiabatic cascade. Some numerical results are presented.

In Chapter V the basic problem is discussed for a cascade of adiabatic reactors with feed heat exchanger and interstage cooling by cold shots of supplementary feed. In so far as the theory is developed for a system with an arbitrary reaction rate function

and arbitrary thermochemistry the results are all new. Much work has been published for reaction mixtures for which the adiabatic temperature rise coefficient is constant. We will review first the case of indirect¹ control;

1. G. Boreskov (Ref.44) gives the conditions for the total mass of catalyst to be stationary. (No numerical methods given). Results of calculations by Russian workers may be found in Refs. (42) and (43).
2. K. Konoki (Refs. 65, 66) gives stationarity conditions. H. Kubota (Ref. 79) treats the case where the temperature must satisfy an upper restraint and applies equations to SO_3 manufacture.
3. F. Horn (Ref. 1) treats the subject in a thesis which forms the basis for subsequent papers.
4. F. Horn and L. Kuchler (Ref. 22) give the stationary condition equations for each² basic problem, showing that they are the same, and give results of calculations on 1, 2, 3 and 4 stage

1. If the subsidiary feed is given the fictitious enthalpy minus infinity then the direct control case becomes indirect.

2. See Chapter III.

reactors.

5. R. Aris treats the problem from the standpoint of dynamic programming in a thesis and also in Refs. (4) and (37), showing that the cost of heat exchange may be accommodated in simple cases without essential modification.

6. F. Horn, (Ref. 36) extends the theory to cover the case where all reactor temperatures must lie in a given interval, and gives an excellent numerical method. He discusses also the case where the objective function depends on the cost of heat exchange and shows that in some special cases the algorithm given for the basic problem needs no essential modification.

7. E. Bartholomé and R. Krabetz (Ref. 38) give the results of some calculations for the water gas shift reaction (including sensitivity¹ calculations) carried out in a two stage cascade.

8. L. Küchler (Ref. 39) presents the results for 1, 2, 3, and 4 stage cascades.

Next we will review the case of direct control:

1. The cold shot problem for air addition and also cold feed addition in SC_2 oxidation is treated by G. Boreskov and others (Refs. 19, 42,

1. See the later part of Chapter V.

43, and 44). Results of calculations are given but the published analysis goes little further than a statement of the problem.

2. K. Konoki (Ref.64) derives the conditions for the total volume to be stationary. His equations are special cases of our equations (5.21), (5.22), and (5.17).

3. R. Aris, in his thesis, and also in Ref. (4), and with Kung You Lee (in Ref. 45) treat the problem from the standpoint of dynamic programming. Calculations made for a three stage cold shot SO_2 converter in which the cost of preheating is allowed for in a simple way are presented.

4. F. Horn (Ref. 40) gives equations for a two stage reactor; these equations are particular cases of K. Konoki's.

5. H. Bakemeier and R. Krabetz (Ref. 11) give equations for the total volume to be stationary for a reactor in which each stage may be preceded by a heat exchanger, or a mixing tee by means of which cold gas (which may be of an alien composition¹) may be added, the particular

1. In the sense of R. Aris (Ref. 4). See also Chapter II.

disposition required being specified by making the elements of a vector 0 or 1. It follows that their equations should reduce to those of K. Konoki for the feed bypass reactor. It appears that they do not, however.

6. H. Bakemeier, H. Detzer, and R. Krabetz (Ref. 41) consider a three stage reactor for ammonia synthesis where the objective function to be minimized is the total high pressure volume. If one sets the volume not occupied by catalyst (i.e. the heat exchange volume) to zero in their equations, one should get Konoki's equations, but this does not happen: there is only one equation which does not agree with Konoki's but it would if a subscript were changed, so the disparity may be due to a misprint.

7. J.M. Douglas (Ref. 35) considers the adiabatic feed bypass reactor without feed preheater as an approximation to a continuous stirred tank reactor, and derives conditions for the optimum distribution of volume and feed. These conditions should be special cases of equations (5.17) and (5.23). The interested reader will

verify that they are. (Douglas considered an irreversible exothermic reaction but for this problem there is no essential distinction between reversible and irreversible reactions).

In Chapter V we start out by deriving the necessary conditions for the total volume to be stationary (a generalization of the work of Konoki and others¹) and discuss methods of solving these equations along with the conditions under which solutions exist and correspond to an overall minimum. Some of the equations have interesting "trivial roots" which are shown to be related to the degeneracy (mentioned above) which arises when the supplementary feed is unreasonably hot. The structure of the equations is such as to favour forward calculation. The case where all fluid temperatures must lie below a given temperature is treated. The sensitivity problem is treated by one method which can be used either for direct or indirect control and by another method suitable for indirect control only.. Some results of numerical calculations using an integration procedure which is a modification of Horn's (Ref. 36) are presented. (The numerical procedure used is about 100 times faster than the method given in 3 above: Ref. (45).)

1. F. Horn in some unpublished work had also derived equations equivalent to Konoki's. It is a pleasure to acknowledge having used them as a check.

Also presented are the corresponding results for the perfectly controlled reactors discussed in Chapter IV.

In Chapter VI the basic problem for U-tube and related reactors is treated, the adjustable variables being the inlet temperature and an internal heat transfer parameter. A perturbation method is used to find the derivatives of the objective function with respect to its arguments, together with a recent iterative gradient hill climbing procedure. Reactors of the empty-full U-tube type, such as the T.V.A. ammonia synthesis reactor are included. The basic problem for the T.V.A. reactor has been treated before but not by the method developed in Chapter VI, which anyway is a general method for U-Tube reactors. The idea of using a pebble heat exchange reactor¹ for a single exothermic reversible reaction is new. (Regenerative reactors of this type have been used in cracking reactions - see e.g. Ref. 9). Various numerical results are presented. A brief review of the relevant work follows:

van Heerden has made a study of autothermal processes, considering primarily the steady state stability analysis, considering the empty-full

1. The U-Tube model can be used to describe the pebble heat exchange (Push-Pull) reactor.

U-tube reactor (Ref. 47), the adiabatic tube with axial diffusion, the continuous adiabatic tank, and the adiabatic (plug flow) tube with feed effluent heat exchange (Ref. 48).

H. Kubota (Ref. 79) has treated the optimization of the empty-full U-tube reactor by simply making many function evaluations. Kubota used a graphical integration procedure. Later (Ref. 54) Kubota used an analogue computer with a conducting paper bivariate function generator - the precision of such calculations is of course questionable. N.S. Zayarnyi (Ref. 56) also used an analogue computer with an elaborate model of an ammonia synthesis reactor. Kuo and Rubin (Ref. 55) considered a complicated concentric tube model. Baddour et al. (Ref. 57) made an extensive study of a T.V.A. reactor considering especially the steady state (Ref. 57) and unsteady state (Ref. 58) stability analysis.

In Chapter VII various reactors are compared for several outlet conversions and the three sets of rate function (1.1) parameters shown in Table 1.1.

Table 1.1.

	1st. set	2nd. set	3rd. set
H	8.7678419,14	1.75356838,7	2.5,3
H'	1.244246,20	2.488492,12	3.54775425,8
A	2.2747861,4	1.13739305,4	5.68696525,3
A'	3.41217915,4	2.2747861,4	1.706089575,4
J	158.5	158.5	158.5

where $a, b = ax10^b$

CHAPTER II

Classification of Tubular Reactors and Idealised Models.

In this chapter we will classify tubular reactors under different headings and consider the steady state heat and material balance equations for idealised models which will be required in later chapters for optimum problems.

PART I : Definitions, Basic Equations, etc.

Ideal Tubular Reactor¹:

An idealised model of a single inlet, single outlet tubular reactor for which:

- 1) The fluid velocity and composition, temperature and pressure are constant across any plane of section.
- 2) There is no longitudinal mixing.

Distributed Feed Reactor²; Ideal Distributed Feed Reactor:

Consider a tubular reactor which has a main feed F_0 and a supplementary feed F_m which is distributed along its length; see Fig 2.1. Such a reactor will be termed - Distributed Feed Reactor.

An idealised model of a distributed feed reactor

-
1. In the sense of Ref. (3) for example; also known as a plug flow reactor Ref. (71)
 2. Has been described as a Cross Flow Reactor (Refs. 3, 27)

which is a generalisation of an ideal tubular reactor, will be called an Ideal Distributed Feed Reactor, and has the following properties:

- 1) The fluid velocity and fluid composition, temperature and pressure are constant across any plane of section. (If the plane of section coincides with a point of addition of F_m , then mixing must be perfect in this plane, in general).
- 2) There is no longitudinal mixing.

For convenience in laying out the theory of the ideal distributed feed reactor we will define some further terms and discuss some elementary properties under the following subheadings:

- a) Basic composition; reference substance; conversion; mixing mass balance; m ; class of functions $w(m)$.

We are concerned only with single reactions. Suppose that the reaction taking place in an ideal distributed feed reactor is represented:

$$\sum v_i M_i = 0 \qquad 2.1$$

where M_i is the chemical formula of the i th substance, and v_i is the stoichiometric coefficient of the i th substance - if it is a product; minus the stoichiometric

coefficient - if it is a reactant, and zero if it is an inert substance. It will be convenient to take the substance represented by $i = 1$ to be a reactant not in excess, to call it the Reference Substance, and to write the equation in such a way that $\nu_1 = -1$.

The Basic Composition of a mixture is the composition it would have if it were converted completely in the reverse direction - i.e. until at least one product were to disappear.

The Basic Molal Flowrate f_{i0} of the i th component in a stream is the value its actual flowrate would have if it were instantly reacted to completion in the reverse direction. For a batch reactor the expression "containing x moles of basic reference substance" will be taken to mean that if converted completely in the reverse direction there would be present x moles of reference substance.

Our scope is limited to reactors where F_0 and F_m have the same basic composition¹.

If a_i is the number of moles of the i th substance in a mixture which contains 1 mole of reference substance and whose composition is the basic composition of the

1. That is to say we will exclude alien cold shots:
c.f. Ref. (4).

reactor feed, and f_i is the flowrate of the i th substance in any stream in the reactor (or reactor feed), then it follows that:

$$f_{i,0} = \alpha_i f_{1,0} \quad 2.2$$

and

$$f_i = f_{i,0} + v_i y f_{1,0} \quad 2.3$$

where y is the conversion of reference substance corresponding to the stream. The composition at any point in the reactor is therefore determined by the variable y , and parameters α_i . If $f_{1,0}$ is also known then the flowrates can all be determined: $f_{1,0}$ will be called the Basic Reference Flowrate and denoted: w

$$f_{1,0} = w \quad 2.4$$

If two streams (whose basic compositions are the same) with basic reference flowrates w_1 and w_2 and conversions y_1 and y_2 respectively are mixed continuously in a chamber of negligible volume (so that no reaction can take place during the mixing), then the resulting stream will have basic reference flowrate w_3 , and conversion y_3 ,

given by:

$$w_3 = w_1 + w_2 \quad 2.5$$

$$(w_1 + w_2) y_3 = w_1 y_1 + w_2 y_2 \quad 2.6$$

as can easily be verified.

Instead of z , the distance from the entrance of the reactor to the plane of section in Fig. 2.1, it is convenient to use m , which is the corresponding void volume if the tube is either unpacked, or packed with inert material; or the mass of catalyst if the tube is packed with solid catalyst. The function $w(m)$ will be used to describe the subsidiary feed addition. We will consider $w(m)$ to be a (non negative) non decreasing function¹. It will be supposed that in addition $w(m)$ is continuous everywhere except at a finite number of points where it may have finite jumps. In this way we can include, for example, a cascade of N adiabatic beds packed with catalyst with "cold shot" intercooling by supplementary feed, for which $w(m)$ would have the form shown in Fig. 2.2.

b) Reaction rate expression: dependence on y and T

For a homogeneous reaction, the reaction rate v ,

1. Otherwise a separation at the walls would be implied, and it is outside our scope to treat such reactors.

i.e. the number of moles of reference substance consumed per unit time, unit volume¹ will depend on the composition, temperature and pressure, so that with a given set of parameters ϕ_i , and a given pressure in mind we may write:

$$v = v(y, T) \quad 2.7$$

For a solid catalysed reaction taking place in a packed tubular reactor we² may also use (2.7) with T as the fluid temperature, and a given particle size and configuration in mind provided that fluid phase diffusion³ is unimportant. (If fluid phase diffusion is important then another variable, such as w would be required). When solid catalyst is present the rate is ordinarily based on the mass of catalyst rather than the volume.

c) Mass balance.

Let the basic reference flowrate and conversion of F_0 be w_0 and y_0 respectively, y_m be the conversion of F_m ; let w and y be the basic reference flowrate and

-
1. Void volume if the tube is packed with inert material.
 2. We are concerned with overall rates or macro-kinetics. The details of mass and heat transfer within a catalyst pellet, are of no concern to us here.
 3. Of mass and heat.

conversion corresponding to m and w^+ and y^+ corresponding to $m + \delta m$. (See Fig. 2.3). In view of 2.5, 6 and 7, we may carry out a steady state mass balance on the element for the reference substance as follows:

$$\text{IN:} \quad w(1-y) + (w^+ - w)(1-y_m)$$

$$\text{OUT:} \quad w^+(1-y^+)$$

$$\text{DESTROYED:} \quad v(y, T) \delta m$$

$$\therefore w^+(y^+ - y_m) - w(y - y_m) = v(y, T) \delta m \quad 2.8$$

If we introduce a new variable x :

$$x = (y - y_m)w \quad 2.9$$

$$\text{and write } x + \delta x = (y^+ - y_m)w^+$$

Then in the limit $\delta m \rightarrow 0$, we get:

$$\frac{dx}{dm} = v(y, T) = v\left(\frac{x}{w} + y_m, T\right) \quad 2.10$$

$$x(0) = (y_0 - y_m)w(0) \quad 2.11$$

If w is constant, i.e. if no subsidiary feed is added, we have an ideal tubular reactor, and if we introduce t , the volume (mass of catalyst) per unit basic reference flowrate:

$$t = \frac{m}{w} \quad 2.12$$

we get

$$\frac{dy}{dt} = v(y, T) \quad 2.13$$

$$y(0) = y_0 \quad 2.14$$

d) Integration of Mass balance equations.

If $T(m)$ and $w(m)$ are given then (2.10) may be integrated. Alternatively T may be specified as a function of x and w , and w as a function of x and m etc. Often T will be specified implicitly by a heat balance, so that the relation between enthalpy conversion and temperature will be required.

If $T(m)$ or $T(y)$ is given (2.13) can be integrated. If $y(T)$ is specified however, and is not easily invertible to give $T(y)$, then (2.13) may be transformed into:

$$\frac{dT}{dt} = \frac{v(y(T), T)}{y'(T)} \quad (2.15)$$

$$\text{where} \quad y'(T) = \frac{dy}{dT} \quad (2.16)$$

(2.15) can be integrated giving $T(t)$ from which y , $y(T(t))$ can be determined, it being necessary to invert $y(T)$ only once: (to determine $T(0)$ the initial condition).

This case arises, as will be seen in the next section, for an adiabatic bed where the reaction mixture is ideal but non linear.

e) Temperature: dependence on conversion and enthalpy: heat balance for mixing of streams

We will consider first the case where the reaction mixture is non ideal and where it is necessary to resort

to experiment to obtain thermochemical data. (In principle) the following experiment might be conducted:

An adiabatic constant pressure batch reactor is quickly charged with feedstock containing one mole of basic reference¹ substance at a suitable temperature T_1 and conversion y_1 ; the temperature and conversion T and y are then determined simultaneously enough times for the yT relation to be satisfactorily deduced. The process is then repeated for several suitably chosen initial temperatures, $T_2, T_3 \dots T_5$.

Suppose the results obtained are represented graphically in Fig. 2.4 (curves $h_1, h_2, h_3 \dots h_5$)

Since the reaction took place adiabatically at constant pressure these curves must be curves of constant enthalpy². If we fix a basis, by making h_1 zero for example, then h_2, h_3, h_4 and h_5 could be obtained from the results of a separate run (curve A) where heat was added at a known rate.

In this manner T could be obtained as a function of y and h :

$$T = T(y, h) \quad (2.17)$$

1. See text under subheading (a) above.

2. Kinetic energy terms are assumed to be negligible.

Next, suppose that we are dealing with an ideal mixture, so that at any given temperature T the partial molal enthalpy, $\bar{H}_i$ of the i th substance is equal to its enthalpy when pure, $H_i(T)$: we may then write, using (2.2) and (2.3):

$$h = \sum (\alpha_i + \nu_i y) H_i(T) \quad (2.18)$$

which gives us y as a function of h and T :

$$y = \frac{h - \sum \alpha_i H_i(T)}{\sum \nu_i H_i(T)} \quad (2.19)$$

It may be either inconvenient or impossible to invert (2.18) so as to obtain T in closed form as an explicit function of y and h .

Calculations are simplified if $H_i(T)$ can be linearly interpolated reasonably well over the range of temperatures which are found in the reactor:

$$H_i(T) = a_i + b_i T \quad (2.20)$$

so that using (2.18), we may obtain T :

$$T = \frac{h - \sum a_i \alpha_i - y \sum a_i \nu_i}{\sum b_i \alpha_i + y \sum b_i \nu_i} \quad (2.21)$$

If $\sum b_i a_i \gg y \sum v_i b_i$, which might occur¹ if either (i) y were small everywhere, (ii) the basic composition were high in inerts, or (iii) the heat of reaction were not strongly temperature dependent, then one could replace y in the denominator of 2.21 with some average value, y_{av} , thus obtaining a linear relation between y , h , and T :

$$T = \frac{h - \sum a_i a_i - y \sum a_i v_i}{\sum b_i a_i + y_{av} \sum b_i v_i} \quad (2.22)$$

It is convenient to define a new variable θ :

$$\theta = \frac{h - \sum a_i a_i}{\sum b_i a_i + y_{av} \sum b_i v_i} \quad (2.23)$$

and to denote the adiabatic temperature rise coefficient by J ,

$$\text{i.e.} \quad J = \frac{- \sum a_i v_i}{\sum b_i a_i + y_{av} \sum b_i v_i} \quad (2.24)$$

$$\text{We may then write: } T = \theta + Jy \quad (2.25)$$

If two streams of basic reference flowrates w_1 and w_2 and enthalpies h_1 and h_2 are mixed adiabatically then h_3 for the resulting stream is given by:

$$h_3(w_2 + w_1) = h_1 w_1 + h_2 w_2 \quad (2.26)$$

1. Such is the case for example in the commercial air oxidation of SO_2 .

the equation holding whether reaction takes place during the mixing or not. If 2.25 holds, it follows that for adiabatic mixing:

$$(T_3 - Jy_3)(w_2 + w_1) = (T_1 - Jy_1)w_1 + (T_2 - Jy_2)w_2 \quad (2.27)$$

Whilst 2.27 may hold well for temperatures T_1 and T_2 which are to be found in the reactor it may not extrapolate well down to the supplementary feed temperature. It may be possible to use a linear relation without incurring serious errors by assigning to the supplementary feed a fictitious temperature.

Consider for example the case of addition of cold shot of conversion y_m , and temperature T_m to a stream of temperature T_1 , and conversion y_1 : (adiabatically and quickly). Suppose the resulting conversion were y_3 and temperature $\bar{T}_3$. If 2.27 were to hold well, then $\bar{T}_3$ would equal T_3 , the point in Fig. 2.5 corresponding to y_3 on the line L joining T_1y_1 to T_my_m . But it does not, so that corresponding points for the mixing lie on the curve C, say. Given this curve C it should not be difficult to choose a fictitious temp T'_m such that the temperature of the mixture predicted by use of the line L' should not be far from $\bar{T}_3$, if one knows approximately what y_3 will be.

In a multistage adiabatic reactor with cold shot cooling the fictitious temperature should be chosen so as to correct for the nonlinearity in the final stages.

One may take 2.24 and 2.25 to define θ , (instead of 2.23), in which case the equation:

$\theta_3(w_2+w_1) = \theta_1 w_1 + \theta_2 w_2$ could be used instead of 2.27, and a fictitious θ_m used.

f) use of h , or θ instead of T in expression for rate.

In an adiabatic reactor h can only change as a result of mixing¹; for this reason it is convenient to consider the rate to be a function of y and h ; we will define:

$$V(y, h) = v(y, T(y, h)) \quad (2.28)$$

Also, if 2.23 and 2.25 hold, we may use U , defined by:

$$U(y, \theta) = v(y, T + Jy) \quad (2.29)$$

g) Rate expressions $v(y, T)$ - general properties for non-autocatalytic reactions.

We will consider non-autocatalytic reactions, i.e. reactions for which:

$$\frac{\partial v}{\partial y} < 0 \quad \text{for all } 0 \leq y \leq 1, T > 0.$$

1. Pressure is assumed to be either constant or without influence and velocity heads are assumed negligible.

One such reaction is described by the function:

$$v = (1-y)H e^{-\frac{A}{T}} - yH'e^{-\frac{A'}{T}}; H' > H > 0; A' > A > 0; (1.1)$$

For the sets of parameters given in table 1.1 this function has contours for $v \geq 0$ of the shape shown in Fig. 2.6. Such hump-shaped contours are well known and are typical of functions used to represent reversible exothermic reactions of industrial importance.

These functions are discussed in books on chemical reactor theory¹.

The locus of the maxima is of importance. This may be obtained considering:

$$\frac{\partial v}{\partial T} = \frac{AH(1-y)e^{-\frac{A}{T}}}{T^2} - \frac{A'H'}{T^2} ye^{-\frac{A'}{T}} = 0$$

from which it follows that the temperature at which the rate is maximum is given by solving for T the equation:

$$T \ln(A'H'y) - T \ln(AH(1-y)) = A' - A$$

for $y_c < y < 1$ and $y_c = AH/(AH+A'H')$

while for $y \leq y_c$, the temperature is infinite. It can be seen that for $v \geq v(y_c, \infty)$ the contours of constant rate in Fig. 2.6 do not have a hump but are monotonic increasing. It is usually the case that y_c is very

1. See References 2, 3, 4, and 5; in particular the last.

small¹. If the lower part of Fig. 2.6 were drawn to a much larger scale in y and smaller scale in T , we would get a diagram like Fig. 2.7.

Such curves are described by R. Aris in his new book (Ref. 5)

y_c is of importance in the theory developed in Chapter IV.

It can be seen from these contours that a straight line of positive slope will intersect a particular contour at most twice. This property is important for the numerical examples based on the theory developed in Chapter V.

PART II : Classification of Ideal Distributed Feed Reactors.

Figure 2.8 represents an ideal distributed feed reactor with a facility for adding (or removing) heat indirectly as the reaction proceeds. $Q(m)$ is the heat added from the beginning (i.e. left hand end in Fig. 2.8) of the reactor up to the place corresponding to a volume (amount of catalyst) m . F_0 and F_m are the main and supplementary feeds².

-
1. For the sets of parameters in table 1.1, y_c is of the order of 0.00001.
 2. It is outside our scope to consider cases where either the basic compositions of E_0 and F_m differ, or $w(m)$ is not strictly non-negative, non-decreasing.

If $y_0 = y_m$ we will refer to the ideal distributed feed reactor as an ideal feed bypass reactor. Apart from this we may classify ideal distributed feed reactors according to their controllability. Using (2.10) and (2.28) we may write the mass balance:

$$\frac{dx}{dm} = V(y_m + \frac{x}{w(m)}, h) \quad (2.32)$$

whilst from (2.26) it is clear that:

$$h = \frac{w(0)}{w(m)} (h_0 - h_m) + h_m + \frac{Q(m)}{w(m)} \quad (2.33)$$

we may therefore regard $Q(m)$ and $w(m)$ as control functions, and define the following terms:

- 1) mixed control : where both $Q(m)$ and $w(m)$ are adjustable.
- 2) perfect mixed control : where $Q(m)$ can be made any¹ arbitrary function and so can $w(m)$.
- 3) direct control : where $w(m)$ is adjustable but $Q(m) - Q(0+)$ is fixed.²
- 4) perfect direct control : where $w(m)$ can be made any arbitrary function¹ but $Q(m) - Q(0+)$ is fixed.²
- 5) indirect control : where $Q(m)$ is adjustable but $w(m)$ is fixed.
- 6) perfect indirect control : where $Q(m)$ can be made any arbitrary function but $w(m)$ is fixed.

1. Within the class of admissible functions - i.e. both must be piecewise continuous. $w(m)$ must be non negative, non decreasing.
2. i.e. $Q(m)$ is allowed a variable (positive or negative) step at $m=0$. (Effectively an adjustable main feed temperature).

7) imperfect control : where none of the conditions 2, 4, 6 above is satisfied. We may classify imperfectly controllable reactors according to their number of adjustable control parameters and their basic structure. Evidently, if the number of adjustable control parameters is finite then control is necessarily imperfect; the converse is not true, as is seen by considering a reactor which comprises a perfectly controlled reactor feeding an adiabatic ideal tubular reactor (of nonzero volume) - the number of control parameters is infinite but control is imperfect.

Examples:

a) Indirect Control

In Figs. 2.9 and 2.12, one parameter reactors (only feed temperature controllable) are represented. The reactors represented in Figs. 2.10 and 2.11 are also¹ one parameter types as far as their operation is concerned, but in design an internal heat exchange

1. The pebble heat exchange reactor (Fig. 2.10) is not a steady state reactor at all, but may be included if certain assumptions - considered in Chapter VI - are reasonable. The reactors represented by Figures 2.11, 2.13, and 2.14 really require consideration of transverse

parameter may be adjusted as well.

In Fig. 2.13 a more flexible reactor is represented.

b) Direct Control

In Fig. 2.15 the $N-1$ cold shot flows and the inlet temperature to the first stage are adjustable during operation whereas in design the $N-1$ catalyst ratios are also adjustable, making $2N-1$ parameters.

c) Mixed Control

During operation of the reactor represented in Fig. 2.16 four parameters may be adjusted independently; in design seven. Fig. 2.14 represents an adiabatic autothermal reactor with adjustable main feed temperature and cold shot fraction. If the internal heat transfer is adjustable in a 1 parameter fashion (independently of the bypass fraction and main feed temperature) then we have mixed control with 3 parameters.

heat and mass transfer for precise calculations; it is reasonable to suppose however that the ideal models used here will provide at any rate an "upper bound" to their performance.

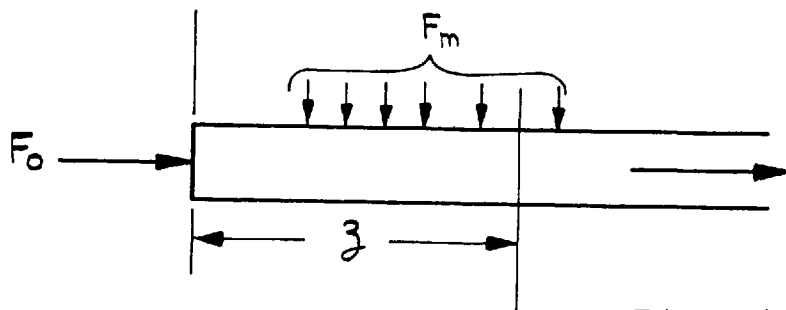


Fig. 2.1.

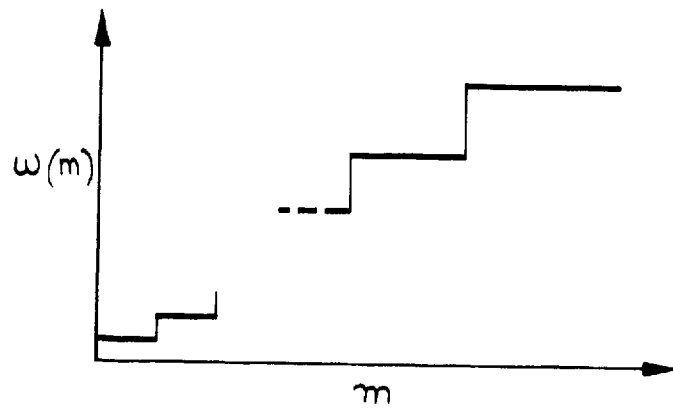


Fig. 2.2.

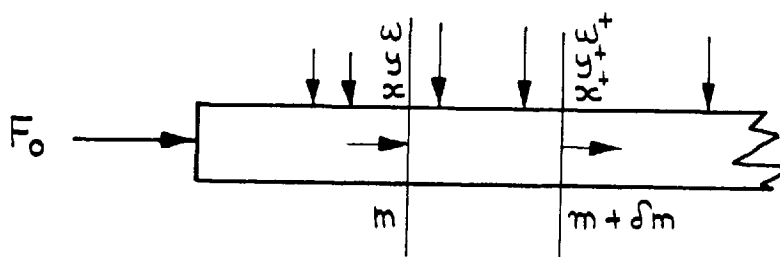


Fig. 2.3.

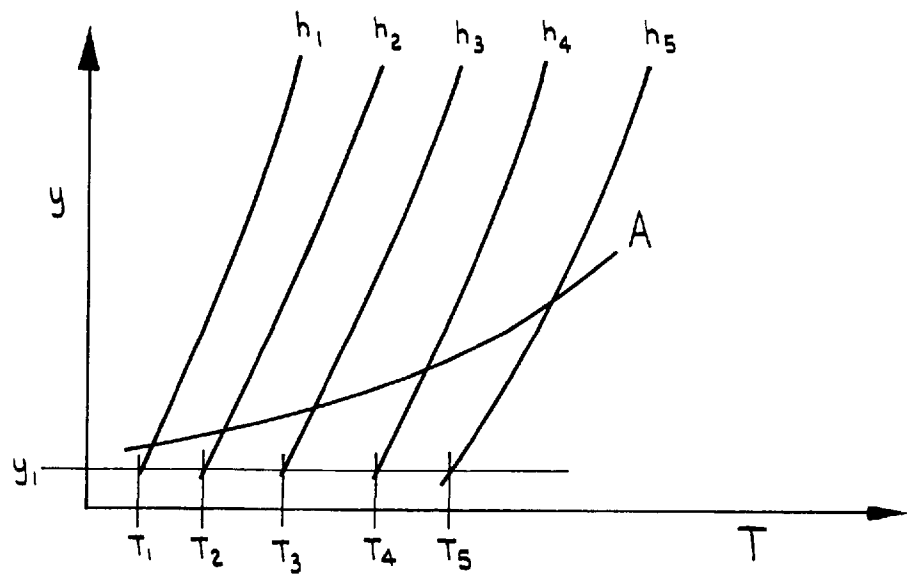


Fig. 2.4.

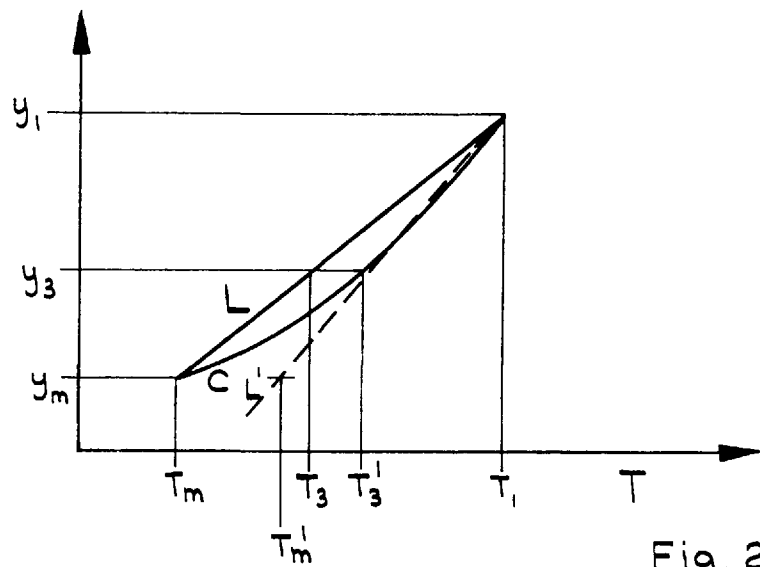


Fig. 2.5.

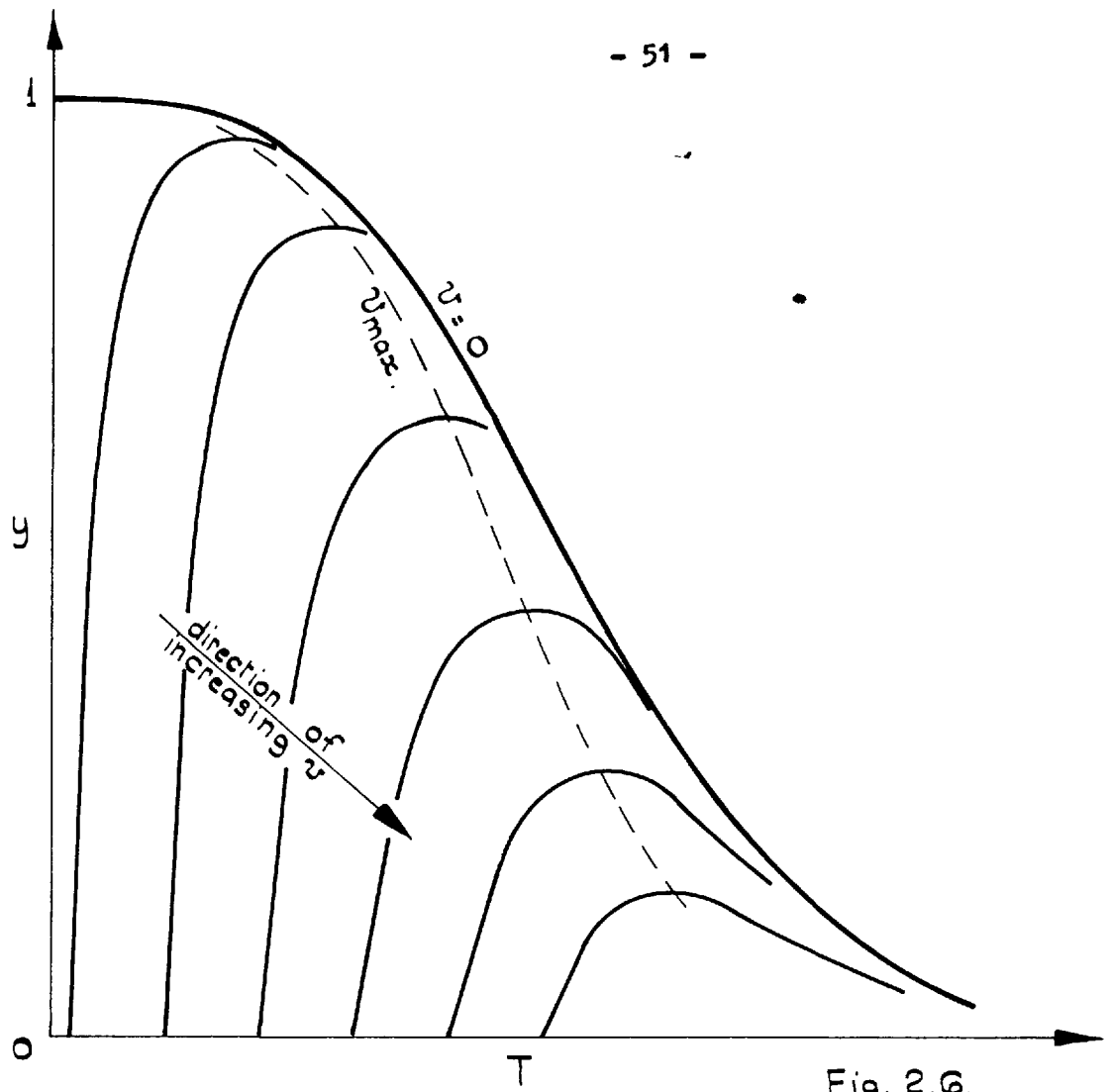


Fig. 2.6.

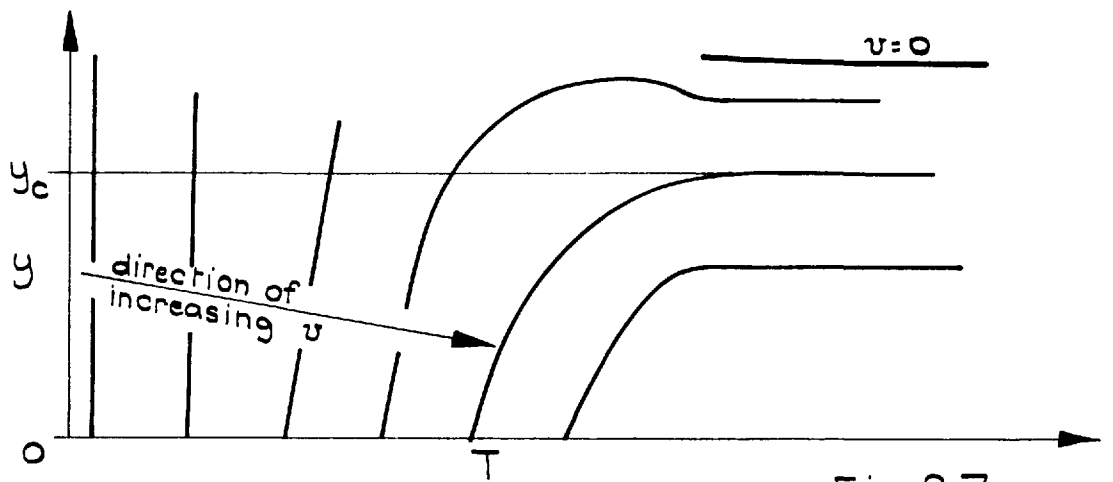


Fig. 2.7.

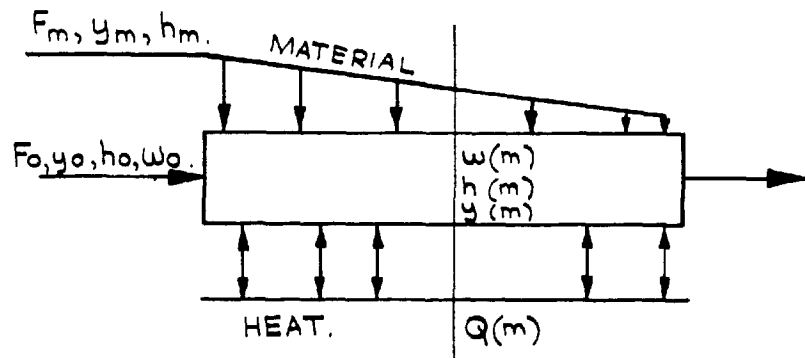


Fig. 2.8.

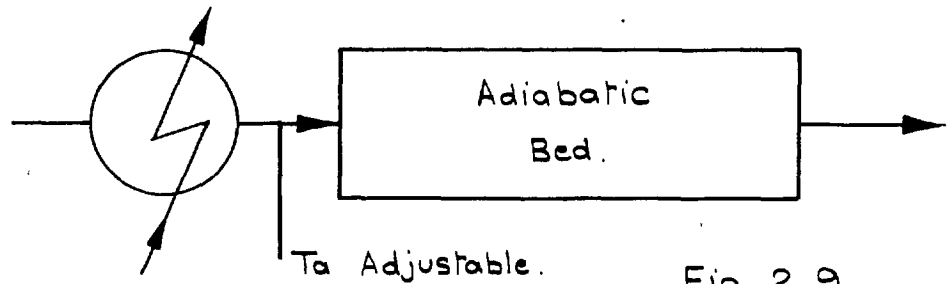
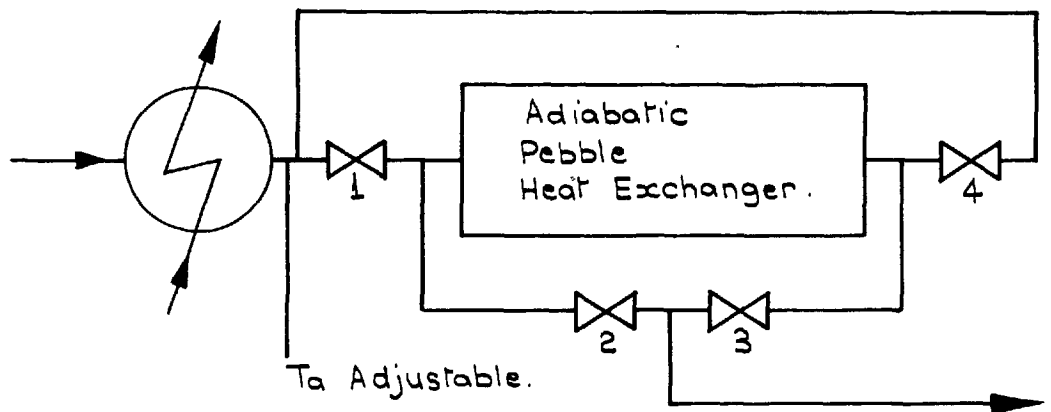


Fig. 2.9.



1 and 3 open, 2 and 4 closed, during first half cycle.
2 and 4 open, 1 and 3 closed, during next half cycle.

Fig. 2.10.

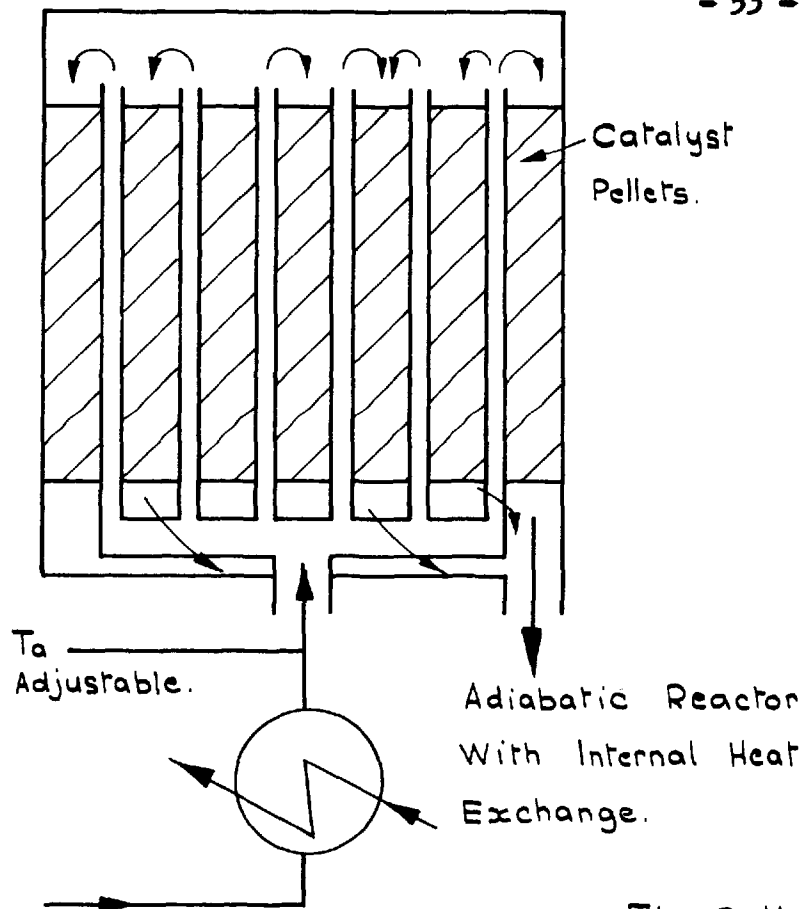


Fig. 2.11.

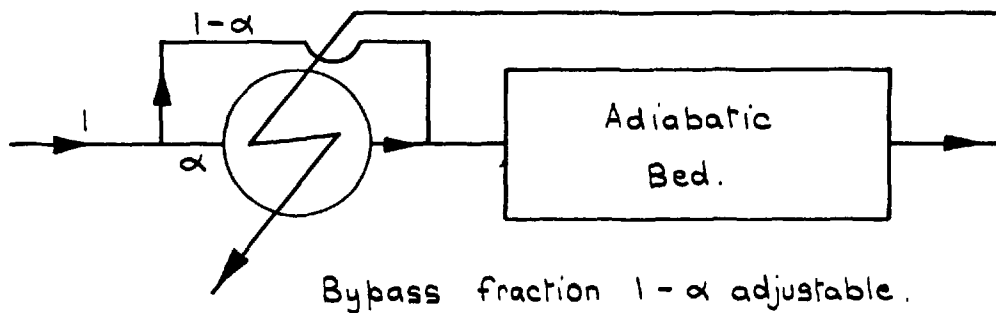


Fig. 2.12.

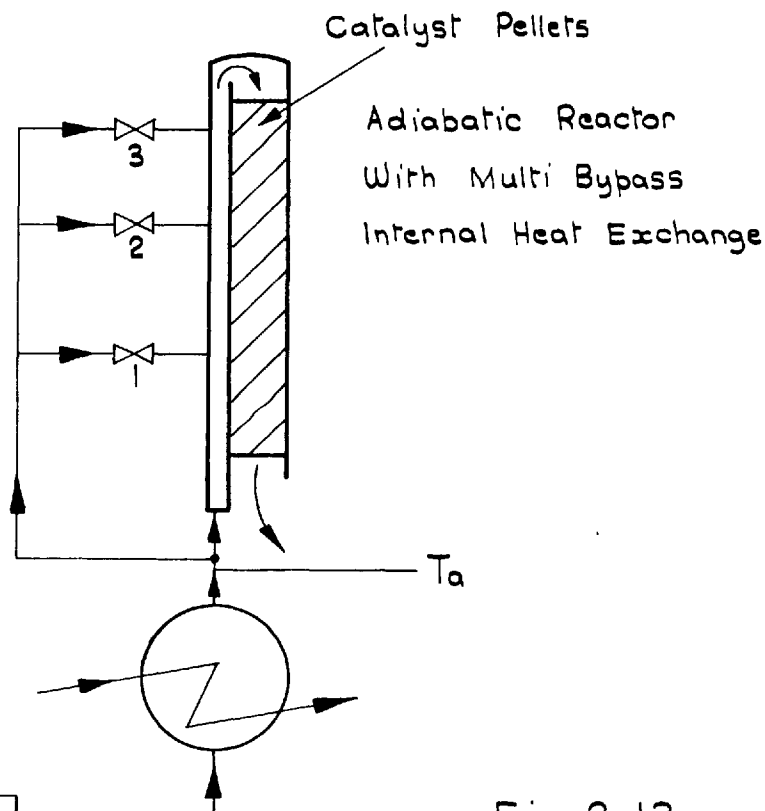


Fig. 2.13.

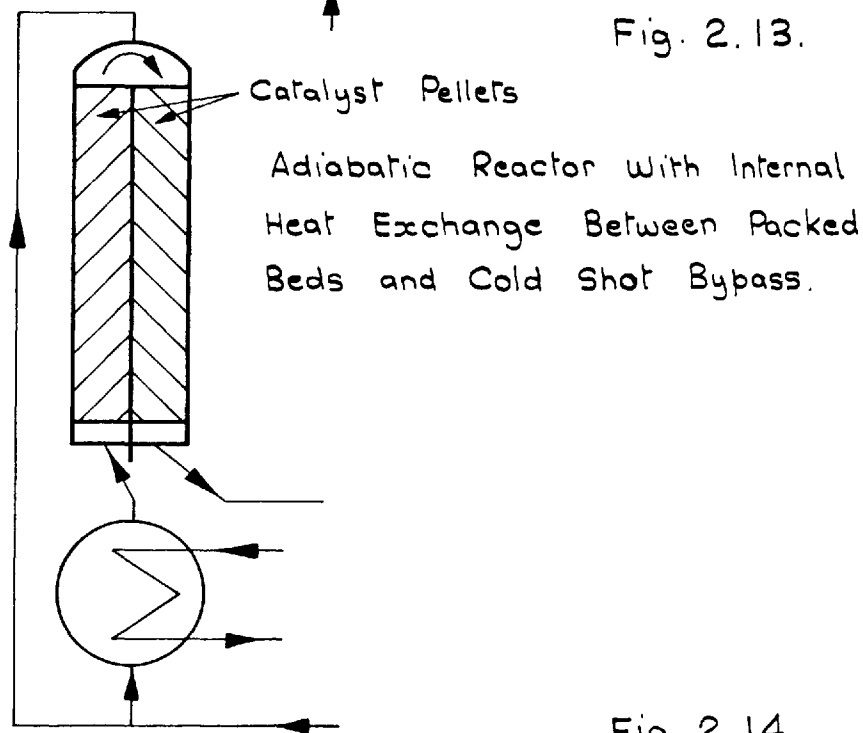
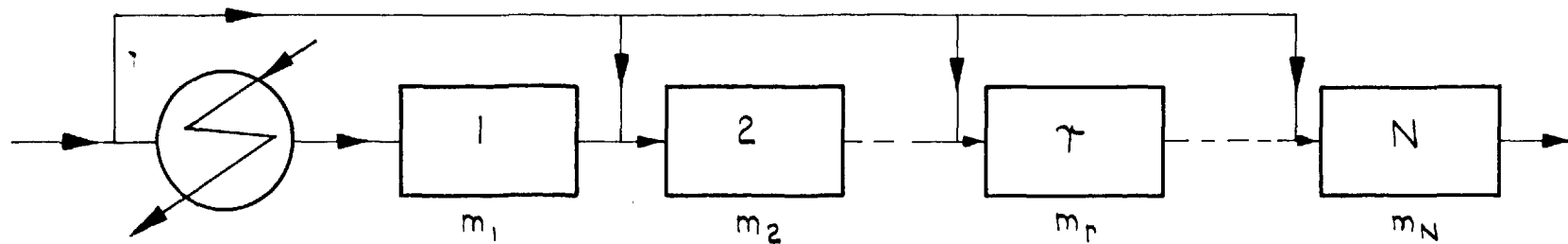
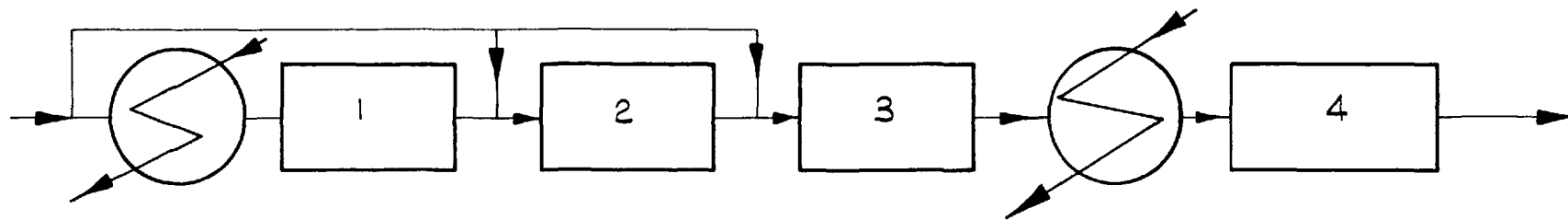


Fig. 2.14.



N stage adiabatic cascade with direct intercooling with cold feed.

Fig. 2.15.



Four stage adiabatic cascade with mixed intercooling.

Fig. 2.16.

CHAPTER III

Optimization Problems For Distributed Feed Reactors.

Two fundamental optimization problems; basic problems (i) and (ii) will be described first.

Given: reactor type, rate expression, basic feed composition, main and subsidiary feed conversions y_o , y_m , and outlet basic reference flowrate, w_f , the problems are:

- (i) minimize¹ the total volume (mass of catalyst), m_f
for given y_f ; ($y_f > y_m$; $y_f > y_o$).
- (ii) maximize² y_f for given m_f .

Unless any statement is made to the contrary it may be taken for granted that we are considering only the ideal distributed feed reactor in what follows.

The "free variables" for the optimization are the functions $w(m)$, $Q(m)$ which will be restricted according to the reactor type being considered. If these

-
- 1. strictly : "find the infimum or greatest lower bound of ..."
 - 2. strictly : "find the supremum or least upper bound of ..."

(These bounds may not be attained although it will generally be assumed, in what follows, that they are)

functions are further restricted by problem specifications (such as $\left| \frac{dQ}{dm} \right| < 100$ everywhere for example), the term restraint will be used to cover the additional restrictions. Also the terms restrained and unrestrained.

Reducible Problems:

It is easy to show, by considering equations (2.32), (2.33) that if basic problem (i) is solved in an unrestrained case for different values of w_f , w_{f_1} and w_{f_2} , say, the corresponding minimum values satisfy the relations:

$$\frac{m_{f_1}^{\mathcal{H}}}{w_{f_1}} = \frac{m_{f_2}^{\mathcal{H}}}{w_{f_2}} = t_f^{\mathcal{H}} \text{ say,} \quad (3.1)$$

and that in fact if instead of minimizing m_f one chose to minimize

$$t_f = \frac{m_f}{w_f} \quad (3.2)$$

the minimum t_f would also be $t_f^{\mathcal{H}}$. Similarly the maximum value of y_f ; $y_f^{\mathcal{H}}$ in basic problem (ii) will not change if m_f and w_f are altered in such a way that the ratio t_f remains constant, i.e. the problem could also be treated equally well in terms of the one quantity t_f as

the two m_f and w_f . Alternatively it may be convenient to consider the problems for one value of w_f , e.g. $w_f = 1$. This reducibility, or scale invariance stems from the rate v being considered a function of intensive variables and would certainly break down if it were not realistic to do so - e.g. for a heterogeneously catalysed reaction in a reactor of fixed cross section with diffusion in the fluid phase controlling.

Provided v can be written $v(y, T)$ then the two problems are still reducible if restraints are placed on intensive variables such as y and T .

Equivalence of basic problems (i) and (ii)

The following remarks about equivalence apply to all distributed feed reactors.

Suppose that basic problem (i) has been solved for all outlet conversions y_f in an interval $[y_1, y_2]$ and that the minimum m_f function is denoted $m_f^*(y_f)$. If it turns out that $m_f^*(y_f)$ is strictly monotonic increasing, then the solution to basic problem (ii) for all m_f in the interval $m_f^*(y_1) \leq m_f < m_f^*(y_2)$ is the function $y^*(m_f)$ which is the inverse¹ of $m_f^*(y_f)$.

1. If $y = f(x)$, a strictly monotonic function, then $g(y)$ is the inverse of $f(x)$ if $x = g(y)$.

For suppose the curve in Fig. 3.1 represents the y_f, m_f^* relation. Then if m', y' is a point on it and we are asked for the y_f^* corresponding to m' in problem (ii), evidently $y_f^* \geq y'$, since a control giving rise to (y', m') is known to exist.¹

Suppose that $y_f^* = y'' > y'$.

Then to y'' there corresponds a minimum volume m'' which according to the strict monotonicity must be larger than m' . This contradicts the optimality of m' so the supposition is false and $y_f^* = y'$.

In a similar manner it may be shown that if the solution to problem (ii) is known for all m_f in a given interval and is strictly monotonic then the solution to problem (i) in the corresponding interval is given by the inverse function.

Basic problem:

When problems (i) and (ii) above are known to be equivalent we shall call them "the basic problem". Also

1. Strictly controls giving rise to values $m' + \epsilon$, for given $y_f = y'$ (ϵ arbitrarily small positive), because $\min [m_f]$ may not exist in the sense that no admissible control giving rise to $\inf [m_f]$ may exist.

the term "reduced basic problem" will be used.

Example:

We will consider a very important control problem: basic problem (i) for the perfect indirectly controlled tubular reactor.

$$\text{Let us use the variable } t = \frac{m}{w} \quad (2.12)$$

To every heat addition policy $Q(t)$ there corresponds a temperature distribution $T(t)$ and vice versa¹: the problem of finding an optimal $Q(t)$ is therefore equivalent to that of finding a $T(t)$ such that for given y_0, y_f, t_f defined by²:

$$\frac{dy}{dt} = v(y, T(t)) \quad (3.3)$$

$$t=0, y=y_0 \quad ; \quad y=y_f, t=t_f \quad (3.4)$$

is minimum. The solution to this problem is well known: the temperature must be chosen so as to maximize the local rate at every point in the reactor. We give here a simple proof: first note that we may exclude

1. More precisely: If C is the set of all piecewise continuous functions, then to every $Q(t) \in C$ there corresponds a $T(t) \in C$

and to every $T(t) \in C$ there corresponds a $Q(t) \in C$.

2. See equation 2.13.

all temperature policies $\bar{T}(t)$ which lead to the rate being zero or negative anywhere in the reactor¹. It is clear then from (3.3) that to every $T(t)$ there corresponds a $T(y)$, so we may write:

$$t_f = \int_{y_0}^{y_f} \frac{dy}{v(y, T(y))} \quad (3.5)$$

from which it follows that to every $T(y)$ there corresponds² a $T(t)$ so that we may transform the problem into one of finding a $T(y)$ which assigns to t_f its minimum value.

Suppose $T^*(y)$ is such that for all $y: y_0 \leq y \leq y_f$:

$$v(y, T^*(y)) \geq v(y, T(y)) \quad (3.6)$$

where $T(y)$ is any admissible function, then in order to show that the corresponding t_f^* is minimum we may

1. See appendix for proof.

2. More precisely: If C is the class of all piecewise continuous functions and $\tilde{T}(t)$ is the set of all temperature profiles which assign to v everywhere a positive value and $\tilde{T}(y)$ is the set of all Ty relations which assign everywhere to v a positive value, then:

to every $T(t) \in C \cap \tilde{T}(t)$ there corresponds a $T(y) \in C \cap \tilde{T}(y)$
 and to " $T(y) \in C \cap \tilde{T}(y)$ " " " $T(t) \in C \cap \tilde{T}(t)$
 where $\cap$ denotes intersection)

consider the difference:

$$t_f^* - t_f = \int_{y_0}^{y_f} \left[\frac{1}{v(y, T^*)} - \frac{1}{v(y, T)} \right] dy \quad (3.7)$$

In view of 3.6, we have

$$t_f^* \leq t_f \quad (3.8)$$

The above proof may be easily extended to cover the case where $T(t)$ must satisfy the restraints:

$$T_1(t) \leq T(t) \leq T_2(t) \quad (3.9)$$

where T_1 and T_2 are given admissible¹ functions satisfying (3.9).

Further, if another control variable $R(t)$ enters into the rate expression so that $v = v(y, T(t), R(t))$ and we are asked for the pair of functions $\{T^*(t), R^*(t)\}$ which leads to the minimum t_f , it can be seen by inspecting the above argument that v must be maximised locally with² respect to both T and R . R need not be continuous. Suppose for example that we have available

-
1. But not absurd functions (such that $v(yT)$ is necessarily ≤ 0 somewhere in the reactor, for example).
 2. van de Vusse and Voetter make use of this for pressure optimization: (Ref.27)

two types of catalyst at different prices, and we wish to minimize the cost of catalyst in a reactor which can have as many sections as necessary, each section containing catalyst of one type or another (see Fig. 3.2).

We may easily transform equation (3.3), introducing instead of t the variable C : the value of catalyst to the left of plane C in Fig. 3.2, obtaining an equation of the form:

$$\frac{dy}{dc} = f(y, T(c), i) \quad (3.10)$$

where $i = 1$ or 2 . $T^*(c)$ and $i^*(c)$ may be found by maximizing f with respect to i and c everywhere.

Since $v > 0$ everywhere along optimal trajectories in the above example it follows that these trajectories are also optimal for problem (ii) above.

Piecewise optimality of trajectories in the case of a perfectly controlled ideal tubular reactor.

Points on an optimal trajectory for a reactor with feed conversion y_1 and outlet conversion y_2 corresponding to conversions y satisfying:
 $y_1 \leq y' \leq y \leq y'' \leq y_2$ are also points on an optimal trajectory

for a reactor with feed conversion y' and outlet conversion y'' for otherwise the former reactor could be improved by altering the control policy in the interval $y' \leq y \leq y''$ which would contradict its optimality. It follows that if $t^*(y)$ is known for the former reactor, then for the latter reactor the corresponding minimum volume (mass of catalyst) is $t^*(y'') - t^*(y')$.

(The optimal trajectories discussed in Chapter V for finite cascades do not have this property although they do exhibit a piecewise optimality which is useful if the $y_f^*(m_f)$ relation is required for several values of N , the number of stages).

Approximate formula for $t_f^*(y_f)$ relation for 1st. order reaction.

There is no difficulty in evaluating the $\{y_f^*, t_f^*\}$ relation for any reasonable reaction rate expression $v(y, T)$ although it is necessary to resort to numerical integration in general. It has been shown (Ref. 23) that for the rate expression (1.1) this relation can be expressed in terms of the incomplete betafunction;

for the important case where $y_0 = 0$ and $y_f \approx 1$ an approximate expression was given; a slightly better approximation¹ is :

$$t_f = \frac{(H')^{\left\{\frac{1}{r-1}\right\}}}{(H)^{\left\{\frac{r}{r-1}\right\}}} \cdot y_f^r \left(\frac{y_f}{1-y_f} \right)^{\left\{\frac{1}{r-1}\right\}} \quad (3.11)$$

$$\text{where } r = A'/A \quad ; \quad r > 1 \quad (3.12)$$

t_f tends to t_f^* as $y_f \rightarrow 1$, the approximation improving as r decreases.

It follows that for $y_0 = 0$ and y_f close to 1 plots of $\log(t_f)$ against $\log\left(\frac{y_f}{1-y_f}\right)$ or $\log(1/(1-y_f))$

should be straight lines of slope $1/(r-1)$. The former plot has been found the more useful for representing exact numerical data because a fairly straight line is obtained even for smallish values of y_f . It also gives rise to fairly straight lines for optimal reactors of various types with rate expression (1.1).

Generalizations Which Stem From Basic Problem: Attainable Regions.

(i) reduced output problem: minimize² a given function

1. See appendix for details.

2. For given basic composition, rate expression, restraints, reactor type, y_0 , y_m .

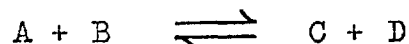
$M(y_f, t_f)$.

Especially important is the case where M satisfies:

$$\left. \begin{array}{l} \frac{\partial M}{\partial y_f} < 0 \\ \frac{\partial M}{\partial t_f} > 0 \end{array} \right\} \quad (3.13)$$

When it is well known that if the solution to the reduced basic problem is known (e.g. if $y_f^*(t_f)$ is available) this problem can easily be solved¹. This type of problem arises in reactor-separator situations:

Suppose we wish to design an optimal unit to produce given amounts of two products C and D per day from materials A and B which react (exothermically) according to:



The flowsheet for the unit is shown in Fig. 3.3. The problem is to minimize the cost of production; this cost may be separated into a reaction cost R and a separation cost S . For a given type of reactor

1. See also Refs. 24, 63, 2.

R will depend on the reactor volume (mass of catalyst) and the control cost. If we can treat the latter as approximately constant then we may write $R=R(m_f)$; $\frac{\partial R}{\partial m_f} > 0$. Similarly $S=S(w_f, y_f)$;

$\frac{\partial S}{\partial w_f} > 0$, $\frac{\partial S}{\partial y_f} < 0$. A material balance gives us $w_f y_f = C$, a constant, so using 3.2, and letting M be the total cost we obtain:

$$M(t_f, y_f) = R(Ct_f/y_f) + S(\frac{C}{y_f}, y_f)$$

from which it is clear that M satisfies (3.13).

In treating this problem we will use the attainable regions concept (Ref. 63).

The y_f^* , t_f curve for the reduced basic problem divides the plane into two regions: only the region on¹ and below the curve containing points which are attainable for the class of reactors in question.

In Fig. 3.4. M contours are also plotted.

It follows from the relations (3.13) that the minimum value of M must lie on the $y_f^*(t_f)$ curve; (point P in the figure). If the basic reduced problem

1. Assuming that the functionals "attain their bounds".

has been solved, the output problem can be considered solved, since the drawing of M contours is generally trivial. If m_f is fixed (such as it would be in most operation problems) then one degree of freedom is lost - in the above example, only the points on OP' (of slope $\frac{C}{m_f}$) could be considered. The optimum would be P' which would be invariant against changes of M (provided 3.13 remains satisfied).

(ii) irreducible output problem

In this case the corresponding generalization of the basic problem is: Minimize $M=M(y_f, w_f, m_f)$ subject to some restraint such as $f(y_f, w_f) = 0$.

A surface $y_f^* = y_f^*(w_f, m_f)$ divides the y_f, w_f, m_f space into two regions, only one of which is attainable by the class of reactors considered. If M has no relative interior minimum on the intersection Γ of $f(y_f, w_f) = 0$ with the attainable region, then it must have its minimum on the border. If this is so, then once the basic problem has been solved it is sufficient to evaluate M for points of the border of Γ and find the minimum by a one dimensional search.

The General Reactor Optimization Problem.

The basic problems discussed above are of importance in situations where the objective function is not influenced by adjusting reactor control variables except insofar as these variations cause changes in the outlet conversion, volume, etc.

Such situations arise for example when the cost of reaction volume (or catalyst) is high and the reaction slow, but heating and cooling relatively inexpensive.

It is sometimes fair to represent the cost of heat exchange in such a way that the resulting problem may be dealt with by the methods for the basic problem without essential modification (Refs. 4, 35, 36, 37: see also Chapter V).

In more general situations however, the reactor control is tied up in a very complicated way with the environmental equipment¹, (or with itself²) and

1. For example a three stage reactor with heat exchange in each stage with other process streams some of whose temperatures influence the performance of the environmental equipment.

2. Such as in a U-tube reactor; See Chapter VI.

in these cases one may be faced with a constrained minimum problem in many variables between which there are complicated restraints. Such problems may be attacked by formal decomposition procedures such as those developed in Ref. (63), (already mentioned), and (70), together with hill-climbing, linear and non linear programming etc. (Refs. 7, 72, 73, 74, 76.) The hill-climbing method described in Ref. 7 was used in a study described in Chapter VI.

Appendix to Chapter III

Part I

"We may exclude all temperature policies $\bar{T}(t)$ which lead to the rate being zero or negative anywhere in the reactor".

The essential step in a proof is given:

We may ignore of course policies which lead to a non positive rate only at isolated points. Suppose then that some policy $\bar{T}(t)$ gives rise to a negative (or identically zero) v over an interval $[t_1, t_2]$. Consider the resulting yt diagram (curve $OA_1A_2A_3A_4$ in Fig. A3.1). Then if we change the control over $[t_1, t_2]$ so that the rate is a positive constant (which is always possible) we can end up at the point A_2' and remove the section $[t_2, t_3]$ thus improving the reactor.

Part II

Approximation to $t_f^*(y_f)$.

It is shown in Ref. 23 that the relation between t_f^* and y_f for the rate expression (1.1) for $y_0 = 0$

is given by:

$$t_f^* = \frac{(H')^{\frac{1}{r-1}} (\tau)^{\frac{r}{r-1}}}{(H)^{\frac{r}{r-1}} (\tau-1)} \int_{y=0}^{y_f} \frac{(y)^{\frac{1}{r-1}}}{(1-y)^{\frac{r}{r-1}}} dy \quad A3.1$$

If we put $\rho = \frac{1}{r-1}$ in the above integral it becomes K:

$$K = \int_{y=0}^{y_f} \left\{ y \left(\frac{y}{1-y} \right)^{\rho-1} \frac{dy}{(1-y)^2} \right\}, \text{ so, noting that}$$

$$\frac{d}{dy} \left(\frac{y}{1-y} \right) = \frac{1}{(1-y)^2}$$

we may integrate by parts, obtaining:

$$K = \left[\frac{1}{\rho} \left(\frac{y}{1-y} \right)^{\rho} y \right]_0^{y_f} - \frac{1}{\rho} \int_0^{y_f} \left(\frac{y}{1-y} \right)^{\rho} dy$$

By putting the numerator = y_f , or zero in the remaining integrand, it is easy to see that K must satisfy:

$$K_a(1-\Delta) < K < K_a$$

where

$$K_a = (r-1)y_f \left(\frac{y_f}{1-y_f} \right)^{\frac{1}{r-1}}$$

we may use K_a as the estimate, obtaining:

$$\hat{t}_f = \frac{(H')^{\frac{1}{r-1}}}{(H)^{\frac{r}{r-1}}} (\tau)^{\frac{r}{r-1}} (y_f) \left(\frac{y_f}{1 - y_f} \right)^{\frac{1}{r-1}} \quad A3.2$$

The estimate given in Ref. 23 was $\hat{t}_f/y_f$ and is consequently worse.

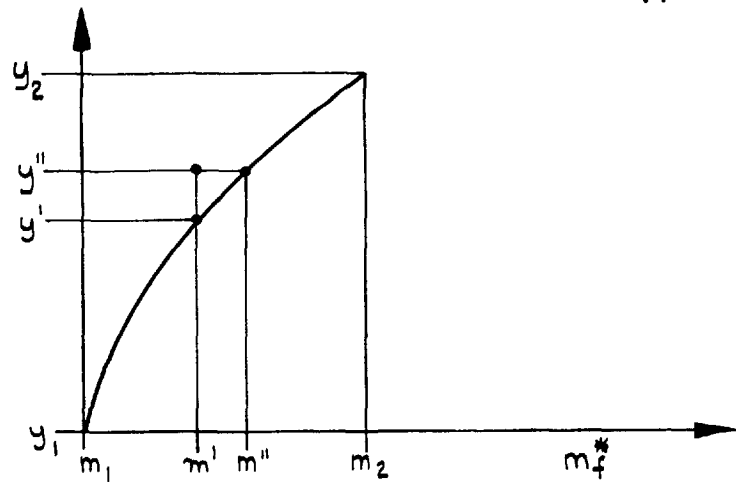
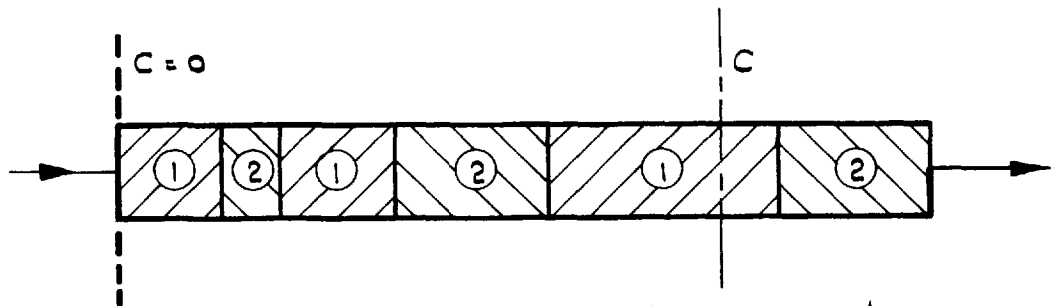


Fig. 3.1.



Tubular Reactor Packed With Catalyst Type 1 and 2 alternately

Fig. 3.2.

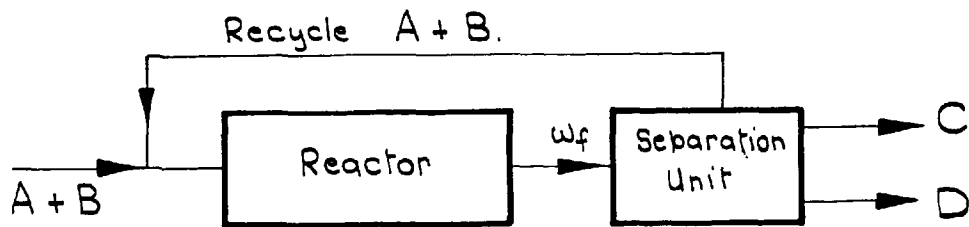


Fig. 3.3.

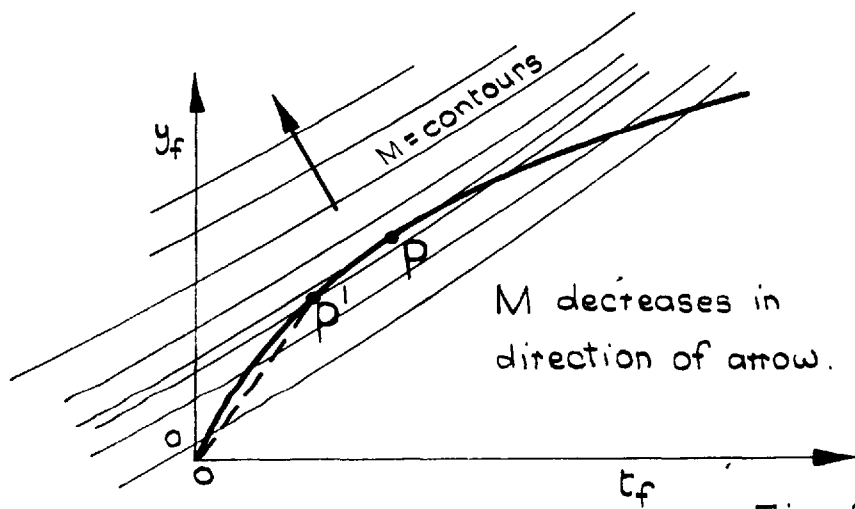


Fig. 3.4.

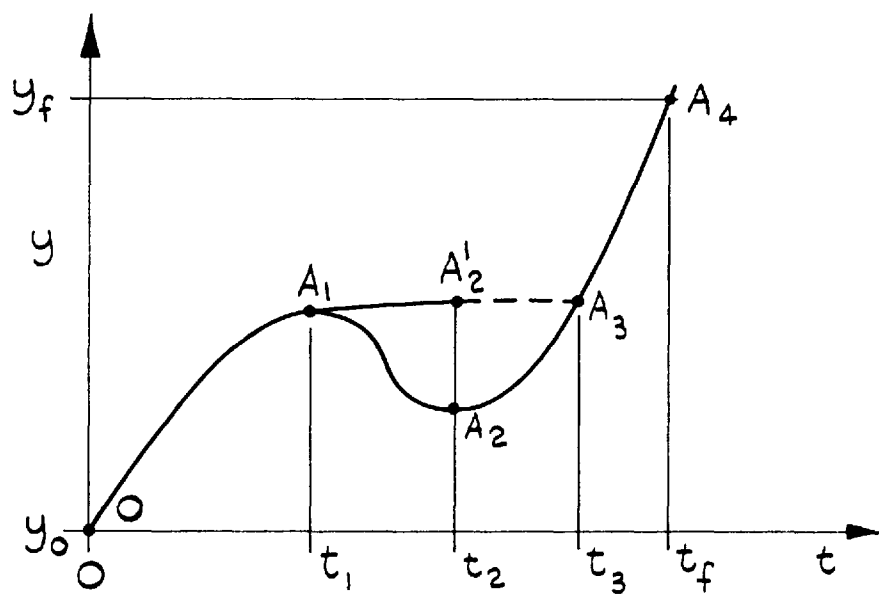


Fig. A3.1.

CHAPTER IV

Optimization of Perfectly Controllable Ideal Distributed Feed Reactors.

In this chapter the solution to the basic problems (i) and (ii) for the three types of perfectly controllable reactors is given.

It may seem to the inexperienced an idle academic exercise to consider perfectly controllable reactors at all since they are so obviously unrealisable¹. Perhaps it will be sufficient to note the following properties they have:

Their performance provides a bound to what can be achieved with any corresponding imperfectly controllable reactor: thus questions like "what possible improvement could be achieved by using a more sophisticated control scheme?" can be answered if the performance of the perfectly controllable reactor has been evaluated. As such they provide a standard of efficiency against which actual reactors may be compared. The batch counterpart of perfect direct control is programmed addition of feed to an adiabatic C.S.T.R. which could be closely approximated in practice. This problem has many variants of which one is treated in a brief sketch at the end of this chapter.

pared, as well as asymptotic results for finite cascades which are sometimes easier to obtain than the finite results themselves.

This chapter will be divided into four parts.

PART I: PERFECT INDIRECT CONTROL

The only case of importance is the case: $w(m)$ constant, i.e. where the ideal distributed feed reactor reduces to an ideal tubular reactor, for which the basic problems were treated in Chapter III.

PART II: PERFECT MIXED CONTROL

It will be shown¹ that both basic problems degenerate to the problem of perfect indirect control of an ideal tubular reactor. If $y_o > y_m$ then no subsidiary feed should be added. If $y_o < y_m$, no main feed should be used; all subsidiary feed being added at $m=0$.

Let us consider first basic problem (i): given y_o, y_m, y_f , find $\min(m_f)$, where $Q(m), w(m)$ may be

1. Except possibly for autocatalytic reactions, or if certain restraints are improved.

chosen from the respective sets of admissible functions.

It is clear from (2.17), (2.32), and (2.33) that (for $w(m)$ given) to every $Q(m)$ there corresponds a $T(m)$ and vice versa, so we may write:

$$\frac{dx}{dm} = v(y_m + \frac{x}{w(m)}, T(m)) \quad (4.1)$$

$$x(0) = w(0)(y_0 - y_m) ; x_f = w_f(y_f - y_m) \quad (4.2)$$

and try to find an optimal¹ $T(m)$ instead of $Q(m)$.

Also, we may disregard all those pairs of functions $\{w(m), T(m)\}$ which lead to a negative or zero rate anywhere². Further, to every admissible pair $\{w(m), T(m)\}$ there corresponds a pair $\{w(x), T(x)\}$ so we may write:

$$m_f = \int_{x_0}^{x_f} \frac{dx}{v(y_m + \frac{x}{w(x)}, T(x))} \quad (4.3)$$

1. This argument can be tightened up in the same way as the corresponding argument for the ideal tubular reactor in Chapter III.

2. See Appendix.

and note that to every pair $\{w(x), T(x)\}$ there corresponds a pair $\{w(m), T(m)\}$. We may thus transform¹ the problem into one of finding the pair $\{w(x), T(x)\}$ which assigns to m_f its minimum value.

Consider first a given $w(x)$; then to minimize m_f , $T(x)$ must be chosen so as to maximise v for all x , for in this way the integrand is minimised² for each x . The optimum $T(x)$ will of course depend on $w(x)$. Let it be $T^*(x, w(x))$:

$$T^*(x, w(x)): v^*(y_m + \frac{x}{w(x)}; T^*) = \max_T v(y_m + \frac{x}{w(x)}; T) \quad (4.4)$$

Putting T^* into 4.3, we obtain:

$$m_f^* = \int_{x_0}^{x_f} \frac{dx}{v(y_m + \frac{x}{w(x)}; T^*(x, w(x)))} \quad (4.5)$$

and must find an optimal $w(x)$.

Let us take the end condition on w to be:

$$w_f = 1 \quad (4.6)$$

1. This argument may be tightened up in the same way as the corresponding argument for the ideal tubular reactor in Chapter III.

2. c.f. ideal tubular reactor in Chapter III.

consider first:

case (i): $y_m = y_o$.

From (4.2) we get: $x_o = 0$, so we only need consider the integrand in computing the variation in $m_f^{\mathbb{K}}$ caused by variation of $w(x)$.

$$\text{Now } v^{\mathbb{K}} = v(y_m + \frac{x}{w}, T^{\mathbb{K}}(x, w)) \quad (4.7)$$

$$\therefore \left(\frac{\partial v^{\mathbb{K}}}{\partial w} \right)_x = - \frac{\partial v}{\partial y} \frac{x}{w^2} + \frac{\partial v}{\partial T} \left(\frac{\partial T^{\mathbb{K}}}{\partial w} \right)_x \quad (4.8)$$

The problem is easily solved if:

$$\left(\frac{\partial v^{\mathbb{K}}}{\partial w} \right)_x > 0 \text{ for all } x :: 0 < x < x_f \quad (4.9)$$

(4.9) will be satisfied if:

$$\text{a) } \frac{\partial v}{\partial y} < 0 \text{ everywhere}^1: \quad (4.10)$$

and

b) if the underlined term in 4.8 vanishes. The underlined term must vanish if T is either unrestrained.

1. We will take (4.10) to be the definition of a non autocatalytic reaction as in Chapter II.

or restrained by a simple inequality such as:

$$T_1 \leq T \leq T_2 \quad (4.11)$$

we consider only cases where (4.9) is satisfied; evidently w must be chosen as large as possible everywhere, i.e.

$$w^{\#}(x) = w_f = 1 \quad (4.12)$$

In this way the local rate is everywhere as large as possible so that if we compare the control $(T^{\#}, w^{\#})$ giving $v^{\#}$ with some arbitrary control $(T^{\#}, w)$, we get:

$$m_f^{\#} - m_f^{\#} = \int_{x=0}^{x_f} \left[\frac{1}{v^{\#}} - \frac{1}{v} \right] dx$$

so that $m_f^{\#} \leq m_f^{\#}$.

case (ii) $y_0 > y_m^1$.

x_0 , the lower limit of (4.5), now becomes an

1.(a) and (b) above assumed satisfied; these conditions imply that for $x < 0$; $(\frac{\partial v^{\#}}{\partial w})_x < 0$.

increasing function of $w(o)$, (see 4.2), so $w(x)$ must again be made as large as possible - i.e. no subsidiary feed should be added.

case (iii) $y_o < y_m$.

x_o , the lower limit of (4.5), now becomes a decreasing function of $w(o)$, so, evidently $w(o)$ should be made zero but $w(m)$ should be identically 1 for all $m > 0$: i.e. no main feed should be used.

The above argument has established what one would find difficult to disbelieve on intuitive grounds: if you have to choose between two feeds of different conversions you should reject the one with the lowest conversion¹, and put the other in all at the beginning. It is instructive to verify the above results by considering the Pontryagin² formulation. (Case (iii) above is too general to be treated by the Pontryagin method on account of the jumps in w at the beginning, but one can allow

1. Except as noted.

2. Refs. 6, 67, 68.

w to have almost a jump by allowing $\frac{dw}{dm}$ to be very large).

PART III: PERFECT DIRECT CONTROL

The mass and heat balance equations are:

$$\frac{dx}{dm} = V(y_m + \frac{x}{w(m)}, h) \quad (2.32)$$

$$h = \frac{w_o}{w(m)} (h_o - h_m) + h_m + \frac{Q(m)}{w(m)} \quad (2.33)$$

We will treat only the adiabatic reactor and consider only non autocatalytic reactions.

Adiabatic reactor with adjustable main feed temperature:

$$\text{Here } Q(m) - Q(o+) \equiv 0 ; m > 0 \quad (4.13)$$

Instead of taking the jump $Q(o+) - Q(o)$ as a variable we can consider $Q(m)$ to be identically

zero and allow $w_o(h_o - h_m)$ to vary. Let us define B:

$$B = w_o(h_o - h_m) \quad (4.14)$$

and put

$$Q(m) \equiv 0 \quad (4.15)$$

so that (2.33) becomes:

$$h = \frac{B}{w(m)} + h_m \quad (4.16)$$

If we put this expression for h into (2.32) we get:

$$\frac{dx}{dm} = V(y_m + \frac{x}{w(m)}, h_m + \frac{B}{w(m)}) \quad (4.17)$$

$$\text{with i.c.: } x(o) = w(o)(y_o - y_m) \quad (4.18)$$

As in Part II above we distinguish three cases:

case (i): Feed bypass reactor: $y_o = y_m$.

Equation (4.18) then becomes: $x(o) = 0$

The basic problems may be restated: for given y_o , h_m , and w_f :

- (i) Find a value for B and an admissible function $w(m)$ such that for given $y_f > y_o$, m_f is minimum
- (ii) Find a value for B and an admissible function $w(m)$ such that for given $m_f > 0$, y_f is maximum.

We will treat the case where $y_0 > y_c$, and where there are no restraints¹ except possibly:

$$B \leq w_f b ; \quad b > 0 \quad (4.19)$$

We will show that problems (i) and (ii) are equivalent, and that the function $y_f^*(m_f)$ and its inverse $m_f^*(y_f)$ may be obtained by some very elementary numerical procedures.

It will be necessary to make use of a simple scale invariance property, which will be established in detail, setting up the equations for future use:

Consider two reactors fed with the same feed-stock, the first described by 4.17, the other by primed variables related as follows:

$$m' = am; \quad w'(m') = aw(m); \quad B' = aB; \quad a > 0. \quad (4.20)$$

The second of these relations being taken to mean that the basic reference flowrate at a section of the second reactor corresponding to a volume m' is

1. See discussion of function $v(y, T)$ for definition of y_c . (Chapter II).

a times the basic reference flowrate in the first reactor at a section corresponding to a volume m . a is a positive constant. We will show that, correspondingly:

$$x'(m') = ax(m) \quad (4.21)$$

from which it follows immediately that:

$$y'(m') = y(m); h'(m') = h(m); T'(m') = T(m) \quad (4.22)$$

i.e. their trajectories in the hy plane are identical.

$$\text{Let } X'(m') = ax(m) \quad (4.23)$$

Putting 4.20 and 4.23 into 4.17 we get:

$$\frac{dX'}{dm'} = V(y_m + \frac{X'(m')}{w'(m')} ; h_m + \frac{B'}{w'(m')}) \quad (4.24)$$

(with i.c. $X'(0) = 0$), whereas if we write heat and mass balances for the second reactor we get simply:

$$\frac{dx'}{dm'} = V(y_m + \frac{x'}{w'(m')} ; h_m + \frac{B'}{w'(m')}) \quad (4.25)$$

with (i.e. $x'(0)=0$). It follows that 4.21 is true and hence 4.22 is true, and of course that problems (i) and (ii) are each reducible;

We will consider only the case $w_f = 1$ (4.6)

Equivalence of problems (i) and (ii)

Consider the single stage ideal adiabatic tubular reactor with adjustable feed enthalpy h_0 (which is in the class of reactors considered). For given $y_0 > 0$ and y_f : $y_0 < y_f < 1$ it is possible to find¹ an h_0 such that a corresponding finite m_f exists. It follows that for the ideal distributed feed reactor considered, to every $y_f < 1$ there corresponds at least one m_f . We will assume that there is also a minimum² which will be denoted m_f^* .

Evidently $m_f^* > 0$. To show that $m_f^*(y_f)$ is a strictly monotonic increasing function it is sufficient to show that given a point $R(m_1, y_1)$ on the

-
1. It is assumed that some reaction will take place however low the temperature.
 2. See discussion about infimum and minimum in Chapter III.

m_f^* , y_f curve, all points for which $y_0 \leq y \leq y_1$ on the straight line joining R to the point $(0, y_0)$ are attainable. (See Fig. 4.1). Suppose the control giving rise to R is $(B, w(m))$. Consider the control $(B', w'(m'))$ where the primed quantities are defined by (4.20) and a is given by:

$$a = \frac{y_2 - y_0}{y_1 - y_0} \quad (4.25b)$$

Suppose the control $\{B', w'(m')\}$ is implemented for all points m'' : $0 \leq m'' < m'$, but at $m'' = m'$, w jumps to 1 . By (4.22), the conversion just before the jump at the end must be y_1 . If the final conversion is y , a mass balance over the jump gives us:

$$ay_1 + (1-a)y_0 = y$$

Substituting for a the right hand side of (4.25b) we get after simplification:

$$y = y_2$$

as required.

The equivalence of the two problems is thus established.

Application of Pontryagin's Maximum Principle.¹

It is convenient to change the conditions of the problem in order to be able to apply Pontryagin's maximum principle. $w(m)$ must be replaced because of the non decreasing restriction; the class of admissible functions will be restricted to those which have a bounded derivative everywhere.

Let $p(m)$ be the new control function:

$$p(m) = \frac{dw}{dm} \quad (4.26)$$

$$0 \leq p \leq P \quad (4.27)$$

It will be shown that (in general) P can always be chosen sufficiently large that p never attains its bound along an optimal trajectory.

It is assumed that with the class of functions $w(m)$ restricted by (4.26) and (4.27) it is always possible to find P large enough for problems (i) and (ii) to be equivalent. In what follows we assume

1. See Refs. 6,

P large enough. Consider problem (ii):

Let us change the notation, putting $\frac{x}{w}$ and write: $V(y_m + \frac{x}{w}, h_m + \frac{B}{w}) \equiv r(x_1, x_2, B)$ so that (4.17) and (4.26) become:

$$\frac{dx_1}{dm} = V(y_m + \frac{x_1}{x_2}, h_m + \frac{B}{x_2}) \equiv r(x_1, x_2, B) \quad (4.28)$$

$$\frac{dx_2}{dm} = p(m) \quad (4.29)$$

with b.c:

$$x_1 = 0 \quad \text{for } m = 0 \quad (4.30)$$

$$x_2 \geq 0 \quad \text{for } m = 0 \quad (4.31)$$

$$x_2 = 1 \quad \text{for } m = m_f \quad (4.32)$$

We wish to find B and p(m) which maximise x_{1f} .

Consider B to be fixed for the moment and let us look for an optimal p(m). According to Pontryagin, along the optimal trajectory there exist adjoint variables λ_1 and λ_2 which are continuous functions of m, do not vanish simultaneously, and satisfy:

$$\frac{d\lambda_1}{dm} = - \lambda_1 \frac{\partial r}{\partial x_1} \quad (4.33)$$

$$\frac{d\lambda_2}{dm} = -\lambda_1 \frac{\partial r}{\partial x_2} \quad (4.34)$$

with boundary conditions¹:

$$\lambda_1 > 0 \quad \text{at } m = m_f \quad (4.35)$$

$$\lambda_2 = 0 \quad \text{at } m = 0 \quad (4.36)$$

(The latter arising from the transversality condition and holding provided $x_2(0) > 0$ which is in general true. The special case $x_2(0) = 0$ is of some theoretical interest and is discussed later).

Also, along the optimal trajectory the Hamiltonian function:

$$H = \lambda_1 r + \lambda_2 p \quad (4.37)$$

must attain its maximum value everywhere, so that p must be chosen to be either 0 or P unless $\lambda_2 = 0$

1. If problem (i) had been set up in Pontryagin fashion the equations would have been the same except for 4.35 which is replaced by $\lambda_1 r > 0$ at $m=0$. The reader will easily show that (for P finite), $r > 0$ along an optimal trajectory, so 4.35 is implied: the Pontryagin equations are thus the same for both problems.

when p may have an intermediate value.

If $\lambda_2 = 0$ for some m , say m_1 , then $p(m)$ may be so chosen that over the interval $[m_1, m_2]$, λ_2 remains identically zero. Such a trajectory is known as a singular¹ trajectory; the corresponding policy will be denoted p_s and the corresponding $w(m)$; w_s . An optimal trajectory may be singular in part, and in general the decision "how long to stay on the singular trajectory" may have to be taken several times. In this case, however the situation is simplified by the "instability" of the singular trajectory: once left it cannot be returned to along an optimal path² so that only one decision need be taken. (4.36) shows that the trajectory must start on the singular curve.

We may express (4.33) as an integral:

$$\lambda_1 = \lambda_1(0) \exp \left\{ - \int_{j=0}^{j=m} \frac{\partial r}{\partial x_1} \cdot dj \right\} \quad (4.38)$$

-
1. See for example Rosonoer, Ref. 67, 68.
 2. for P large enough: See equation 4.59.

From (4.35) and the fact that the exponential function takes on only positive values, λ_1 must be positive everywhere. Because the adjoint equations (4.33 and 34) are linear and homogeneous and because H is linear in the λ_s we may take $\lambda_1(0)$ to be 1

$$\lambda_1(0) = 1 \quad (4.39)$$

Hence, integrating (4.34) and using the above results:

$$\lambda_2 = \int_{\xi=0}^m \left\{ -\frac{\partial r}{\partial x_2} \exp \left(- \int_{\eta=0}^{\eta=\xi} \frac{\partial r}{\partial x_1} d\eta \right) \right\} d\xi \quad (4.40)$$

λ_2 is zero at $m=0$. If the singular trajectory is to be followed it is sufficient to satisfy: $S=0$ (4.41)

$$\text{where } S \equiv - \frac{\partial r}{\partial x_2} \quad (4.42)$$

from $m=0$ onwards. To show that the singular locus

is unstable we consider its mapping in the (hy) plane.

The singular locus in the (hy) plane and the optimum policy: reduction to finite choice:

By (4.42) and the definition of x_2 and r :

$$S = - \frac{\partial}{\partial w} \left[V(y_m + \frac{x}{w}, h_m + \frac{B}{w}) \right] \quad (4.43)$$

$$\therefore S = + \frac{\partial V}{\partial y} \cdot \frac{x}{w^2} + \frac{\partial V}{\partial h} \frac{B}{w^2} \quad (4.44)$$

Hence, using (2.9) and (4.16), we get:

$$S = + \frac{1}{w} \left[(y - y_m) \frac{\partial V}{\partial y} + (h - h_m) \frac{\partial V}{\partial h} \right] \quad (4.45)$$

Now the rate contours in the hy plane would be expected to have the shape shown for the curves v_0, v_1 , etc. in Fig. 4.2. Also drawn in Fig. 4.2 is the locus of points of tangency from (h_m, y_m) to the rate contours. It is clear from (4.45) that this locus divides the plane into two regions: + and - where S is respectively positive and negative, and that on the locus S vanishes. To follow the locus is of course to maximise the rate with

respect to w at all points¹.

We are now in a position to consider the integration of the Pontryagin equations starting from $m=0$. Let us ignore for the moment the boundary condition (4.32): that is to say the equations will be integrated up to some final value of m which need not be the specified m_f .

case (a): $B > 0$.

Our initial point is on the $y = \text{constant}$ line to the right of O (in Fig. 4.2).

Suppose it is P_1 . Then whatever our initial choice of p , S will be negative, so that λ_2 will start taking on negative values: in order to maximize H , (4.37), p must be made zero for $m=0+$. For subsequent values of m , λ_2 will continue negative by 4.40, so that the control is: $p=0$ for all $m>0$, and the trajectory will run vertically upwards tending to intersect the equilibrium line as $m \rightarrow \infty$.

1. We have chosen the point O in fig. 4.2 in such a way that the rate increases with conversion, at constant h , there. This is the most difficult case to treat.

(If the initial point is P_2 the situation is hopeless since y decreases monotonically, whilst P_3 cannot be left at all).

Suppose the initial point is P_4 : then the optimum policy requires $p=P$ for $m=0+$. Since P is large this means that the trajectory would be directed (almost) towards 0.

P_5 is the important point. Here $S=0$ so that the singular curve may be followed. (We note that the singular curve must always be followed in the direction of increasing w , i.e. from P_5 to P_u . P_u is not attainable¹ because there $h = h_m$). It follows from equation 4.40 and Fig. 4.2 that the singular curve is unstable because, supposing the - region is entered at some point, then λ_2 will take on negative values requiring a $p=0$ policy thereafter, (and the corresponding situation occurs if the +region is entered from the singular curve²).

1. In an exceptional case, discussed later, it is shown that the trajectory can start at P_u .

2. See equation 4.59 for the control p_s required to follow the singular trajectory.

Case (b): $B < 0$:

The following assertions can easily be verified:

- (i) There exists a point P_6 such that for all starting points on $y=y_m$ (Fig. 4.2) to the left of it, the optimal trajectory is a line $h = \text{constant}$.
- (ii) For starting points between 0 and P_6 (Fig. 4.2) the optimal¹ trajectories start out as $h = \text{constant}$ lines and then switch (almost) towards 0. (It will normally turn out that these trajectories may be ignored).
- (iii) From P_6 the optimal trajectories¹ comprise the line $h = \text{constant}$ up to P_7 (Fig. 4.2) on the curve $S=0$, a portion of this curve (towards P_u) branching off (perhaps) either (almost) towards 0 or else along an $h = \text{constant}$ line.

1. In the sense that they satisfy the Maximum Principle.

Case (c): $B=0$: The MT(Tank Tube¹) Reactor:

If $B = 0$, it is clear from 4.14 that either:

$$w_0 > 0 ; h_0 = h_m$$

$$\text{or} \quad w_0 = 0 ; h_0 \text{ has any value,}$$

$$\text{in particular} \quad w_0 = 0 ; h_0 = h_m .$$

The first alternative makes the start the point 0 in Fig. 4.2, which cannot be left at all² (since the control $p = P$ must be applied for $m = 0+$).

The second alternative would permit the point P_u to be attained at $m=0$ by a variety of routes³. In particular the singular trajectory from P_5 to P_u may be followed (limiting case of trajectory described earlier) or the path P_6, P_7, P_u (another limiting case) may be taken. Finally a jump from 0 to P_u is possible.

1. See Refs. 32 and 33.

2. $(\frac{\partial h}{\partial y})_v$ at 0 in Fig. 4.2 is negative: in other instances it may be positive, simplifying the problem.

3. If $w_0 = 0$, the b.c. (4.36) must be replaced by $\lambda_2 \leq 0$. For $\lambda_2 < 0$ only trivial trajectories result.

Once arrived at P_u of course it is possible to continue either vertically downwards (Fig. 4.2) - evidently a trajectory which may be ignored - or vertically upwards; this latter alternative one cannot fail to identify as a continuous stirred tank reactor feeding a tubular reactor.

Exercise of finite choice:

It follows from the above discussion that the optimal trajectory which fits the problem specifications must be selected from the following six types:

$T_1, T_2, \dots, T_6$ defined¹ by:

$$\left. \begin{array}{l} T_1 : p = 0 \\ T_2 : p = 0 \text{ then } p = P \\ T_3 : p = p_s \\ T_4 : p = p_s \text{ then } p = 0 \\ T_5 : p = p_s \text{ then } p = P \\ T_6 : p = 0 \text{ from } P_6 \text{ to } P_7 \text{ (Fig. 4.2) then } \\ p = p_s, \text{ then } p = 0 \end{array} \right\} (4.46)$$

1. p_s being the policy required to follow the singular trajectory.

Let us consider these in turn.

T_1 : this corresponds to a one stage adiabatic ideal tubular reactor; evidently we need consider only reactors with an optimum inlet temperature.

T_2 : Suppose we have the attainable region in the y_f m_f plane for trajectories of type T_1 and that its border is the curve $OC_1C_2C_3$ in Fig. 4.3. Then the border of the attainable region for the trajectories of type T_2 may be obtained by drawing a tangent¹ from O to the curve; obtaining the curve OC_2C_3 . (Usually it will turn out that $OC_1C_2C_3$ is not as shown in the Fig. but convex upwards so that it will itself be the border of the attainable region for trajectories of type T_1 and T_2).

In order to deal with the cases T_3 , T_4 and T_5 we will consider how the singular trajectory in the (h,y) plane maps into the (x,w) plane for different values of B . To this end let us consider two reactors one with the control policy $\{B, w(m)\}$ - so chosen that the singular curve is followed, starting from P_5 at $m=0$,

1. See argument used to prove equivalence of problems (i) and (ii). (P is supposed to be very large).

and the other with policy $\{B', w'(m')\}$, where the primed quantities are defined by (4.20) and $a > 1$.

It follows from (4.22) that the trajectory for the latter reactor is also singular. In Fig. 4.4 we have the hy plane with the singular locus sketched; in Fig. 4.5 the (x, w) plane with lines of constant y , the curves B and B' corresponding to the controls $\{B, w(m)\}$; $\{B', w'(m')\}$. The relation between these two curves can be seen by considering the mapping of the point P_7 from Fig. 4.4 onto P_7 and P_7' respectively in Fig. 4.5. In view of (4.20), (4.21) and (4.22) we have for the distances P_7A and $P_7'A$:

$$P_7'A = aP_7A$$

It is important to notice that points Q_1 and Q_1' on B and B' which have the same value of x , i.e. x_1 , map back into the hy plane as shown: i.e. Q_1' is closer (along the singular curve) to P_5 than is Q_1 . The same is true for any other two points: e.g. Q_2 and Q_2' .

Since the rate V decreases monotonically along the singular curve as it is traversed from P_5 to P_u

it is clear that the rate corresponding to some point on B' is higher than the rate for a point on B with the same x .

Next we will make use of these properties in an integral formulation of the original problem i.e. where $w(m)$ is allowed to jump.

Integral Formulation.

It is easy to see that the problem may be transformed in to finding the $[B, w(x)]$ which minimises:

$$m_f = \int_{x=0}^{x=x_f} \frac{dx}{r(x, w(x), B)} \quad (4.47)$$

subject to $w(x)$ being nondecreasing and $w(x_f)=1$ (4.48)

Suppose that $y_f > y_{\max}$ (See Fig.4.4). Then trajectories of type T_3 and T_5 must be ruled out. However for $y_f < y_{\max}$ we cannot rule these trajectories out a priori.

We will show that T_5 is never optimal if B is free.

Suppose some control $[B, w_1(x)]$ is imposed so that the singular trajectory is followed up to some point

R_1 at which point $x = x_f$ but $w < 1$ (see Fig. 4.4). Let there then be a step in w to bring it up to 1. It is clear that for this value of B the chosen $w_1(x)$ cannot be improved since it minimizes the integrand (4.47) for every value of x . In particular, no trajectory of the type T_5 which terminates under the control $p=P$ can improve on $w_1(x)$.

We now increase B from B_1 to B_2 , again following the singular trajectory until x_f is reached with $w < 1$, (at R_2 in figures 4.4 and 4.5), and then finishing off with a step to bring w up to 1.

It follows from what was established about the rates at corresponding points Q_1, Q_1' at the end of the last section that m_{f_1} associated with the control $[B_1, w_1(x)]$ is larger than m_{f_2} associated with the control $[B_2, w_2(x)]$, and also that the control $[B_+, w_+(x)]$ where the singular trajectory is followed all the way is therefore better than any possible trajectory with $B < B_+$. Thus all trajectories of type T_5 may be rejected in favour of trajectories of type T_3 .

Evaluation of the $y_f(m_f)$ relation for trajectories of type T_4 .

Suppose we wish to find these $y_f(m_f)$ curves corresponding to the three type T_4 trajectories $P_5C_1\bar{C}_1; P_5C_1C_2\bar{C}_2; P_5C_1C_2C_3\bar{C}_3$, in Fig. 4.6. The calculations may be shortened by making use of the scale invariance property: all the information required concerning the singular trajectory may be obtained by one integration along it up to C_3 .

We choose some suitable value of B' , say

$$B' = 1 \quad (4.49)$$

and $w' = w'_s \quad (4.50)$

so that equation (4.25) becomes:

$$\frac{dx'}{dm'} = V(y_m + \frac{x'}{w'_s} ; h_m + \frac{1}{w'_s}) \quad (4.51)$$

or $\frac{dx'}{dm'} = V(y_m + \frac{x'}{w'} ; h_m + \frac{1}{w'}) \quad (4.52)$
max over w'

(with i.c. $x'(0) = 0$). (4.52) is integrated through positive values of m' until the point C_1 is reached;

where the variables x' , w' and m' have the values x'_{e_1} , w'_{e_1} , m'_{e_1} , respectively. These three variables are stored, and then a is chosen such that the corresponding $w_{e_1} = 1$, and x_{e_1} and m_{e_1} calculated.

From 4.20 it follows that:

$$a = w'_{e_1} \quad (4.53)$$

$$\text{so that } x_{e_1} = \frac{x'_{e_1}}{w'_{e_1}}; \quad B = 1/w'_{e_1}; \quad m_{e_1} = \frac{m'_{e_1}}{w'_{e_1}} \quad (4.54)$$

We then simply evaluate the ym relation over the curve $C_1\bar{C}_1$ (in Fig. 4.6) by integrating:

$$\frac{dy}{dm} = V(y; h_{e_1}) \quad (4.55)$$

$$\text{with i.c. : } y=y_{e_1} \text{ at } m = m_{e_1} \quad (4.56)$$

through increasing values of m until $\bar{C}_1$ is reached.

To evaluate the ym relation over the curve $P_5C_1C_2\bar{C}_2$ we need go back only to the point C_1

(in Fig. 4.6) and integrate (4.52) through increasing values of m' from the initial condition $x' = x'_{e_1}$, $m' = m'_{e_1}$ until C_2 is reached, store x'_{e_2} , m'_{e_2} , w'_{e_2} , rescale to get the new initial conditions for (4.55), and so on. In this way the $y_f(m_f)$ relation for trajectories of type T_4 may be obtained. If this relation is plotted for different values of the switching point C , a family of curves in the y_f, m_f diagram would be obtained; the best ym relation for the entire family may be obtained by constructing the envelope.

Evaluation of the y_f, m_f relation for trajectories of type T_6 :

The part of the trajectory from P_7 (Fig. 4.2) onwards can be dealt with by the method used for T_4 trajectories above. We must also find P_6 , and evaluate the P_6P_7 part.

There are three obvious methods based on guessing h_0 such that λ_2 and $\frac{d\lambda_2}{dm}$ vanish simultaneously

at the intersection of $h = h_0$ and $S = 0$ (Fig. 4.2): one may integrate 4.28, 4.29, 4.33, and 4.34 forwards; or 4.28 and 4.29 forwards, (storing relevant intermediate information) and 4.33 and 4.34 backwards, or evaluate 4.40 together with 4.47.

Alternatively, by changing the integration variables in both integrals from volume (mass of catalyst) to conversion (noting that x_2 and h are constant) and integrating by parts it can be seen that the following alternative equations may be used:

$$F(y_e) = \frac{y_m - y_e}{V_e} + \int_{y_0}^{y_e} \frac{dy}{V} + (h_0 - h_m) \int_{y_0}^{y_e} \frac{\partial V}{\partial h} \frac{dy}{V^2} = 0 \quad (4.57)$$

$$\frac{dF}{dy_e} = 0 \quad (4.58)$$

These two conditions are the "subsidiary feed too hot" conditions, which apply also to the finite cascade treated in Chapter V.

Again one would obtain a family of curves in

the y_f, m_f diagram, the optimal relation being given by the envelope.

Selection of best envelope¹:

It would appear that (for the subsidiary feed condition represented in Fig. 4.2), the T_4 envelope would be optimal for low y_f , then the T_6 envelope (the transition corresponding to the MT reactor) and finally the envelope for the single stage adiabatic tube with adjustable feed temperature. (For high subsidiary feed temperatures the T_6 envelope degenerates to a point, of course).

Rate of addition of subsidiary feed: Details of method used for the special case $y_m = 0$:

The singular trajectory maps into the relation:

$$S(y, h) = 0$$

in the hy plane. Bearing in mind equation 4.6, we may obtain for the rate of addition of subsidiary

1. See above discussion and also section on numerical results.

feed:

$$h_s = \frac{dw_s}{dm} = \frac{V \frac{\partial S}{\partial y}}{(y-y_m) \frac{\partial S}{\partial y} + (h-h_m) \frac{\partial S}{\partial h}} \quad (4.59)$$

p_s will be finite provided:

$$(y-y_m) \frac{\partial S}{\partial y} + (h-h_m) \frac{\partial S}{\partial h} \neq 0 \quad (4.60)$$

If $y_m > y_c$, then 4.60 will be satisfied in general, so that $w(m)$ will not jump even if permitted to do so.

If $y_m \leq y_c$, and in particular if $y_m = 0$, it would appear that p_s would exceed P at $m=0$ however large P might be, so that we would have to consider the case where P is assigned some reasonable value:

One is often interested in the $\bar{y}_f^*$, m_f relation for $y_f > 0.1$ and $y_m = y_o = 0$. One could (with some labour) compute this relation for given values of P and estimate in some way the limiting relation as P

tends to infinity. It seems plausible that this limiting relation would be the solution to the problem where $w(m)$ is allowed jumps: (this is no proof). Alternatively one could get:

- (i) an upper bound on y_f^{∞} (for given m_f) by proceeding as above for $y_0 = y_m = y_c + \text{some small number}$.
- (ii) A lower bound by considering some non optimal trajectory such as: adiabatic from $y = 0$, h large to the curve $S=0$ (Fig. 4.2), and thereafter following T_4 .

It has turned out that for the rate functions defined by equation 1.1 and table 1.1, these bounds are almost identical and that in fact one may (for $y_0 = y_m = 0$) start out on the intersection of the curve $S=0$ with the line $y = 0.0005$, and let m' be considered zero there without introducing appreciable error. Alternatively the small correction can be estimated from the data for perfect indirect control by (for example) putting $y=0$ in the denominator of the integrand A.3.1. This latter procedure was used in the numerical calculations on which the results shown in this thesis are based.

Optimal policy with B restrained.

Suppose that for B free, and some specified y_f , m_f^* corresponds to a T_4 trajectory with $B = B_1$. If a restraint B_2 is placed on B so that $B_1 > B_2 > 0$, then it is clear that the optimal trajectory will have $B = B_2$ and may be of type T_3 , T_4 , or T_5 .

B might be so restrained in a practical situation if the feed preheater were undersized and of such a type that the heat load is independent of $w(o)$: e.g. an electrically heated device.

Programming details for evaluation of type T_4 trajectories.

Programming is simplified if the switch points C are specified in terms of m' . In this way no equation need be solved to determine m' . Alternatively switching may be specified to take place as soon as h falls below a certain value.

Instead of integrating (4.52) the corresponding integral may be evaluated: there being numerical advantages especially if y_0 is close to zero. Expressing (4.55) as an integral however is not recommended unless special precautions are taken about

the pole which the integrand has on the equilibrium line¹.

Some thought should be given to specifying the m_f values corresponding to $\bar{C}_1, \bar{C}_2$, etc. If a variable step length method such as Runge Kutta Merson is used for the integration of (4.55) then these m_f values can be specified to be much larger than the values one would expect to be sufficient, because, as the trajectories (4.55) run into the equilibrium line, v becomes so small that the step length is automatically enlarged very quickly so that not much unnecessary computation is in fact done. Alternatively, after a little experience, it is not difficult to specify a suitable small number and program the integration to stop when it exceeds the reaction rate.

Case (ii) $y_o < y_m$.

For P very large this problem presumably degenerates to case (i), since, by using very little main feed (if it is sufficiently hot) it is possible by

1. See Chapter V.

mixing it with subsidiary feed to achieve any value of h required and a conversion close to y_m .

Case (iii) $y_o > y_m$.

Besides being of little practical interest this problem appears to be difficult (it appears that the classical calculus of variations is inadequate and also Pontryagin's Maximum Principle does not[†] apply), so it will not be treated.

Problems for the tank reactor.

Suppose a liquid phase catalytic reaction is to take place in an adiabatic (atmospheric pressure) stirred tank of volume M_f (Fig. 4.7), which may be operated as follows:

- 1) A charge of raw material containing w_o moles of¹ basic reference substance (which need not fill the tank completely) is dumped in quickly.
- 2) Catalyst is added and agitation commenced.
- 3) Cold raw material of enthalpy h_m /mole basic reference substance is added according to some sequence

1. See definition in Chapter II.

†. At any rate to basic problem (ii).

$w(t)$ where t is time, until the tank is full, when it is dumped quickly.

The cycle is then repeated.

One reason for having an adiabatic tank might be that the reaction mixture (including catalyst) could be extremely corrosive, but the raw material innocuous.

There are many optimization problems which may be formulated¹; we will consider the following problem:

For fixed time from filling to emptying t_f , find $w(t)$, a nonnegative, non decreasing function, and w_0 and h_0 such that (for given $y_0=y_m$), the quantity

$$x_f = w_f(y_f - y_0)$$

is maximised.

The system could be described by the differential equations:

$$\dot{x}_1 = x_2 \left(V(y_m + \frac{x_1}{x_2}, h_m + \frac{B}{x_2}) \right)$$

$$\dot{x}_2 = p(t)$$

1. Siebenthal and Aris considered others (Ref. 29) but they used an incorrect heat balance.

where x_1 , x_2 and B have the same meaning as before, but p depends on t , and V is the rate not per unit volume but per mole of basic reference substance. The boundary conditions would be $x_1 = 0$ and $x_2 \geq 0$ at $t=0$, and at $t=t_f$:

$$M(x_1, x_2, h) = M_f$$

(M volume of liquid in the reactor). It would probably not be serious¹ to replace this boundary condition by: $x_2 = 1$, giving us a problem of the same form as before except with the function $x_2^+ V$ instead of V . We would obtain a singular trajectory in the h y plane given by:

$$\frac{\partial}{\partial x_2} (x_2^+ V)_{x_1} = 0$$

$$\text{i.e.} \quad \frac{\partial V}{\partial y} = (y - y_m) \frac{\partial V}{\partial y} + (h - h_m) \frac{\partial V}{\partial h}.$$

It seems that one might not have to go far to find functions $V(y, h)$ having the property that there are no solutions, one solution, or more than one solution to the above equation for positive (and

1. A simplification Siebenthal and Aris used: strictly $x_2 = \text{constant}$.

reasonable) values of y , h , y_m , h_m .⁺ Anyway, for given V this situation would have to be explored as a prelude to finding optimal trajectories.

Numerical Results:

In the case where J , the adiabatic temperature rise coefficient is constant, if h is replaced by θ and $V(y, h)$ by $U(y, \theta)$ in all the above equations in this chapter, the resulting equations are valid¹.

Trajectories of type T_4 for the second set of rate function parameters (equation and Table 1.1) for the case $y_0 = y_m = 0.01$, $w_f = 1$, $J = 158.5$, and $T_m = 300^\circ\text{K}$ are shown² in Fig. 4.8. Also shown in Fig. 4.8 is the corresponding curve for perfect indirect control. The envelope of the trajectories T_4 in Fig. 4.8 is optimal for the range of conversions y_f shown.

-
1. See discussion about θ and U in Chapters II and V.
 2. The coordinates are transformed to $\log m_f$ and $\log (y_f/(1-y_f))$.

Fig. 4.8 was obtained by making two separate computer runs, one at tighter error specifications than the other. It was found in this way, that in order to obtain a relative precision in conversion temperature, and volume of 1 part in 100,000, 45 integration steps along the singular trajectory were required from the start to¹ the point:

$$y = 0.9038099$$

$$T = 605.5867,$$

whereas from 4 to 11 steps were sufficient for the $p=0$ portions of the trajectory to obtain the curves in Fig. 4.8 as accurately as they could be drawn to a scale twice that shown. To compute the above singular trajectory, and ten $p=0$ branches (requiring 77 integration steps) less than 2.5 seconds were required on an I.C.T. Atlas computer.

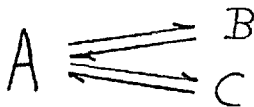
The singular controls m' , w' and the corresponding x' are presented² in Table 4.1.

The remaining numerical results are discussed in Chapter V.

-
1. For low conversions the errors were slightly larger.
 2. Defined in terms of θ : e.g. $w'_s = 1/(\theta - \theta_m)$

Part IV: The Principle of Maximizing the Local Rate.

It has been shown above that the optimal policy for the basic problem for indirect or mixed control of an ideal distributed feed reactor is one of local rate maximization with respect to temperature. This simple result is a special property of single reactions and cannot be generalized to cover all cases where more than one independent reaction is taking place: for suppose we consider an ideal tubular reactor in which the reactions:



are carried out. The feed is pure A; C is the desired product which must be produced at a given rate in a stream in which the conversion of A to C is given; X_{C_f} , in a reactor of minimum volume. If X_B and X_C are the fractions of A converted to B and C, and v_B , v_C are the rates, then we may write equations of the form:

$$\frac{dX_B}{dt} = v_B(X_B, X_C, T(t))$$

$$\frac{dX_C}{dt} = v_C(X_B, X_C, T(t))$$

Proceeding as for a single reaction we may assume that $v_C > 0$ along the optimal trajectory and write:

$$t_f = \int_{X_C=0}^{X_C=X_{Cf}} \frac{dx_C}{v_C(X_B, X_C, T)}$$

from which it is tempting to surmise that by choosing T everywhere such that v_C is maximised, t_f is minimised. This however is incorrect, the reason being that by choosing a $T(t)$ we imply an $X_B(t)$ so that choosing $T(t)$ to maximise v_C everywhere will imply a function $X_B(t) = \bar{X}_B(t)$ say. The $T(t)$ which maximised v_C everywhere is then only the best amongst the set of temperature profiles which made $X_B(t) = \bar{X}_B(t)$. And this of course is in general an "extremely small subset" of the set of all temperature profiles. It is also clear that there is no such objection in the case of single reactions.

Appendix to Chapter IV Part II

... "we may disregard those pairs of functions $\{w(m), T(m)\}$ which lead to a negative or zero rate anywhere."

We may ignore pairs of functions which lead to v being negative or zero only at isolated points.

Suppose that $w(m)$ is strictly increasing. Then if the rate is negative over an interval, there are several possible types of wx diagrams of which we will consider only the one shown in Fig. A4.1: curve OABCDE. This can evidently be improved by removing a section of the reactor corresponding to ABCD and changing the control $w(x)$ so that w jumps from point A to point D. The other cases can be treated in a similar way.

If $w(m)$ is constant then the above method may be used perhaps in conjunction with the method in Part I of the appendix to Chapter III.

T A B L E 4.1.

Singular Controls.

Second set of rate function parameters

$y_o = y_m = 0.01$; $T_m = 300^\circ\text{K}$; $J = 158.5^\circ\text{K}$.

Note: $a, -b = ax10^{-b}$

m'	x'	w'
0	0	8.835,-4
1,-7	6.9244,-5	1.2062,-3
3,-7	1.2731,-4	1.3047,-3
1,-6	2.3748,-4	1.4312,-3
3,-6	4.0262,-4	1.5718,-3
1,-5	6.8162,-4	1.7672,-3
3,-5	1.0404,-3	1.9970,-3
1,-4	1.5395,-3	2.3198,-3
3,-4	2.0614,-3	2.6900,-3
1,-3	2.6721,-3	3.1910,-3
2,-3	3.0388,-3	3.5299,-3
3,-3	3.2605,-3	3.7466,-3
4.5,-3	3.4894,-3	3.9777,-3
6,-3	3.6572,-3	4.1510,-3
8,-3	3.8303,-3	4.3325,-3
1.2,-2	4.0847,-3	4.6033,-3
1.8,-2	4.3535,-3	4.8932,-3
2.5,-2	4.5835,-3	5.1436,-3
5,-2	5.1119,-3	5.7237,-3
7.5,-2	5.4528,-3	6.1006,-3
2.2,-1	6.5033,-3	7.2688,-3
6.6,-1	7.8677,-3	8.7942,-3
2	9.6821,-3	1.0829,-2

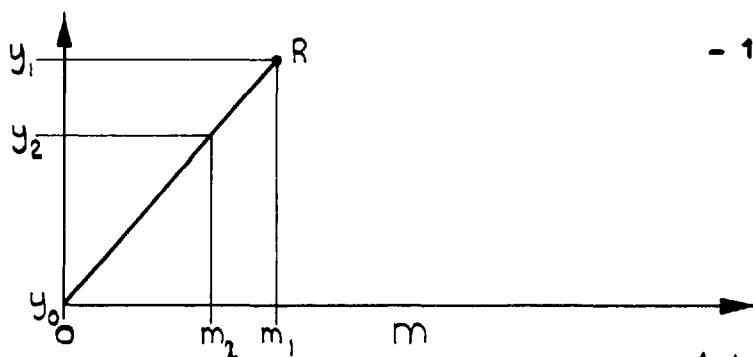


Fig. 4.1.

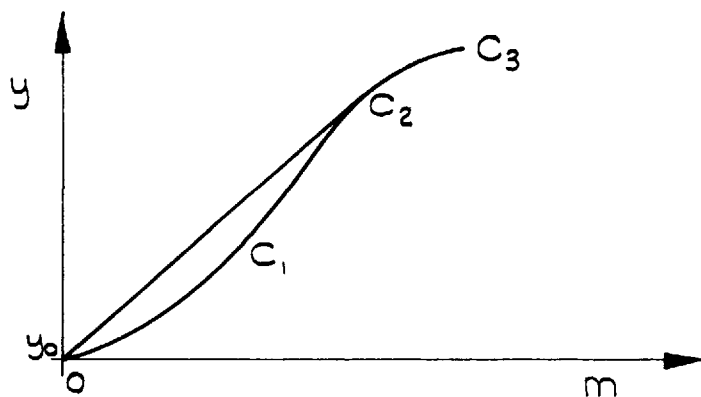


Fig. 4.3.

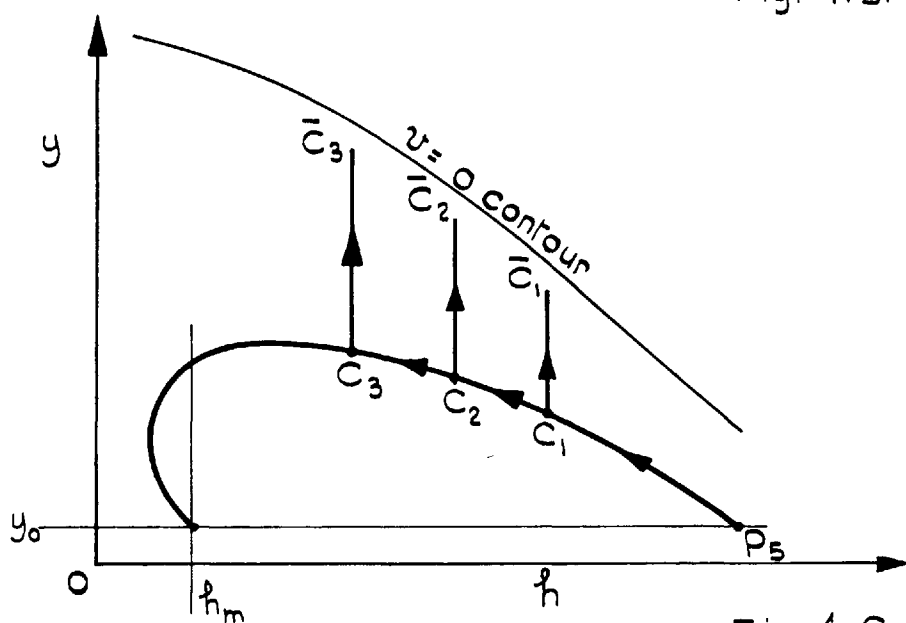
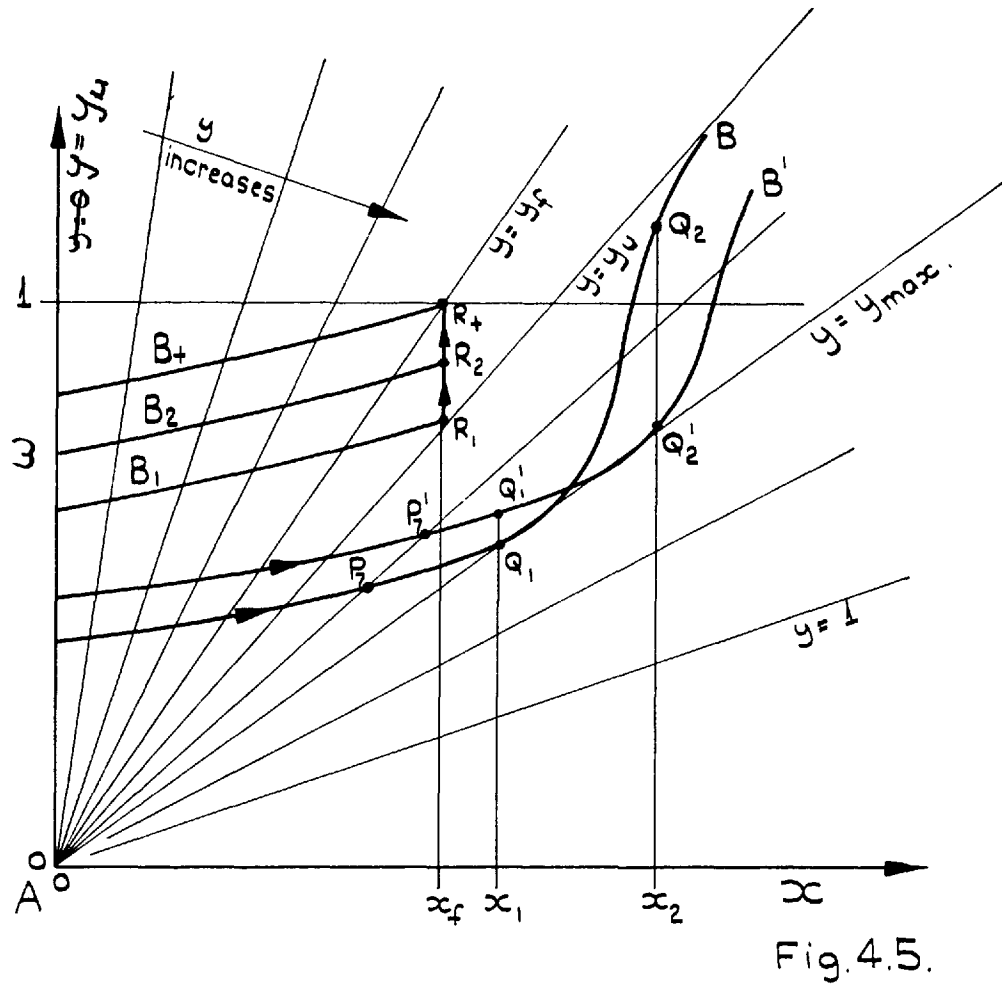
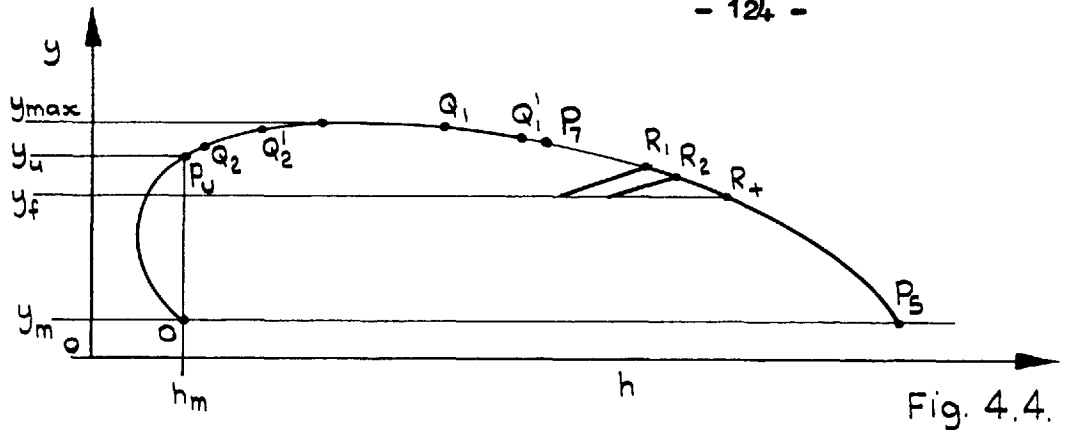


Fig. 4.6.

(For figs 4.2., 4.4. and 4.5., please turn over.)



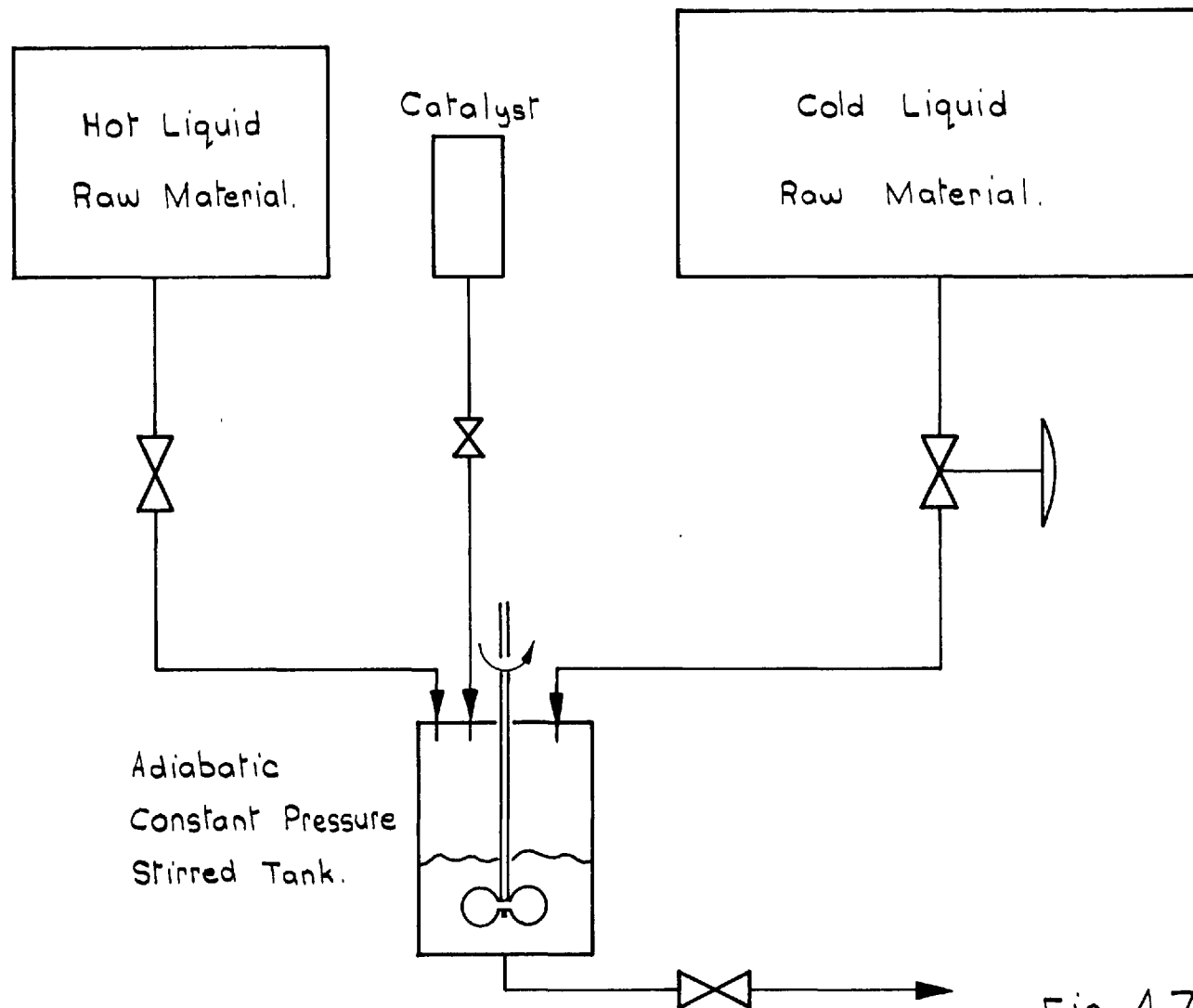


Fig. 4.7.

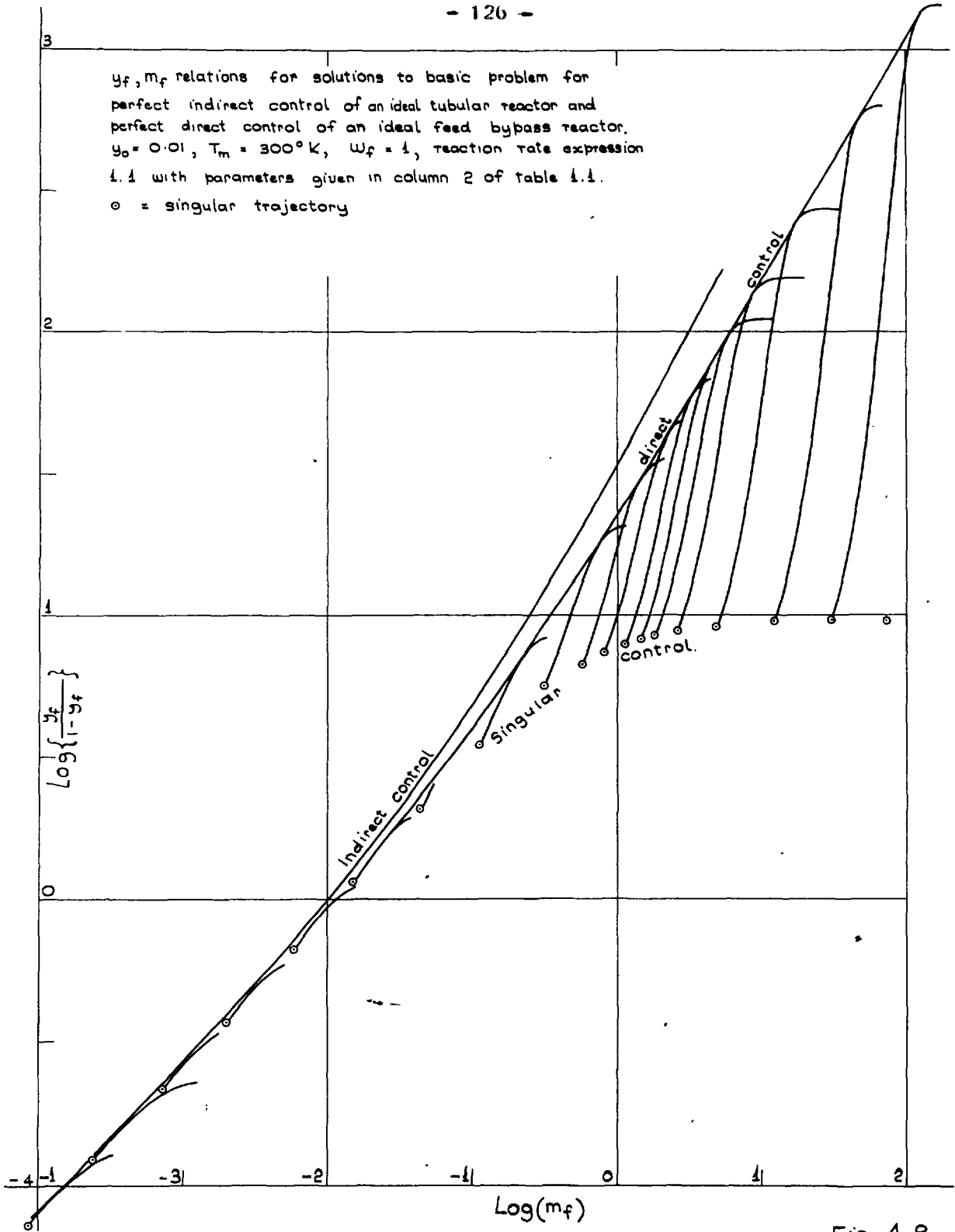


Fig. 4.8.

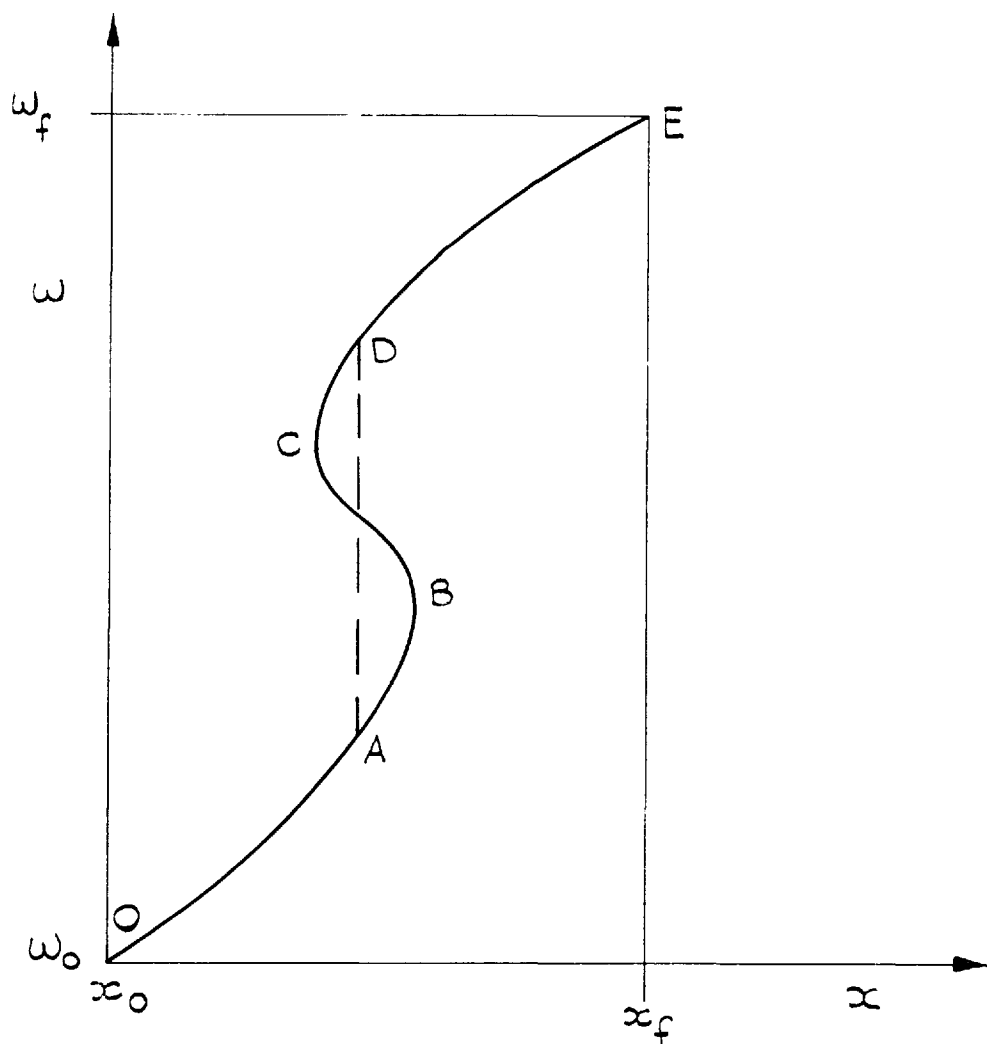


Fig. A 4.1.

CHAPTER V

Optimization of a Cascade of Adiabatic Ideal Tubular Reactors with Interstage Cooling.

In this chapter the basic problem for the N stage reactor represented in Fig. 5.1. will be treated.

The main and supplementary feeds will be taken to have the same basic composition.

The above reactor is directly controlled. By giving h_m the (fictitious) value $-\infty$, however, the indirectly controlled case may be included in the same mathematical model.

If restraints are imposed they will be on temperatures only so the basic problem is reducible.

V.I. Derivation of Optimum Condition Equations for problem (i).

If the w_K is the basic reference¹ flowrate in the K th stage, y_{a_K} and y_{e_K} are its inlet and outlet

1. See Chapter II for definition.

conversions and h_K its enthalpy/mole basic reference substance, then the total N stage volume (mass of catalyst) is given¹ by:

$$M = \sum_{K=1}^N w_K \int_{y_{a_K}}^{y_{e_K}} \frac{dy}{V(y, h_K)} \quad (5.1)$$

An enthalpy balance for the mixing between the j th and $j+1$ th stages gives:

$$\frac{w_{j+1}}{w_j} = \frac{h_j - h_m}{h_{j+1} - h_m} \quad ; \quad j=1, 2 \dots N-1 \quad (5.2)$$

1. It may easily be shown that in an optimal reactor for $y_{a_1} \geq y_m$, the rate V must everywhere be positive, so an integral formulation is justifiable. There may be an advantage to be gained from making $V < 0$ if $y_{a_1} < y_m$, however, but this case is rather absurd because, the performance of the class of reactors itself could be improved by merely allowing mixing of subsidiary feed to take place before the first stage. (See corresponding case in Chapter IV).

This difference equation being easily solved,
giving:

$$w_j = w_N \left\{ \frac{h_N - h_m}{h_j - h_m} \right\}; \quad j=1, 2 \dots N-1 \quad (5.3)$$

(alternatively 5.3 may be determined by means of a single enthalpy¹ balance round the stages $j, j+1 \dots N$).

A mass balance for the mixing² between the j th and $j+1$ th stages gives:

$$\frac{w_{j+1}}{w_j} = \frac{y_{e_j} - y_m}{y_{a_{j+1}} - y_m}; \quad j=1, 2 \dots N-1 \quad (5.4)$$

Consider the minimization of M for given y_{e_N}, y_{a_1} , and w_N . We must solve a constrained minimum problem because, by (5.1) M is formally a function of $\{h_1, h_2 \dots h_N, y_{a_2} \dots y_{a_N}\}$ and $\{w_1, w_2 \dots w_{N-1}, y_{e_1}, y_{e_2} \dots y_{e_{N-1}}\}$ but these are

1. See discussion in Chapter II.

3. The volume of interstage piping is assumed to be negligible if a homogeneous reaction is considered.

constrained by (5.3) and (5.4). We may use these relations to express the latter set of variables in terms of the former, regarding M to be a function of the former¹ set only:

$$M = M(h_1, h_2 \dots h_N, y_{a_2}, \dots y_{a_N})$$

and solve the resulting unconstrained minimum problem.

In finding the derivatives of M with respect to these variables it will be convenient to have expressions for:

$$\frac{\partial y_{e_j}}{\partial h_i}, \quad \frac{\partial y_{e_j}}{\partial y_{a_i}}, \quad \frac{\partial \omega_j}{\partial h_i}, \quad \frac{\partial \omega_j}{\partial y_{a_i}}$$

From (5.2) and (5.4) we get:

$$y_{e_j} = y_m + \frac{(y_{a_{j+1}} - y_m)(h_j - h_m)}{h_{j+1} - h_m} \quad (5.5)$$

1. This set of variables is particularly simple to work with if only the unconstrained problem is considered; this derivation does not cover the case $h_i = h_m$ for all i : the final relations 5.17, 5.23, and 5.24 persist however even when $h_i = h_m$ as may be seen by developing the theory in terms of the set of independent variables: $(h_1, w_1, w_2 \dots w_{N-1}, y_{a_2}, \dots y_{a_N})$. See also Chapter I and Ref. 35.

$$\frac{\partial y_{e_j}}{\partial h_i} = \frac{(h_{j+1} - h_m)(y_{a_{j+1}} - y_m) \delta_{ij} - (y_{a_{j+1}} - y_m)(h_j - h_m) \delta_{j+1,i}}{(h_{j+1} - h_m)^2}$$

$$\text{where } \delta_{ij} = \begin{cases} 1 & \text{for } i=j \\ 0 & \text{for } i \neq j \end{cases} \quad (5.6)$$

Using (5.4):

$$\frac{\partial y_{e_j}}{\partial h_i} = \left\{ \frac{y_{a_{j+1}} - y_m}{h_{j+1} - h_m} \right\} \left\{ \delta_{ij} - \frac{\omega_{j+1}}{\omega_j} \delta_{j+1,i} \right\} \quad (5.7)$$

Differentiating (5.5), with respect to y_{a_i}

$$\frac{\partial y_{e_j}}{\partial y_{a_i}} = \left\{ \frac{h_j - h_m}{h_{j+1} - h_m} \right\} \delta_{j+1,i} \quad (5.8)$$

Using (5.2):

$$\frac{\partial y_{e_j}}{\partial y_{a_i}} = \left\{ \frac{\omega_{j+1}}{\omega_j} \right\} \delta_{j+1,i} \quad (5.9)$$

Differentiating (5.3) with respect to h_i :

$$\frac{\partial w_j}{\partial h_i} = \frac{w_N \delta_{iN}}{h_j - h_m} - \frac{w_N (h_N - h_m)}{(h_j - h_m)^2} \delta_{ij} \quad (5.10)$$

Using (5.3):

$$\frac{\partial w_j}{\partial h_i} = \frac{w_N \delta_{iN}}{h_j - h_m} - \frac{w_j \delta_{ij}}{h_j - h_m} \quad (5.11)$$

Differentiating (5.3) with respect to y_{a_i} :

$$\frac{\partial w_j}{\partial y_{a_i}} = 0 \quad (5.12)$$

It is convenient to¹ define t_i and t'_i by:

$$t_i = \int_{y_{a_i}}^{y_{e_i}} \frac{dy}{V(y, h_i)} \quad (5.13)$$

$$t'_i = \int_{y_{a_i}}^{y_{e_i}} \left[\frac{1}{V^2} \frac{\partial V}{\partial h} \right] dy \quad (5.14)$$

Differentiating M with respect to y_{a_i} , using

(5.1), (5.9), (5.12) and (5.13), and reducing we get:

$$\frac{\partial M}{\partial y_{a_i}} = w_i \left\{ \frac{1}{V_{e_{i-1}}} - \frac{1}{V_{a_i}} \right\}; \quad i=2, 3 \dots N \quad (5.15)$$

1. To be strictly consistent with equation 2.12, we should subscript t_i again, getting t_{if} , or t_{ie} , but there should be no confusion if we drop these suffixes.

Differentiating M with respect to h_i , using (5.1), (5.7), (5.11), (5.13) and (5.14) and reducing, we

$$\text{get: } \frac{\partial M}{\partial h_i} = + \frac{\omega_i (y_{a_{i+1}} - y_m)}{V_{e_i} (h_{i+1} - h_m)} (1 - \delta_{Ni}) - \frac{\omega_i (y_{a_i} - y_m)}{V_{e_{i-1}} (h_i - h_m)} (1 - \delta_{li}) \\ - \omega_i t'_i + \omega_N \delta_{iN} \sum_{k=1}^{N-1} \frac{t_k}{h_k - h_m} - \frac{\omega_i t_i (1 - \delta_{iN})}{h_i - h_m} \quad (5.16)$$

For M to be an unrestrained minimum, all these first derivatives must vanish, i.e.

$$\frac{\partial M}{\partial y_{a_i}} = 0 \quad (5.15a)$$

$$\frac{\partial M}{\partial h_i} = 0 \quad (5.16a)$$

It follows from (5.15) and (5.15a) that:

$$V_{a_i} = V_{e_{i-1}} ; i=2, 3 \dots N \quad (5.17)$$

Thus the well known rate matching condition¹ (which seems so reasonable intuitively) also holds in this case of complex thermochemistry.

1. See Chapter I for review of previous work.

For $i \neq N$, from (5.16) and (5.16a):

$$\frac{t_i}{h_i - h_m} = -t'_i + \frac{y_{a_{i+1}} - y_m}{V_{e_i}(h_{i+1} - h_m)} - \frac{(1-\delta_{i1})(y_{a_i} - y_m)}{V_{e_{i-1}}(h_i - h_m)}; i \neq N \quad (5.18)$$

If we sum the above equation from $i = 1$ to $N-1$ cancel terms, we get:

$$\sum_{i=1}^{N-1} \frac{t_i}{h_i - h_m} = - \sum_{i=1}^{N-1} t'_i + \frac{y_{a_N} - y_m}{V_{e_{N-1}}(h_N - h_m)} \quad (5.19)$$

whereas for $i=N$, from (5.16) and (5.16a):

$$\sum_{K=1}^{N-1} \frac{t_K}{h_K - h_m} = t'_i + \frac{y_{a_N} - y_m}{V_{e_{N-1}}(h_N - h_m)} \quad (5.20)$$

Subtracting (5.19) from (5.20):

$$\sum_{i=1}^N t'_i = 0 \quad (5.21)$$

Using (5.2) and (5.4) we may simplify (5.18):

$$0 = t_i + (h_i - h_m)t'_i - \frac{y_{e_i} - y_m}{V_{e_i}} + \frac{(1-\delta_{i1})(y_{a_i} - y_m)}{V_{e_{i-1}}}; i \neq N \quad (5.22)$$

It is convenient to define a function $F_i(y_i)$, where y_i is the conversion somewhere in the i th stage as follows:

$$\left. \begin{aligned} F_i(y_i) &\equiv \int_{y_{a_i}}^{y_i} \frac{dy}{V(y, h_i)} + (h_i - h_m) \int_{y_{a_i}}^{y_i} \frac{\partial V}{\partial h} \frac{dy}{V^2} - \frac{y_i - y_m}{V(y_i, h_i)} \\ &\quad + \frac{(1 - \delta_{ii})(y_{a_i} - y_m)}{V_{e_{i-1}}} ; i \neq N \\ F_N(y_N) &\equiv \sum_{i=1}^{N-1} t'_i + \int_{y_{a_N}}^{y_N} \frac{\partial V}{\partial h} \cdot \frac{dy}{V^2} \end{aligned} \right\} \quad (5.23)$$

(where the integrands are evaluated for $h = h_i$).

The optimum condition equations may be written concisely:

$$V_{a_i} = V_{e_{i-1}} \quad i = 2, 3 \dots N \quad (5.17)$$

$$F_i(y_{e_i}) = 0 \quad i = 1, 2 \dots N \quad (5.24)$$

V.II: Solution of Optimum Condition¹ Equations:

Outline:

Guess h_1 , evaluate F_1 for y_1 increasing from

1. It will be assumed in what follows that $h_{a_1} > h_m$ unless otherwise stated. It will also be assumed that the rate contours have the shape shown in fig. 5.2. (This may not be the case for a reaction which is autocatalytic, or for a reaction mixture which is strongly non ideal, so that equations 5.17 and 5.24 may have more or less solutions than those considered in what follows).

y_{a_1} , (and along with it the contributions to t_1) stopping when (5.24) is satisfied. Then use 5.2, 5.4, and 5.17 to get y_{a_2} , h_{a_2} , and calculate stage 2 in the same way as stage 1. Continue until (5.24) has been (suitably) satisfied for the last stage.

In general the resulting y_{e_N} will not satisfy its boundary condition. Reguess h_1 and repeat.

Details:

Consider first the derivative: $F'_i = \frac{dF_i}{dy_i}$ (5.25)

By differentiating (5.23) and cancelling terms we obtain:

$$F'_i = \frac{1}{V_i^2} \left\{ [h_i - h_m] \frac{\partial V_i}{\partial h_i} + (y_i - y_m) \frac{\partial V_i}{\partial y_i} \right\}, \quad i \neq N \quad (5.26)$$

$$F'_N = \frac{1}{V_N^2} \frac{\partial V_N}{\partial h_N} \quad (5.27)$$

Next consider the rate contours v_1 , v_2 , etc. in Fig. 5.2 and the locus L_1 of points of tangency to them from 0 the supplementary feed point. L_1 divides

the plane into two regions + , and - ; it is clear from 5.26 that for $i \neq N$, F'_i is positive in the + region, negative in the - region and zero on L_1 . Consider F'_i for $h = h_1$ (see Fig. 5.2) evaluated at points A and above. As y increases from y_m to y'' (at the intersection with L_1), F'_i goes through positive values to zero. As y increases further, F'_i decreases, and as $y \rightarrow y'$ on the equilibrium line, $F'_i \rightarrow -\infty$ as a pole¹ of order 2.

The hy plane is also divided into two regions by the locus L_2 of the maxima of the rate contours. It is evident from (5.27) that below this broken line F'_N is positive, on it F'_N is zero, and above it F'_N is negative. F'_N also tends to $-\infty$ as a pole of order 2 as the equilibrium line is approached along the line $h = h_N$.

Now consider F'_i . We note that for i neither 1 nor N , F'_i is zero at the beginning of the i th stage:

$$F'_i(y_{a_i}) = 0 ; \quad i \neq N, \quad i \neq 1 \quad (5.28)$$

1. $V(y, h)$ for h constant is assumed to have a simple zero on the equilibrium line.

The corresponding y_{a_i} are therefore solutions of (5.24) which may be disregarded in general¹. For the first stage:

$$F_1(y_{a_1}) = \frac{y_m - y_{a_1}}{V_{a_1}} \quad (5.29)$$

We distinguish two cases:

case (i): $y_m = y_{a_1}$:

Here $F_i(y_{a_i}) = 0$ for $i < N$; to calculate an N stage reactor we may proceed as follows:

First we choose h_1 . This gives a starting point (h_1, y_{a_1}) : A in Fig. 5.2. If we were to evaluate F_1 for values of y_1 from y_{a_1} to y' , the equilibrium conversion, we would get a unimodal curve such as the one in Fig. 5.3 with a pole of order 1 at $y = y'$.

1. These solutions correspond to leaving out a stage or more. If in a practical case, 1,2,3,4 ... N stage reactors are all calculated (using the optimal condition equations) ignoring the roots (5.28) when one or more of these should have been selected, then an "optimal" r stage reactor ($r < n$) will be found which is better than an optimal $r+1$ stage reactor, so the error will be brought to light. The significance of (5.28) when $h_{a_1} \leq h_m$ is discussed later (c.f. Chapter IV).

$F_1(y)$ has then a non trivial zero between y'' and y' . In order to find this zero, y_{e1} , $F_1(y_1)$ is evaluated along with the two integrals on the right hand side of (5.23) for increasing values of y_1 until F_1 becomes negative, when y_{e1} is found by a suitable non linear equation solving routine. (t_1 and t'_1 are then evaluated as well). Suppose $h_1 y_{e1}$ is the point B in Fig. 5.2. which is on the v_6 contour. Now by (5.17) the optimum starting point for the next stage would also be on the v_6 contour, and by (5.2) and (5.4) it would be on the straight line joining B and O, somewhere between them; therefore it would be the point C. It is a simple matter to program a digital computer to find the point C, the only pitfall being to allow the computer to find the point B instead (which satisfies (5.2), (5.4), and (5.17) trivially). A simple search routine evaluating $v - v_{e1}$ for points on OB starting from some suitable point between O and B may be used to box in C. If a negative value of $v - v_{e1}$ has been found but not a positive one, then the next point to be tried should be suitably closer to B;

if a positive value of $v-v_{e_1}$ has been found but not a negative one, then the next point should be closer to 0. Once C has been boxed in there should be no further difficulty.

An optimum starting point for stage 2 need not exist however; suppose that (h_1, y_{e_1}) were on the v_1 contour, instead of the v_6 contour. Then it is clear from Fig. 5.2 that no optimum starting point for the second stage can be found: i.e. for the particular h_1 chosen there would be no optimal reactor with more than one stage¹.

Assuming that the point C has been determined, and along with it the ratio w_2/w_1 , we proceed to evaluate the integrals on the right hand side of (5.23), and will in general find some point D where $F_2 = 0$ which would be the optimal end point for the second stage, E for the beginning of the third stage, etc. In this way we develop a trajectory satisfying the optimum condition equations, storing t_i , t'_i , and the ratios w_{i+1}/w_i and finally arrive at the beginning

1. This possibility has not occurred in the numerical examples treated.

of the last (Nth) stage.

For the last stage there are four possibilities, depending on $F_N(y_{a_N})$. The only one encountered in numerical calculations so far is represented by curve 1 in Fig. 5.4. $F_N(y)$ has only one zero for $y > y_{a_N}$. The remaining possibilities are covered by curves 2, 3, 4: For curve 4 there is no solution to the optimum condition equations with N (non empty) stages (for the value of h_1 chosen). For curve 3 there is a solution (just) while for curve 2 there are two.

To cater for the above possibilities, $F_N(y_{a_N})$ should be computed: if positive or zero, then calculation should proceed as for the earlier stages. If negative, then y_N'' , (see Fig. 5.2.) should be determined, and the two integrals:

$$\int_{y_{a_N}}^y \frac{dy}{V(h_N, y)} \quad ; \quad \int_{y_{a_N}}^y \frac{dy}{V^2(h_N, y)} \cdot \frac{\partial V}{\partial h}$$

evaluated, along with F_N , for values of y from

y_{a_N} to y''_N .

If F_N changes sign during this procedure, then the corresponding root y_p in Fig. 5.4 should be determined, and also t_N , these quantities being stored; then calculation should proceed to determine y_q as before. The values of M for the two reactors satisfying the optimum condition equations for exit conversion y_p and y_q can then easily be determined from the values already stored. If $F_N(y''_N) = 0$, calculation of F_N should stop, and M for the reactor satisfying the optimum condition equations for exit conversion y''_N determined. (If $F_N(y''_N) < 0$ calculation should also stop, no optimal reactor being possible!)

The reactor(s) calculated above will not in general satisfy the boundary condition on y_{e_N} , as a result of h_1 having been guessed incorrectly, but the calculations may be repeated for several h_1 and points on the m_f^x, y_f curve obtained. Intermediate values may be obtained by interpolation. (It may happen that in an attempt to get the required y_{e_N} , h_1 has to be lowered so much that the equations (5.2), (5.4), (5.17) cannot be satisfied. In such

a case the optimal reactor would have less than N (perhaps only one) nonempty stage(s). In other words the supplementary feed is unreasonably hot: see also corresponding case when $h_{a_1} \leq h_m$, discussed later, and Chapter IV.

If optimal reactors for 1,2,3 ... N stages are to be calculated¹, then we can take advantage of the fact that for given h_1 , the first $K-1$ stages of an optimal K stage reactor ($K \leq N$) are identical to the first $K-1$ stages of an optimal N stage reactor.

case (ii) $y_{a_1} > y_m$.

From (5.29) we see that $F_1(y_{a_1}) < 0$. If a starting point can be found in the + region of Fig. 5.2., the equation $F_1(y_1) = 0$ may have solutions (for $y_1 > y_{a_1}$). If there are two solutions, then the one for the smallest y should be ignored, of course.

Indirect Control:

The equations (5.17) hold for indirect control. If we let $h_m \rightarrow -\infty$ in (5.3) we get $w_j = w_N$, for all j ,

1. It is prudent to do this anyway in order to determine whether an optimal N stage reactor has empty stages.

so that (5.4) becomes $y_{a_i} = y_{e_{i-1}}$, whilst from (5.16) we obtain:

$$\frac{\partial M}{\partial h_i} = -w_N t'_i$$

so that for M to have an unrestrained minimum, the following equations must be satisfied:

$$V(y_{e_{i-1}}, h_i) = V(y_{e_{i-1}}, h_{i-1}) \quad (5.17a)$$

$$y_{e_{i-1}} = y_{a_i} \quad i=2 \dots N \quad (5.4a)$$

$$t'_i = 0 \quad i=1 \dots N \quad (5.30)$$

It is easy to see that for each value of i (and for y_{a_i}, h_i below L_2 in Fig. 5.2) equations (5.30) have two solutions, a trivial one for $y_{a_i} = y_{e_i}$ and another which lies between L_2 and the equilibrium line, so that for each non trivial solution of (5.30) it is always possible to find an $h_i < h_{i-1}$ to satisfy (5.17a).

The algorithm outlined above for the directly controlled case may be used here. It is sufficient to give h_m a large negative value. If optimal 1,2,3... N stage reactors are to be calculated then use may be

made of the fact that (for given h_1) all parts of the optimal trajectory are optimal. Also, if the $m_f^*(y_f)$ relation is required for several values of N and for several y_{a_1} , use may again be made of the piecewise optimality of the trajectories.

Behaviour as N tends to infinity:

The optimal trajectories discussed in Chapter III and Chapter IV part III are plausible limiting cases of the trajectories discussed above, the key role being played by the locus of points of tangency from the subsidiary feed condition to the contours of constant rate: L_1 in Fig. 5.2.

Forward vs. Backward Method of Calculation

The algorithm outlined above is an example of the forward calculation procedure, i.e. a "first stage" unknown is guessed, the equations for the first stage are then dealt with, then the second stage equations and so on up to the end of the N th stage. We will compare this procedure with the backward method¹.

(i) Indirect Control: Because of the bidiagonal structure of the equations one can in principle equally well guess h_N and proceed backwards as guess

1. Because of the topology of the problem either of these methods should be used.

h_1 and proceed forwards. If m_f^* is required for several y_f and one y_{a1} , then the forward procedure would be best, since to every h_1 there would correspond a point on the m_f^*, y_f curve: if m_f^* is required for one y_f and several y_{a1} then it is best to proceed backwards.

(ii) Direct control: There is probably nothing to be gained by using the backward method even if one is interested in m_f^* for several y_{a1} and one y_f because the equations are complicated by the term $\sum_{j=1}^{N-1} t'_j$

for stage N. This term arises from the essential asymmetry of the problem: w_N being fixed. If the forward procedure is used the $2N-1$ dimensional problem becomes a 1 dimensional problem (as in the indirect case). Starting at the last stage and proceeding backwards would require a two dimensional

guess: h_N and $\sum_{j=1}^{N-1} t'_j$ (or some equivalent quantities)

would have to be guessed, and only for the correct guess of this latter quantity would the backward

calculation terminate in such a way for the trajectory to be optimal for the value of h_N in question. The backward method is of course related to dynamic programming which has been shown to be inefficient in this case. (Ref. 45.)

Numerical Details (Forward Calculation).

There is only one point which deserves special attention: the evaluation of the integrals t_j and t'_j . It turns out that for moderate values of N and for y_f close to 1, the optimum adiabatic trajectories end up very close to the equilibrium line. Consider an adiabatic trajectory such as the vertical through A in Fig. 5.2. At $y=y'$, $V(h_1, y)$ has a simple zero (we have supposed). The factors $\frac{1}{V}$ and $\frac{1}{V^2}$ in the respective integrands would therefore cause trouble if ordinary numerical integration were used. Excellent results have been obtained by interpolating $\frac{1}{V}$ close to the equilibrium line by simple functions which could be integrated in closed form and which also have simple poles there¹.

1. A method mentioned by F. Horn in Ref. 36.

The function:
$$\frac{y - y'}{b(y - y') + c} \quad (5.31)$$

was used to interpolate $V(h_i, y)$ close to the equilibrium line¹, and further away $\frac{1}{V(h_i, y)}$ was interpolated by:

$$a(y - y') + b + \frac{c}{y - y'} \quad (5.32)$$

Provided $V(h_i, y)$ is a decreasing function of y the above interpolation can be used very successfully for values of y far from y' . The function

$$a_1 + b_1(y - y') + c_1(y - y')^2 \quad (5.33)$$

was used to interpolate $\frac{\partial V}{\partial h}$ so that by using (5.33) together with (5.32) or (5.31), the contributions to t'_j over a sub-interval could be determined by evaluating the resulting simple functions.

Provided $V(h_i, y)$ decreases as y goes from y_a to y_e the above interpolation method can be used satisfactorily throughout the whole interval but some

1. The function 1.1 with the three sets of parameters in table 1.1 and $J=158.5^\circ\text{k}$ was used.

slight errors arise if V goes through a maximum, so the following strategy was used¹ to find the non-trivial y_e .

(i) y' was determined precisely.

(ii) $y''' = 0.995y' + 0.005 y_a$ was calculated.

(iii) Evaluation of the integrals t and t' was initiated, (starting from y_a). The integrals were evaluated over sub intervals $[y_a, y_a + k_1]$; $[y_a + k_1, y_a + k_2 + k_1]$, etc.,² three point Simpson's rule quadrature being used provided that v was increasing over the sub-interval. As soon as v started decreasing, then the interpolation methods (formulae (5.32) and (5.33)) were switched to³. At the right hand end of each sub-interval $F(y)$ was evaluated. If $F(y)$ was negative at the right hand end of the first sub interval a fault⁴ loop was entered, otherwise

-
- 1.. For most of the calculations done for the second set of parameters in table 1.1.
 2. The method of assigning k_1 will be discussed later.
 3. The N th stage requires additional logic to cover the possibility of two roots and no roots; so does the first stage unless $y_{a_1} = y_m$, so the procedure will be described for an intermediate stage in order to avoid tedious detail.
 4. never occurred in an actual calculation.

integration continued unless $F(y)$ became negative at the right hand end of some sub-interval (in which case a routine was entered in order to determine y_e and all other relevant end values). If $F(y)$ was positive at the left hand end of a sub-interval which contained y''' , then the right hand end of that sub-interval was made y''' . If $F(y''')$ was also positive, then (5.31) and (5.33) were used to interpolate V and $\frac{\partial V}{\partial h}$. The base points y''' and $\frac{1}{2}(y''' + y')$ were used for (5.31) and (5.33), the additional base point for (5.33) being y' . (In this way $F(y)$ could be evaluated by a routine based on the primitive functions for the interpolated integrands for any reasonable y between y''' and y'). $F(y)$ was evaluated for $y = y_1, y_2 \dots$ where these were generated by:

$$y_1 = \frac{1}{2}(y''' + y'); y_2 = \frac{1}{2}(y_1 + y'); y_3 = \frac{1}{2}(y_2 + y'), \text{ etc.}$$

(until a value y^+ was found such that $F(y^+) \leq 0$, when y_e was determined by a root finding routine, and all other relevant variables were calculated).

The widths of the successive sub-intervals k_1, k_2, k_3 , etc. were determined by a rather crude procedure based on the second differences of the function $V(h_i, y)$ as follows:

i) A small positive number e' and a positive integer R were specified.

2) A trial number $k = 0.02 (y' - y_a)$ was calculated.

3) k was used as a trial interval width, V being calculated at the left hand end: V_1 , at the mid-point: V_2 , and at the right hand end: V_3 .

$$\text{If } \frac{V_1 - 2V_2 + V_3}{V_1 + 4V_2 + V_3} < e'$$

then k was considered acceptable, a success was counted, and calculation proceeded on this basis. Otherwise the success count was set to zero, k halved, V_2 replaced V_3 , a new V_2 was calculated and the test repeated. After each step was calculated (i.e. the contributions to t and t' evaluated etc.) the success count was compared with R . If it was less than R , k was used unchanged as the trial width for the next

interval. Otherwise $2k$ was used. (Thus if successive steps were successful after the first few, the interval width would be doubled at every step).

For values of e' from 0.002 to 0.01, ten to twenty five steps were required per stage for $y_{a_1} = 0$ and y_{e_N} up to 0.999. The results for a one stage reactor were checked by the perturbation method described in Chapter VI and found to be in excellent agreement for $e' = 0.01$ and 0.002.

The above method has the advantage that it is a one parameter method in the sense that the accuracy is determined (principally) by e' : the step adjustment criterion however is best suited to the interpolation methods used in the latter part of the integration interval. (If $V(h_1, y)$ is linear in y then the interpolation is exact). For the 1st set of parameters in table 1.1 however, a considerable contribution to the integrals t and t' is made during the former part of the integration interval for low values of h_{a_1} , so a two parameter modification of

the above method was used in which the steplength changing criterion during the Simpson's rule integration¹ was based on $\bar{e}$, the largest of two numbers calculated at each trial step. One of these numbers was the modulus of ratio of the estimated² truncation error to the estimated contribution to t , and the other the corresponding number for t' . A small number e'' was assigned, and if:

$$\bar{e} < e''/32$$

then the step was considered successful and the proposed step length for the next step was made twice that for the current step. If $e'' < \bar{e}$ the step was considered unsuccessful and repeated with halved step length, while for $\frac{e''}{32} \leq \bar{e} \leq e''$ it was considered successful and the proposed step length for the next step remained the same as for the current step.

-
1. In the latter part of the integration interval the interpolation method was used.
 2. The Merson estimate, (Ref.8) was used: for an integral the Merson method degenerates to Simpson's rule (with an added point for error estimation).

A study was made to determine reasonable values for e' , e'' and other parameters such as the precision required in the determination of y' , etc.¹ In the worst case considered (1st set of reaction rate parameters, $T_{a1}=550^{\circ}\text{K}$, $T_m=300^{\circ}\text{K}$, $y_{a1} = 0$, two stages) with $e' = 0.001$, and $e'' = 0.0001$, and the tolerance² on $y' = 0.000,000,001$, all relevant numbers were calculated with a precision of 1 part in 100,000 or better: 58 and 33 steps being required in the first and second stages³. (Even with the tolerances relaxed so that 15 and 9 steps were required for the first and second stages respectively, the largest corresponding relative error was $1/200$).

On an I.C.T. Atlas with the above method 1,2, and 3 stage reactors may be calculated for one value of h_{a1} in at most 1 second. Allowing for the difference in

1. By reducing them successively until all relevant numbers (such as exit conversion, inlet temperature, stage flowrates, etc.) became constant.

2. A tolerance on y' of 1 part in 1 million would probably have been adequate, but this tolerance was obtainable easily on the I.C.T. Atlas anyway.

3. These tolerances were used in "production runs."

speeds of the computers used, this makes our method over 100 times as fast as the method described in (Ref.45) which is not surprising¹.

1. See section on Forward vs. Backward method of calculation.

V.III Results of Calculations:

The $M_{\min}$, y_{e_N} relation for $w_N=1$, $y_{a_1} = 0$, and all sets of reaction rate function (1.1) parameters to be found in Table 1.1, was determined for indirect control, and for direct control with cold shot temperatures of both 300 and 600°K, for various values of y_{e_N} from about 0.1 to about 0.99, and for 1,2,3,4 and infinitely many stages.¹

$M_{\min}$, y_{e_N} graphs for the indirectly controlled reactors are presented in Chapter VII, together with the corresponding curves for U-tube and other indirectly controlled reactors.²

In the following three sections the results for the directly controlled reactors are discussed.

(i) The $M_{\min}$, y_{e_N} relations for $T_m=600^\circ\text{K}$, "Cold shot too hot" degeneracy:

In Fig. 5.11 the $M_{\min}$, y_{e_N} relations for the first set of reaction rate parameters are shown. The

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1. Except as noted later.
 2. The corresponding optimal controls are discussed in sub-section (iii) below.

reduction in $M_{\min}$ gained by using two stages instead of one is seen to be modest at low outlet conversions but approximately a five fold volume reduction is possible for $y_e = 0.9$ whilst for conversions approaching the critical value represented by the point A, the improvement dwindles to zero.

A of course corresponds to the "cold shot too hot" degeneracy and occurs for an inlet temperature between 584 and 585°K, i.e. lower than the cold shot temperature. In this critical case the function $F_1(y)$ has not the form shown in Fig.5.3, but that of Fig.5.10. Evidently in this case each of the two zeros of $F_1(y)$, y_{a_1} or y'' are equally good.

It would appear that for all $N=3,4,\dots$ degeneracy also occurs at the point A in Fig.5.11, however, this has not been confirmed numerically because (for various unimportant reasons) the programmes used were workable for $T_{a_1} < T_m$ only if $N \leq 2$, but were otherwise satisfactory, so the curves for $N > 2$ in Fig. 5.11 terminate at points corresponding to $T_{a_1} = 600^\circ\text{K}$ (the MT reactor in the variational

case).

The MT reactor (point B) requires only 7 % of the volume required by the corresponding optimal single stage reactor and approximately 40% of the volume required by the corresponding optimal four-stage reactor.¹ For $y_{eN} \approx 0.9$, however, only about 15% less volume is required for $N = \infty$ than for $N=4$ and for lower conversions the reduction in volume decreases steadily.

The $M_{\min}$, y_{eN} relations for the second set of rate parameters have the same form as those in Fig.5.11. Complete results for some selected values y_{eN} are to be found in Tables 5.1, 5.2, and 5.3; the degeneracy occurs at an inlet temperature between 580 and 581°K and the critical outlet conversion is approximately 97%. At $y_{eN} = 0.9$, the 4,3,2 and 1 stage reactors require approximately 5, 12, 23 and 100 percent more volume respectively than the ∞ staged reactor,² and there is no y_{eN} for which the 4,3,2,1 staged

1. Not shown in Fig. 5.11 so as to prevent crowding: see also Table 5.3.

2. These figures were obtained graphically and have an estimated relative precision of $\pm 20\%$.

reactors compare much less favourably with the perfectly controlled reactor.

Results for the third set of reaction rate function parameters may also be found in Tables 5.1 to 5.3. Because the effect of N was not very marked the $N=\infty$ case was not investigated. At $y_{eN} \approx 0.85$ the ratio of 1 stage $M_{\min}$ to 4 stage $M_{\min}$ is maximum and is approximately 1.21. The corresponding 4 stage to 2 stage maximum ratio is only about¹ about 1.06.

(ii) The $M_{\min}$, y_{eN} relation for $T_m = 300^\circ\text{K}$.

The 600°K cold shot was selected especially to investigate the degeneracy. Cold shots used industrially are ordinarily so cold that this degeneracy cannot occur for practicable outlet conversions; 300°K is a reasonable temperature for a water-scrubbed gas.

The results are represented in Tables 5.1 to 5.3 and the $M_{\min}$, y_{eN} curves in Figs. 5.12 to 5.14.

Some curves have been cut short or omitted entirely to prevent crowding. For example, the perfor-

1. See footnote 2 on previous page.

mance of a three stage optimal reactor is so close to that of a four stage reactor, that even for $y_{e_N} = 0.98$, for the first set of rate function parameters, it requires approximately 11% more volume, and for the second and third sets approximately 6% and 2% respectively. For $y_{e_N} = 0.98$ and the second set of rate function parameters, 5% more volume is required when $N = 4$ than when $N = \infty$. The case $N = \infty$ was not investigated for the third set of rate function parameters because its performance was not expected to differ significantly from that of the four stage reactor: for $y_{e_N} = 0.98$ it turned out that the two stage reactor required approximately 10% more volume than the four stage reactor.

It can be seen from the results presented that the volume (or mass of catalyst) economy due to increasing N is larger the smaller is N , ($N > 0$) and is most significant for A'/A small ($A'/A > 1$). It is hoped that those faced with designing a reactor in a hurry will find the relative orders of magnitude to

be of use.

(iii) The optimal controls.

The case $N = \infty$, ($y_0 = y_m = 0$) is not of much interest because of the infinite initial temperature.

The optimal inlet temperatures as functions of y_{e1} for a one stage reactor are represented in Fig. 5.15. For given y_0 , the optimal inlet temperatures are uniformly higher the higher the activation energies: the optimal inlet temperature is a compromise between a high rate in the first part of the reactor ~~at a~~ ^{and} consequently of a low rate in the last part, and vice-versa, so the effect is intuitively reasonable.

As may be observed by considering Tables 5.1 to 5.6, for each set of rate parameters, and for every given y_{eN} , the optimal inlet temperatures are increasing functions of the number of stages, as one would expect; for all values of N studied the variation of optimal inlet temperature with reaction rate parameters was of the same qualitative form as for $N=1$.

The distribution of volume between the stages

is also to be found in Tables 5.1-6. In table 5.1, $w_1 t_1 / M$ is the fraction of the total volume in stage 1. This figure is of importance because it is in general fixed at the design stage and cannot be altered easily afterwards: it is interesting to note that (with the exception of the cases where T_{a1} is close to the degeneration temperature when it evidently cannot be of much importance anyway), the figure¹ is fairly constant: 0.125-0.245. In Tables 5.2-3 and 5.5-6 the same type of distributional invariance may be noted for the three and four stage reactors. This relative invariance has been noticed before for indirect control: it does not follow that the effects of maldistribution of volume can be well compensated by adjustment of the remaining free variables (although this would seem likely) and in fact this subject is treated theoretically later on.

The optimal trajectories in the yT plane may easily be constructed from the information presented in Tables 5.1 to 5.6.

1. Slightly more variable for indirect control.

V.IV Consideration of Preheating cost.

Suppose that the cost of preheating is allowed for by minimizing not M (equation 5.1) but

$$K = M + \overset{+}{F}(w_1, h_1)$$

where $\overset{+}{F}$ is an arbitrary (well behaved) function.

Then the same type of argument given at the beginning of the chapter may be used to obtain the modifications to equations (5.16) and (5.16a) required: (it is obvious that equations 5.17 still hold).

Also, evidently for i neither 1 nor N ,

$$\frac{\partial K}{\partial h_i} = \frac{\partial M}{\partial h_i}$$

whereas for $i=1$, using equation (5.11):

$$\frac{\partial K}{\partial h_1} = \frac{\partial M}{\partial h_1} + \overset{+}{\frac{\partial F}{\partial h_1}} + \overset{+}{\frac{\partial F}{\partial w_1}} \left\{ \frac{w_N \delta_{1N}}{h_1 - h_m} - \frac{w_1}{h_1 - h_m} \right\}$$

If we note that the underlined term depends on variables for the N th stage only if $N=1$, it is clear that the calculation may proceed in the forward direction without essential modification. The alteration

to equations (5.23) and (5.24) required being easy to find. It is worth pointing out however, that unless $F(w_1, h_1)$ is linear in w_1 , the problem loses its reducibility, i.e. in order to start the calculation w_1 and h_1 have to be specified and the reactor will be optimal only for the ensuing y_{e_N} and w_N . (The reader will not fail to notice that the reactor with heat feedback considered in Ref. 41 can not be dismissed so simply because F in addition to depending on w_1 and h_1 would depend on h_N and y_{e_N}).

V.V. Transformation of Optimum Condition Equations:
T as Integration Variable.

If the function $y(T, h)$ is given explicitly but is not easily invertible to get $T(y, h)$ it would be worthwhile to set up the equations with T as independent variable so that $y(T, h)$ does not have to be inverted every time the rate $v(y, T)$ is calculated.

It is sufficient to transform (5.1), (5.13) and (5.14), writing:

$$y = y(h, T); \quad y_T = \left(\frac{\partial y}{\partial T}\right)_h; \quad y_h = \left(\frac{\partial y}{\partial h}\right)_T \quad (5.34)$$

$$V(y, h) = v(y(h, T), T) \quad (5.35)$$

so that:

$$\frac{\partial V}{\partial h} = \frac{\partial v}{\partial T} \left(\frac{\partial T}{\partial h} \right)_y = - \frac{y_h}{y_T} \frac{\partial v}{\partial T} \quad (5.36)$$

$$\text{and } t_i = \int_{T_{a_i}}^{T_{e_i}} \frac{y_T dT}{v(y, T)}, \quad t'_i = - \int_{T_{a_i}}^{T_{e_i}} \frac{y_h \cdot \frac{\partial v}{\partial T}}{v^2(y, T)} dT \quad (5.37)$$

where the last integrals are evaluated over the path $y=y(h_i, T)$. And M is as before:

$$M = \sum_{i=1}^N t_i w_i \quad (5.38)$$

(Alternatively the equivalent equations obtained from equations A5.14, A5.15, and A5.16 by setting their left hand side equal to zero may be used).¹

In the indirectly controlled case (5.17a) could be replaced by: $v(y_{a_{i+1}}, T_{a_{i+1}}) = v_{e_i}$, (5.17b)

this equation could be solved for $T_{a_{i+1}}$, and h_{i+1} found by solving $y_{a_{i+1}} = y(h_{i+1}, T_{a_{i+1}})$.

1. See Appendix.

In the directly controlled case several inversions of the function $y(h, T)$ to find T would be required in order to solve (5.2), (5.4), and (5.17) simultaneously by guessing only one quantity, (such as $y_{a_{i+1}}$). If $T_{a_{i+1}}$ and h_{i+1} are both guessed, then no inversion would be required.

V. VI. Optimum conditions with Temperature Restraints.

(i) General case: T must satisfy:

$$T_1 \leq T \leq T_2 \quad (5.39)$$

The optimum condition equations 5.17 and 5.24 may still be used provided that the rate expression is suitably modified so that the rate is made ≤ 0 if 5.39 is violated but otherwise unchanged. Suppose for example that $v(y, T)$ is replaced by $\bar{v}(y, T)$ defined by:

$$\begin{aligned} \bar{v}(y, T) = & \begin{aligned} & v(y, T) \cdot \exp(-K^2(T-T'_1)^2) \cdot \text{for } T \leq T'_1 \\ & v(y, T) \cdot \text{for } T'_1 \leq T \leq T'_2 \\ & v(y, T) \cdot \exp(-K^2(T-T'_2)^2) \cdot \text{for } T \geq T'_2 \end{aligned} \end{aligned} \quad (5.40)$$

where T'_1 and T'_2 are suitably close to T_1 and T_2 respectively and K is suitably large, then the basic

algorithm given above should work satisfactorily provided the initial choice of h_1 doesn't imply the violation of (5.39).

(ii) Only maximum temperature limited:

$$T \text{ must satisfy : } T \leq T_2 \quad (5.41)$$

One may proceed as above, with $T'_1 = 0$. Alternatively the problem may be formulated in terms of a set of free variables $\{T_{e_1}, T_{e_2} \dots T_{e_N}\}$, since the highest (fluid) temperature in each stage must occur at the end¹. If we choose the set:

$$S_4 : \{T_{e_1}, \dots T_{e_N}, h_1 \dots h_{N-1}\} \text{ and write:}$$

$$W(T_{e_1}, \dots T_{e_N}, h_1 \dots h_{N-1}) \equiv M(h_1 \dots h_N, y_{a_2} \dots y_{a_N}); \quad (5.42)$$

then (it is shown in the appendix that):

$$\frac{\partial W}{\partial T_{e_j}} = w_j y_T \left\{ \frac{1}{v_{e_j}} - \frac{1}{v_{a_{j+1}}} \right\}, \quad j=1, 2 \dots N-1; \quad (5.43)$$

$$\frac{\partial W}{\partial T_{e_N}} = - \frac{y_T(e_N)}{y_R(e_N)} \left\{ \frac{\partial M}{\partial h_N} + (1 - \delta_{N1}) w_N \frac{(y_m - y_{e_{N-1}})}{(h_m - h_{N-1})} \left(\frac{1}{v_{e_{N-1}}} - \frac{1}{v_{a_N}} \right) \right\} \quad (5.44)$$

$$\frac{\partial W}{\partial h_j} = w_j \left\{ \left(\frac{1}{v_{e_j}} - \frac{1}{v_{a_{j+1}}} \right) \left(\frac{y_{e_j} - y_m}{h_j - h_m} \right) + \left(\frac{1}{v_{e_{j-1}}} - \frac{1}{v_{a_j}} \right) \left(\frac{y_{e_{j-1}} - y_m}{h_{j-1} - h_m} \right) (1 - \delta_{ij}) \right\} + \frac{\partial M}{\partial h_j}; \quad j \neq N \quad (5.45)$$

1. We exclude systems where the mixing is so strongly non ideal that although ΔH is negative $\left(\frac{\partial h}{\partial y}\right)_T$ is positive.

We will also use the relation¹:

$$\frac{\partial M}{\partial h_j} = \left\{ \frac{w_j}{h_m - h_j} \right\} F_j(y_{e_j}) \quad ; \quad j \neq N \quad (5.46)$$

Modifications which may be made to basic algorithm to take (5.41) into account:

We will consider only case (i), i.e. $y_{a_1} = y_m$. As before, h_1 is guessed and the first stage is calculated, $F_1(y_1)$ being evaluated for increasing y_1 , until either it becomes zero, or T reaches T_2 . In the former case, the following relation must be satisfied:

$$\frac{\partial W}{\partial T}_{e_1} = 0$$

so that the starting conditions for the next stage may be obtained as before, so that (for $N > 2$), $F_2(y)$ will have one trivial zero for $y = y_{a_2}$ and one other. In the latter case we must have²:

$$\frac{\partial W}{\partial T}_{e_1} \leq 0, \text{ i.e. : } v_{a_2} \leq v_{e_1}$$

and $\frac{\partial W}{\partial h_1} = 0$, so that the starting rate for

1. See (5.16) and (5.23).

2. equality occurring if the nontrivial zero of $F_1(y_1)$ occurs at $T=T_2$.

the next stage may be found by solving 5.47 (for $j=1$):

$$\left. \begin{aligned} \frac{F_j(y_{ej})}{h_m - h_j} + \left(\frac{1}{V_{ej}} - \frac{1}{V_{a_{j+1}}} \right) \left(y_{ej} - \frac{y_{ej} - y_m}{h_j - h_m} \right) \\ + \left(\frac{1}{V_{e_{j-1}}} - \frac{1}{V_{a_j}} \right) \left(\frac{y_{ej} - y_m}{h_{j-1} - h_m} \right) (1 - \delta_{ij}) = 0 \\ y_e(h_j, T_2) = 0 \end{aligned} \right\} \quad (5.47)$$

For $j=1$, the V_{a_2} obtained from (5.47) will automatically be less than V_{e_1} as required by the temperature restraint. For other values of j , $V_{a_{j+1}}$ may not be less than (or equal to) V_{e_j} and so should be tested. (If $V_{a_{j+1}}$ satisfying (5.47) exceeds V_{e_j} then there is no N stage optimal reactor for the h_1 chosen). It follows that for an optimal reactor, if the j th stage ($j+1 < N$) terminates at a temperature restraint¹, then $V_{a_{j+1}} < V_{e_j}$, so that $F_{j+1}(y_{a_{j+1}}) < 0$. Thus $F_{j+1}(y)$ will have two roots, and the one for the smallest y (being in the + region of fig. 5.2) should be ignored.

The last stage should terminate either at $T=T_2$ or when $\frac{\partial W}{\partial T}$ is zero. It is easy to show that $\frac{\partial W}{\partial T}$ may have two zeros along the line $h = h_N$.

If T is to be used as an integration variable

1. Where $F_j(y_j)$ is not simultaneously zero.

then the above equations can easily be transformed (as above); alternatively an algorithm based on the equations A 5.14, A 5.15, and A 5.16, could be devised.

V.VII. Equations for linear enthalpy relation.

If equation (2.22) holds accurately, then the above equations will remain true if all variables h_j are replaced by θ_j (equation 2.23) and all $V(y, h)$ by $U(y, \theta)$ (see 2.28, 2.29).

If we put $y_{a_1} = y_m$, then for $N=2$ we obtain Horn's equations, whilst for $y_m = 0$ we obtain Konoki's. (Refs. 40 and 64).

V.VIII. Sufficient Conditions For a Minimum: Sensitivity of Minimum:

(i) Sufficient Conditions

To confirm that a calculated stationary point in fact corresponds to a minimum one may consider the matrix H_1 of second derivatives of M with respect to the set $S_1 = \{y_{a_2} \dots y_{a_N}, h_1 \dots h_N\}$ and verify that it is positive definite.

For indirect control it is elementary to show

that the elements of H_1 are given by¹:

$$\begin{aligned}\frac{\partial^2 M}{\partial y_{a_i} \partial y_{a_j}} &= \frac{1}{V_{a_i}^2} \left(\frac{\partial V_{a_i}}{\partial y_{a_j}} - \frac{\partial V_{e_{i-1}}}{\partial y_{a_j}} \right) \\ \frac{\partial^2 M}{\partial h_j \partial y_{a_i}} &= \frac{1}{V_{a_i}^2} \left(\frac{\partial V_{a_i}}{\partial h_j} - \frac{\partial V_{e_{i-1}}}{\partial h_j} \right)\end{aligned}\quad (5.49)$$

$$\begin{aligned}\frac{\partial^2 M}{\partial h_i \partial h_j} &= -\delta_{ij} t_j'' \\ \text{where } t_j'' &= \int_{y_{a_j}}^{y_{e_j}} \frac{1}{V_j^3} \left\{ V_j \frac{\partial^2 V_j}{\partial h_j^2} - 2 \left(\frac{\partial V_j}{\partial h_j} \right)^2 \right\} dy\end{aligned}$$

If the variables are ordered $\{h_1, y_{a_2}, h_2, y_{a_3}, \dots, y_{a_N}, h_N\}$ (and the matrix correspondingly), then it may be seen from (5.49) that H_1 is tridiagonal, but it is not easy to see under what conditions it is positive definite (for realistic rate functions).

The elements of H_1 may be evaluated numerically; a method similar to the one mentioned above for determining t_j and t'_j may be used for t''_j .

If H_1 is written:

$$H_1 = \begin{bmatrix} d_1 & e_1 & & & \\ e_1 & d_2 & e_2 & & \\ & e_2 & d_3 & e_3 & \\ & & & \ddots & \\ & & & & d_{n-1} & e_{n-1} \\ & & & & e_{n-1} & d_n \end{bmatrix}$$

1. These relations hold only for stationary points.

(where $n = 2N-1$) then it is well known that the determinants $\Delta_1, \Delta_2 \dots \Delta_K \dots \Delta_n$ formed from H_1 by taking the first row and column, first and second rows and columns, etc. satisfy the relations:

$$\begin{aligned}\Delta_1 &= d_1 \\ \Delta_2 &= d_2 \Delta_1 - e_1^2 \\ \Delta_3 &= d_3 \Delta_2 - e_2^2 \Delta_1 \\ \Delta_K &= d_K \Delta_{K-1} - e_{K-1}^2 \Delta_{K-2} \\ \Delta_n &= d_n \Delta_{n-1} - e_{n-1}^2 \Delta_{n-2}.\end{aligned}$$

The elements of H_1 would be calculated either from 1 to n or from n to 1. In order to test for positive definiteness, it is therefore sufficient to carry over (at most) four quantities from the end of one stage to the beginning of the next.

For the directly controlled case the matrix H_1 is more complicated, being a five band matrix with the last row and column filled (i.e. not identically zero). The second derivatives with respect to h_i and h_j (when they are not zero) are extremely complicated.

(ii) Sensitivity Problems: Statements:

Knowing H_1 enables sensitivity calculations to be made easily: i.e. the question "how sensitive is the

optimum M to variations of members of the set S_1 ?" is easily answered. These questions are however relatively unimportant. An important sensitivity problem arises as follows:

Based on a given reaction rate expression an optimal N stage reactor is designed, the optimum catalyst distribution being calculated, as well as the optimum enthalpies for each stage. When the reactor is fabricated provision is made for the adjustment of the h_i but not for the redistribution of catalyst, so that errors in the calculated optimal values of h_i (arising from the inaccurate reaction rate expression) can be compensated for, but errors in the catalyst ratios $m_1:m_2 \dots : m_N$ cannot. One wants to know how serious this is.

To fix ideas suppose that we know the true data, but the person who computes the optimal reactor works with (slightly) inaccurate data. Let us consider the maximization of y_f problem. For the given amount of catalyst we know that the corresponding y_f max is A in Fig. 5.5. Because of errors the actual point will

be B, rising to C when the h_i have been readjusted. C will be below A in general because the catalyst distribution will be wrong. How is the distance AC related to these errors?

We begin by stating the optimization problem in different terms, choosing the set of variables:

$$S_2 = \{h_1, h_2 \dots h_N, m_1, m_2 \dots m_N\}$$

and trying to find the values corresponding to the $\max y_{e_N}$ for given $M = m_1 + m_2 \dots + m_N$, and w_N, y_{a_1}, y_m and h_m . To specify the distribution we introduce new variables ψ_i , such that:

$$\left. \begin{aligned} m_i &= \sum_{K=1}^{K=N} P_{iK} \psi_K \\ M &= \psi_N \sqrt{N} \end{aligned} \right\} \quad (5.50)$$

where the P_{iK} form a constant orthonormal matrix

$P = \parallel P_{iK} \parallel$ so that the problem⁺ is transformed

⁺Such a matrix may be constructed by starting with the last column: $N^{-\frac{1}{2}} \{1, 1, \dots, 1\}$ and working back according to the Schmidt procedure.

into an unconstrained maximization with variables $S_3 = \{h_1 \dots h_N, \psi_1 \dots \psi_{N-1}\}$. [Changing ψ_K ($K \neq N$) by 1 will make the corresponding image in m space move unit distance in the hyperplane $\sum m_i = M$. Changing another ψ_K ($K \neq N$) will make the image move in an orthogonal direction (again in the hyperplane $\sum m_i = M$), while changing ψ_N will make the image move normal to the hyperplane].

We may specify distance and direction in the above hyperplane from the point corresponding to A in Fig. 5.5, and ask for the change in y_f if the variables $h_1, h_2 \dots h_N$ are simultaneously adjusted so as to maximize y_f for the new values $m_1, m_2 \dots m_N$, i.e. ask for the distance AC in Fig. 5.5. We may specify a small distance and ask for the direction in the hyperplane which gives rise to the largest change in y_f max (when the h_i are again adjusted so as to make y_f maximum for the new values of m), etc.

Methods for treating these problems will be discussed in the following section:

Solution of sensitivity problems in terms of matrix H_2

It will be assumed that H_2 , the matrix of second derivatives of y_{e_N} with respect to the members of the set S_2 (evaluated at the overall optimum) is known: methods of finding H_2 will be discussed later. Let the variables be so ordered that H_2 may be partitioned into four submatrices A_{11} , A_{12} , A_{21} , A_{22} , as shown:

$$H_2 = \left[\begin{array}{cc|cc} A_{11} = \left\| \frac{\partial^2 y_{e_N}}{\partial m_i \partial m_j} \right\| & & A_{12} = \left\| \frac{\partial^2 y_{e_N}}{\partial m_i \partial h_j} \right\| & \\ \hline & & & \\ A_{21} = \left\| \frac{\partial^2 y_{e_N}}{\partial h_i \partial m_j} \right\| & & A_{22} = \left\| \frac{\partial^2 y_{e_N}}{\partial h_i \partial h_j} \right\| & \end{array} \right] \quad (5.51)$$

Suppose also that at the optimum point the elements $\bar{B}_i$ of a (column) vector $\bar{B}$ are evaluated:

$$\bar{B} = [\bar{B}_i] = \left[\frac{\partial y_{e_N}}{\partial m_i} \right] \quad (5.52)$$

Then we may expand y_{e_N} in a Taylor series about the optimum point (where its value is $y_{e_N}^*$), ignoring third and higher order terms and letting $\phi, \bar{\phi}$ be (column)

vectors with elements δh_i , δm_i respectively:

$$\phi = [\delta h_i] ; \Phi = [\delta m_i] \quad (5.52a)$$

$$y_{e_N} = y_{e_N}^* + \bar{B}^T \Phi + \frac{1}{2} [\Phi^T \ ; \ \phi^T] \begin{bmatrix} A_{11} & A_{12} \\ A_{21} & A_{22} \end{bmatrix} \begin{bmatrix} \Phi \\ \phi \end{bmatrix} \quad (5.53)$$

where the superscript T denotes transposition. If we make use of the relation $A_{12}^T = A_{21}$, we may write (5.53):

$$y_{e_N} - y_{e_N}^* = \bar{B}^T \Phi + \frac{1}{2} \Phi^T A_{11} \Phi + \frac{1}{2} \phi^T [2A_{21} \Phi + A_{22} \phi]; \quad (5.54)$$

we wish to find ϕ as a function of Φ such that y_{e_N} is conditionally maximum.

By differentiating and setting to zero we obtain:

$$\phi = - A_{22}^{-1} A_{21} \Phi \quad (5.55)$$

which can be seen to be the required relation by putting:

$$\phi = - A_{22}^{-1} A_{21} \Phi + E \quad (5.56)$$

into (5.54), when we obtain:

$$y_{e_N} - y_{e_N}^* = E^T A_{22} E + K \quad (5.57)$$

where K is independent of E (and E^T). Now A_{22} is

necessarily negative definite so it follows that y_{e_N} is maximised by $E=0$. Putting the optimal expression for ϕ into (5.54) we get the conditional maximum, $\tilde{y}_{e_N}$:

$$\tilde{y}_{e_N} = y_{e_N}^{\pi} + B^T \bar{\phi} + \frac{1}{2} \bar{\phi}^T [A_{11} - A_{12} A_{22}^{-1} A_{21}] \bar{\phi}; \quad (5.58)$$

If χ is a column vector whose elements are $\delta\psi_K$

$$\chi = [\delta\psi_K] \dots \quad (5.59)$$

then, using (5.50):

$$\bar{\phi} = P\chi \quad (5.60)$$

Putting this into (5.58), we get:

$$\tilde{y}_{e_N} = y_{e_N}^{\pi} + \delta\psi_N \underbrace{\sum_{i=1}^N P_{iN} \bar{B}_i}_{\text{underlined}} + \frac{1}{2} \chi^T P^T [A_{11} - A_{12} A_{22}^{-1} A_{21}] P \chi; \quad (5.61)$$

where the underlined term is all that remains of $B^T P \chi$ (because $y_{e_N}^{\pi}$ is a maximum with respect to free variations of the first $N-1$ of the ψ_K).

If $\chi_N = 0$, then 5.61 gives us points on the line ABC, in Fig. 5.5, for various $\bar{\phi}$. The direction of greatest sensitivity (in the hyperplane $m_1 + m_2 + \dots + m_N = M$) is that of the eigenvector with largest eigenvalue of

the matrix obtained by deleting the last row and column of the matrix:

$$P^T [A_{11} - A_{12} A_{22}^{-1} A_{21}] P \quad (5.62)$$

By allowing χ_N to vary as well one gets points in a little semicircle around A in Fig. 5.5, so the analysis can therefore be extended to cover for example the case where M and y_f are fixed and w_N is to be maximised conditionally.

Optimum Condition Equations based on S_3 as variables:

Solution of sensitivity problem when H_2 is unknown.

If y_{eN} is expressed as a function of the variables of the set $S_2 = \{h_1 \dots h_N, m_1 \dots m_N\}$ then the conditions that the first derivatives with respect to the h_j should vanish¹ are;

$$V_{e_j} t'_j - \left(\frac{1}{h_j - h_{mm}} \right) \left\{ -t_j V_{e_j} - \frac{(y_{a_j} - y_m)(1 - \delta_{ij}) V_{e_j}}{V_{a_j}} + y_{e_j} - y_m \right\} = 0 \quad \text{for } j \neq N \quad (5.63a)$$

$$V_{e_N} t'_N + \sum_{i=1}^{N-1} \left\{ \prod_{j=i+1}^{j=N} \frac{V_{e_j}}{V_{a_j}} \right\} V_{e_i} t'_i = 0 \quad (5.63b)$$

1. See appendix for derivation.

Equations (5.63a) for $j \neq 1$ in general have a trivial root at $y_{e_i} = y_{a_i}$ and one other root: (this is also true for $i=1$ if $y_{a_1} = y_m$). Equation (5.63b) may have no roots, one or two roots. [If y_{e_N} is to be a maximum with respect to variations of the m_i (constrained by $\sum dm_i = 0$) then equations (5.17) must be satisfied as well. Equations (5.63a) together with (5.17) imply (5.18), and (5.63b) together with (5.17) imply (5.21)].

To investigate the sensitivity near the point A (Figs. 5.5 and 5.6) we may proceed as follows.

We first find a segment of the line O' in h space (Fig. 5.7) which corresponds to points on the $(y_{e_N}^*, M)$ curve: 0 Fig. 5.6, in the neighbourhood of A. Here we construct a set of $n-1$ mutually orthogonal lines O'_1, O'_2 , etc. which are orthogonal to the direction of O' at A' , and choose first a few suitable points on O'_1 , say. We then find the corresponding points in the space of m_i by solving equations (5.63) (if this is possible) and also the corresponding points in the y_m plane. In this way the mapping of the lines O'_1, O'_2 , etc. onto the corresponding lines O_1, O_2 in Fig. 5.6

and O_1'' , O_2'' in Fig. 5.8 is determined. We require of course the mapping of points in Fig. 5.8 into Fig. 5.6 in order to solve this sensitivity problem; by this method points in each of these figures are generated simultaneously; the required mapping may be found by interpolation.

It goes without saying that for large deviations from the line O' in h space this method is superior to the one based on H_2 given above. For small deviations the H_2 method has the strong advantage that one can find the mapping from the m space to the h space without any of the difficulty that one would evidently have with this method (especially if N is large) - that is if the labour involved in determining H_2 is discounted.

Solution of sensitivity problem: special method for indirect control

We make use of the piecewise optimality of the¹ trajectories. Suppose the basic problem has been solved for a one stage reactor for a large number of values

1. See page 144 of this chapter. Alternatively, put $h_m = -\infty$ in 5.63a.

of the parameter y_{a_1} , resulting in a family of curves such as those in Fig. 5.9., curves $C_1, C_2, \dots C_6$. Suppose we wish to know $\widetilde{y}_{e_3}$ with m_1, m_2, m_3 given, as shown in fig., for $y_{a_1} = 0$. It is sufficient to find the point corresponding to m_1 on C_1 , hence y_{e_1} ; interpolate the curve between C_2 and C_3 (C_7 : broken line); find on it the point y_{e_2} corresponding to m_2 ; and hence, finally $\widetilde{y}_{e_3}$. (That this method is explained in geometrical terms should not be taken to imply that a paper and pencil construction is recommended; corresponding numerical techniques may be devised to suit the nature of the relations represented by $C_1, C_2 \dots C_6$ in particular cases).

Determination of the matrix H_2

(i) Indirect Control

Expressions for the elements of the matrix H_2 may be determined by first finding the derivatives of the "eliminated variables" with respect to the members of the set S_2 , and using these to find the second derivatives by total differentiation. Although straightforward, this procedure would be extremely

tedious. Even in the indirectly cooled case, much labour is involved, and the following procedure is less troublesome:

For the i th stage we have:

$$t_i = \int_{y_{a_i}}^{y_{e_i}} \frac{dy}{V(y, h_i)}$$

so that t_i may be considered formally as a function of y_{e_i} , y_{a_i} and h_i :

$$t_i = L_i(y_{e_i}, y_{a_i}, h_i) \quad (5.64)$$

Let us drop the suffix for the moment. The sets of first and second derivatives of L with respect to its arguments may easily be obtained and used to get the corresponding sets of 1st. and second derivatives of:

$$y_e = F(h, t, y_a) \quad (5.65)$$

With respect to its arguments using implicit differentiation, using also the relations

$$\frac{\partial F}{\partial h_i} = \frac{\partial L}{\partial h_i} = 0$$

(which hold for a maximum/minimum) to simplify the expressions.

We obtain:

$$\left. \begin{aligned} \frac{\partial F}{\partial t} &= V_e ; \quad \frac{\partial F}{\partial y_a} = \frac{V_e}{V_a} ; \quad \frac{\partial F}{\partial h} = V_e t' \\ \frac{\partial^2 F}{\partial t^2} &= V_e \frac{\partial V_e}{\partial y} ; \quad \frac{\partial^2 F}{\partial y_a \partial t} = \frac{V_e}{V_a} \frac{\partial V_e}{\partial y} \\ \frac{\partial^2 F}{\partial h \partial t} &= \frac{\partial V_e}{\partial h} ; \quad \frac{\partial^2 F}{\partial y_a^2} = \frac{V_e}{V_a^2} \left(\frac{\partial V_e}{\partial y} - \frac{\partial V_a}{\partial y} \right) \\ \frac{\partial^2 F}{\partial h \partial y_a} &= \frac{1}{V_a} \left[\frac{\partial V_e}{\partial h} - \frac{V_e}{V_a} \frac{\partial V_a}{\partial h} \right] ; \quad \frac{\partial^2 F}{\partial h^2} = V_e t'' \end{aligned} \right\} \quad (5.66)$$

(See also (5.49))

Next, the stages are connected together, writing:

$$\begin{aligned} y_{e_N} &= F_N(h_N, t_N, y_{a_N}) \\ &= F_N(h_N, t_N, F_{N-1}(h_{N-1}, t_{N-1}, F_{N-2}(\dots h_2, t_2, F_1(h_1, t_1, y_{a_1}))) \dots) \end{aligned} \quad (5.67)$$

That is to say y_{e_N} , is implicitly a function of $h_1, h_2, \dots, h_N, t_1, t_2, \dots, t_N$, (y_{a_1} will be considered a constant). If we then write:

$$y_{e_N} = y_{e_N}(h_1 \dots h_N, t_1 \dots t_N) \quad (5.68)$$

we may express the first and second derivatives of (5.68) in terms of the quantities in (5.66). We note that:

$$\frac{\partial y_{e_N}}{\partial t_p} = \frac{\partial F_p}{\partial t_p} \prod_{i=p+1}^{i=N} \frac{\partial F_i}{\partial y_{a_i}} ; \quad \frac{\partial y_{e_N}}{\partial h_p} = \frac{\partial F_p}{\partial h_p} \prod_{i=p+1}^{i=N} \frac{\partial F_i}{\partial y_{a_i}} \quad (5.69)$$

and in particular that by interchanging t and h in one of these equations, the other is obtained.

By differentiating the first of (5.69) with respect to t_q FOR $q \geq p$, we obtain:

$$\frac{\partial^2 y_{eN}}{\partial t_q \partial t_p} = \frac{\partial F_p}{\partial t_p} \prod_{i=p+1}^{i=N} \frac{\partial F_i}{\partial y_{a_i}} \left[\frac{\frac{\partial^2 F_q}{\partial t_q \partial y_{a_q}}}{\frac{\partial F_q}{\partial y_{a_q}}} + \frac{\partial F_q}{\partial t_q} \left\{ \frac{\frac{\partial^2 F_{q+r}}{\partial y_{a_{q+r}}^2}}{\frac{\partial F_{q+r}}{\partial y_{a_{q+r}}}} \right\}_{r=1}^{r=N-q} \prod_{S=1}^{S=r-1} \frac{\partial F_{q+s}}{\partial y_{a_{q+s}}} \right] \quad (5.70)$$

[(5.70) will¹ give the WRONG result if $q \neq p$). If $q < p$ the corresponding derivatives may be found by interchanging p and q on the right hand side of 5.70)].

If $p=q$,

$$\frac{\partial^2 y_{eN}}{\partial t_p^2} = \prod_{i=p+1}^{i=N} \frac{\partial F_i}{\partial y_{a_i}} \left[\frac{\partial^2 F_p}{\partial t_p^2} + \left(\frac{\partial F_p}{\partial t_p} \right)^2 \left\{ \frac{\frac{\partial^2 F_{p+r}}{\partial y_{a_{p+r}}^2}}{\frac{\partial F_{p+r}}{\partial y_{a_{p+r}}}} \right\}_{r=1}^{r=N-p} \prod_{S=p+1}^{S=p+r-1} \frac{\partial F_S}{\partial y_{a_S}} \right] \quad (5.71)$$

Similarly for $q > p$:

$$\frac{\partial^2 y_{eN}}{\partial t_q \partial t_p} = \frac{\partial F_p}{\partial t_p} \prod_{i=p+1}^{i=N} \frac{\partial F_i}{\partial y_{a_i}} \left[\frac{\frac{\partial^2 F_q}{\partial t_q \partial y_{a_q}}}{\frac{\partial F_q}{\partial y_{a_q}}} + \frac{\partial F_q}{\partial t_q} \left\{ \frac{\frac{\partial^2 F_{q+r}}{\partial y_{a_{q+r}}^2}}{\frac{\partial F_{q+r}}{\partial y_{a_{q+r}}}} \right\}_{r=1}^{r=N-q} \prod_{S=1}^{S=r-1} \frac{\partial F_{q+s}}{\partial y_{a_{q+s}}} \right] \quad (5.72)$$

1. The convention $\sum_{j=\alpha}^{j=\beta} a_j = 0$; $\prod_{j=\alpha}^{j=\beta} a_j = 1$ for $\beta < \alpha$ is used here as elsewhere.

The corresponding formulae for $p < q$ may be obtained by simultaneous interchange of h and t on both sides of (5.72).

For $p=q$, we get:

$$\frac{\partial^2 y_{eN}}{\partial h_p \partial t_p} = \prod_{i=p+1}^{i=N} \frac{\partial F_i}{\partial y_{a_i}} \left[\frac{\partial^2 F}{\partial h_p \partial t_p} + \frac{\partial F_p}{\partial t_p} \cdot \frac{\partial F_p}{\partial h_p} \sum_{r=1}^{r=N-p} \frac{\frac{\partial^2 F_{h+r}}{\partial y_{a_{p+r}}^2}}{\frac{\partial F_{p+r}}{\partial y_{a_{p+r}}}} \prod_{s=p+1}^{s=p+r-1} \frac{\partial F_s}{\partial y_{a_s}} \right] \quad (5.73)$$

Finally $\frac{\partial^2 y_{eN}}{\partial h_p \partial h_q}$ may be obtained from (5.70) or (5.71) by interchanging h and t on both sides.

In this way, (if one notes that $m_i = wt_i$ where w is constant) it is easy to see how to get the elements of H_2 . For a two stage reactor the expressions are quite simple, and are given in the following table (the corresponding variables from the set S_2 have been written across the top and down the left hand side for convenience):

Elements of H_2 for a two stage reactor with indirect intercooling.

	m_1	m_2	h_1	h_2
m_1	$\frac{V_{e2}}{\omega^2} \left\{ \frac{\partial V_{e1}}{\partial y} + \frac{\partial V_{e2}}{\partial y} - \frac{\partial V_{a2}}{\partial y} \right\}$	$\frac{V_{e2}}{\omega^2} \frac{\partial V_{e2}}{\partial y}$	$\frac{1}{\omega} \cdot \frac{V_{e2}}{V_{a2}} \frac{\partial V_{e1}}{\partial h_1}$	$\frac{1}{\omega} \left\{ \frac{\partial V_{e2}}{\partial h_2} - \frac{V_{e2}}{V_{a2}} \frac{\partial V_{a2}}{\partial h_2} \right\}$
m_2		$\frac{V_{e2}}{\omega^2} \frac{\partial V_{e2}}{\partial y}$	0	$\frac{1}{\omega} \frac{\partial V_{e2}}{\partial h_2}$
h_1			$V_{e2} t_1''$	0
h_2				$V_{e2} t_2''$

(The elements below the principal diagonal may be found by symmetry, of course).

If A^* is the matrix:

$$\begin{bmatrix} 1 & 0 & 0 \\ -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

then for y_{e2} to be a maximum with respect to variations of h_1 , h_2 , m_1 , m_2 , (the latter constrained by: $m_1 + m_2 = \text{constant}$), the matrix $\tilde{H}_2 = A^{*T} H_2 A^*$ must be negative definite. It is easy to verify from the

relations given that $\tilde{H}_2$ is negative definite if and only if the corresponding matrix H_1 is positive definite.

(ii) Direct Control.

The reader will appreciate that some of the elements of the matrix H_2 in this case will be exceptionally complicated - so much so in fact that even having derived them, the problem of checking that a computer had been programmed correctly to evaluate them would be far from trivial.

Some progress is being made towards computer differentiation, (not numerical differentiation), i.e. the computer uses the rules for differentiating elementary functions together with routines for calculating these functions to compute complex derivatives. There are many difficulties still to be overcome (such as programming the machine to cancel terms, etc.). (Ref. 75).

Such a method might be applied in this case.

Appendix to Chapter V

Part I.

Derivation of $\frac{\partial W}{\partial T_{e_i}}$; $\frac{\partial W}{\partial h_j}$; Proof of equations (5.43, 5.44, 5.45)

By definition:

$$W = W(T_{e_1}, T_{e_2} \dots T_{e_N}, h_1, h_2 \dots h_{N-1}) = \sum_{i=1}^{i=N} t_i w_i ; \quad (A5.1)$$

$$y \equiv y(h, T); \quad y_T = \left(\frac{\partial y}{\partial T}\right)_h; \quad y_h = \left(\frac{\partial y}{\partial h}\right)_T \dots \dots \dots; \quad (5.34)$$

$$t_i = \int_{T_{a_i}}^{T_{e_i}} \frac{y_T dT}{v(y, T)}; \quad t'_i = - \int_{T_{a_i}}^{T_{e_i}} \frac{y_h \frac{\partial v}{\partial T} dT}{v^2} \quad ; \quad (5.37)$$

(where the integrals are taken over the path $y=y(h_i, T)$).

It will be convenient to define in addition:

$$r(h, T) \equiv \frac{y_T}{v(y(h, T), T)} \quad (A5.2a)$$

and

$$L'_i = \int_{T_{a_i}}^{T_{e_i}} \left[\frac{\partial r}{\partial h} \right]_{h=h_i} \cdot dT \quad (A5.2b)$$

We will require:

$$\frac{dh_N}{dT_{e_N}}; \quad \frac{\partial w_j}{\partial h_i}; \quad \frac{\partial w_j}{\partial T_{e_i}}; \quad \frac{\partial y_{a_j}}{\partial h_i}; \quad \frac{\partial y_{e_j}}{\partial h_i}; \quad \frac{\partial T_{a_i}}{\partial h_i}; \quad \frac{\partial y_{a_j}}{\partial T_{e_i}}; \quad \frac{\partial T_{a_j}}{\partial T_{e_i}}.$$

Note that h_N is determined by T_{e_N} alone, there being only one h_N which will allow y_{e_N} to satisfy its boundary condition for each T_{e_N} . It follows that:

$$\frac{dh_N}{dT_{e_N}} = - \frac{y_T(e_N)}{y_h(e_N)} \quad (A5.3)$$

We recall that:

$$\frac{w_{j+1}}{w_j} = \frac{h_j - h_m}{h_{j+1} - h_m} \quad ; \quad j=1, 2 \dots N-1 \quad ; \quad 5.2$$

$$w_j = w_N \left\{ \frac{h_N - h_m}{h_j - h_m} \right\} \quad ; \quad j=1, 2 \dots N-1 \quad ; \quad 5.3$$

$$\text{and } \frac{w_{j+1}}{w_j} = \frac{y_{e_j} - y_m}{y_{a_{j+1}} - y_m} \quad ; \quad j=1, 2 \dots N-1 \quad ; \quad 5.4$$

Differentiating (5.3) with respect to h_i , ($i \neq N$) and using 5.3 again:

$$\frac{\partial w_j}{\partial h_i} = - \frac{w_j \delta_{ij}}{h_j - h_m} \quad ; \quad (A5.4)$$

Differentiating (5.3) with respect to h_N , and using A5.3:

$$\frac{\partial w_j}{\partial T_{e_i}} = - \frac{w_N}{h_j - h_m} \cdot \frac{y_T(e_N)}{y_h(e_N)} \cdot \delta_{iN} ; j \neq N; \quad (A5.5)$$

In calculating $\frac{\partial y_{a_j}}{\partial h_i}$, we note that changing h_i (the remaining h_j and T_{e_j} being kept constant) affects (of the y_{a_j}) only y_{a_i} (except for $i=1$ when it is fixed by the boundary condition), and $y_{a_{i+1}}$. We will derive

first $\frac{\partial y_{a_i}}{\partial h_i}$, $i \neq 1$, noting that $y_{e_{i-1}}$ is fixed because $T_{e_{i-1}}$ and h_{i-1} are fixed, and w_{i-1} is also fixed, we put $j=i-1$ in (5.4), and differentiate with respect to w_i :

$$dy_{a_i} = - (y_{e_{i-1}} - y_m) w_{i-1} \cdot \frac{dw_i}{w_i^2}$$

so that with (A5.4) for $i=j$, and using (5.2) for

$$j=i-1, \quad \frac{\partial y_{a_i}}{\partial h_i} = \frac{y_{e_{i-1}} - y_m}{h_{i-1} - h_m} ; i \neq 1 \quad (A5.6)$$

$$\text{From (5.34) : } \frac{\partial y_{e_j}}{\partial h_i} = \delta_{ij} y_h(e_j) \quad (A5.7)$$

We can use this to derive $\frac{\partial y_{a_{i+1}}}{\partial h_i}$. Rearranging (5.4) and varying w_i , y_{e_i} , and $y_{a_{i+1}}$,

$$w_{i+1} dy_{a_{i+1}} = w_i dy_{e_i} + (y_{e_i} - y_m) dw_i$$

Hence, using (A5.4) and (A5.7) for $i=j$, we get:

$$\frac{\partial y_{a_{i+1}}}{\partial h_i} = \frac{w_i}{w_{i+1}} y_h(e_i) - \frac{y_{e_i} - y_m}{h_i - h_m} \cdot \frac{w_i}{w_{i+1}} \quad ; \quad (A5.8)$$

which can be put together with (A5.6) resulting in:

$$\frac{\partial y_{a_j}}{\partial h_i} = \delta_{ij} (1 - \delta_{ij}) \left(\frac{y_{e_i} - y_m}{h_i - h_m} \right) + \delta_{i+1,j} \left(\frac{w_i}{w_{i+1}} \right) \left(y_h(e_i) - \frac{y_{e_i} - y_m}{h_i - h_m} \right) \quad (A5.9)$$

To derive $\frac{\partial T_{a_j}}{\partial h_i}$, we note as above that we need only consider $j=i$ and $j=i+1$. From (A5.8) we obtain:

$$\frac{\partial T_{a_{i+1}}}{\partial h_i} = \frac{1}{y_T(a_{i+1})} \left\{ y_h(e_i) - \frac{y_{e_i} - y_m}{h_i - h_m} \right\} \frac{w_i}{w_{i+1}}$$

For $j=i$, we may proceed in the same way, using (A5.6) (except for the underlined term which must be added):

$$\frac{\partial T_{a_i}}{\partial h_i} = \frac{(1 - \delta_{1i})}{y_T(a_i)} \cdot \frac{(y_{e_{i-1}} - y_m)}{h_{i-1} - h_m} - \frac{y_h(a_i)}{y_T(a_i)} \quad ; \quad (A5.10)$$

Putting these last two equations together:

$$\frac{\partial T_{a_j}}{\partial h_i} = \frac{1}{y_T(a_j)} \left\{ \delta_{i+1,j} \left(y_h(e_i) - \frac{y_{e_i} - y_m}{h_i - h_m} \right) \frac{w_i}{w_j} \right. \\ \left. + \delta_{ij} \left[(1 - \delta_{1i}) \left(\frac{y_{e_{i-1}} - y_m}{h_{i-1} - h_m} \right) - y_h(a_i) \right] \right\} \quad (A5.11)$$

If T_{e_i} is varied, $i \neq N$, then y_{e_i} changes as well, and consequently $y_{a_{i+1}}$, so that from (5.4), we get:

$$\frac{\partial y_{a_{i+1}}}{\partial T_{e_i}} = \frac{y_T(e_i) w_i}{w_{i+1}} \quad i \neq N$$

hence

$$\frac{\partial T_{a_{i+1}}}{\partial T_{e_i}} = \left\{ \frac{w_i}{w_{i+1}} \right\} \left\{ \frac{y_T(e_i)}{y_T(a_{i+1})} \right\} \quad i \neq N$$

so that::

$$\frac{\partial T_{a_j}}{\partial T_{e_i}} = \delta_{i+1,j} \cdot \frac{w_i}{w_j} \cdot \frac{y_T(e_i)}{y_T(a_j)} \quad ; \quad i \neq N \quad ; \quad (A5.12)$$

If $i=N$, varying T_{e_i} varies h_N , which in turn varies y_{a_N} , so, using (A5.10) and (A5.3):

$$\frac{\partial T_{a_N}}{\partial T_{e_N}} = - \frac{y_T(e_N)}{y_h(e_N)} \left\{ \frac{(1-\delta_{IN})}{y_T(a_N)} \times \frac{(y_{e_{N-1}} - y_m)}{(h_{N-1} - h_m)} - \frac{y_h(a_N)}{y_T(a_N)} \right\} \quad (A5.13)$$

Using relations (5.37), (A5.1), (A5.2), (A5.4), (A5.11),

we may therefore write:

$$\begin{aligned} \frac{\partial W}{\partial h_i} = & \omega_i L'_i - \frac{\omega_i t_i}{h_i - h_m} - \frac{\omega_i t_{i+1}}{y_T(a_{i+1})} \left\{ y_{h(e_i)} - \frac{y_{e_i} - y_m}{h_i - h_m} \right\} \\ & - \frac{\omega_i t_{a_i}}{y_T(a_i)} \left\{ \frac{(1-\delta_{ii})(y_{e_{i-1}} - y_m)}{h_{i-1} - h_m} - y_{h(a_i)} \right\} \end{aligned} \quad (A5.14)$$

And, using relations (5.37), (A5.1), (A5.2a), (A5.12), (A5.5), for $i \neq N$

$$\frac{\partial W}{\partial T_{e_i}} = \omega_i y_T(e_i) \left\{ \frac{1}{v_{e_i}} - \frac{1}{v_{a_{i+1}}} \right\}; \quad i \neq N \quad (A5.15)$$

Equation (5.43) is thus proven.

Similarly:

$$\frac{\partial W}{\partial T_{e_N}} = \omega_N t_N - \frac{\omega_N y_T(e_N)}{y_h(e_N)} \left\{ \sum_{j=1}^{N-1} \frac{t_j}{h_j - h_m} + L'_N + \frac{y_h(a_N)}{v_{a_N}} - \frac{(1-\delta_{IN})(y_m - y_{e_{N-1}})}{v_{a_N}(h_m - h_{N-1})} \right\} \quad (A5.16)$$

In order to establish equations 5.44 and 5.45 we first prove a simple lemma:

$$L'_i = \frac{y_h(e_i)}{v_{e_i}} - \frac{y_h(a_i)}{v_{a_i}} - t'_i \quad (A5.17)$$

we will drop the suffix i in the proof:

Note that:

$$\frac{\partial r}{\partial h} = \frac{v y_{hT} - y_T y_h \frac{\partial v}{\partial y}}{v^2}$$

But $y_T \frac{\partial v}{\partial y} = \frac{dv}{dT} - \frac{\partial v}{\partial T}$ where the total derivative is understood to be the limit of $\Delta v / \Delta T$ along the constant h reaction path. We may then use (A5.2b) and write:

$$L' = \int_{T_a}^{T_e} \left\{ \frac{v y_{hT} - y_h \frac{dv}{dT} + \frac{\partial v}{\partial T} y_h}{v^2} \right\} dT$$

Integrating the middle term by parts:

$$- \int_{T_a}^{T_e} \frac{y_R \frac{dv}{dT}}{v^2} dT = \left[\frac{y_R}{v} \right]_{T_a}^{T_e} - \int_{T_a}^{T_e} \frac{v y_{RT}}{v^2} dT$$

hence

$$L' = \frac{y_R(e)}{v_e} - \frac{y_R(a)}{v_a} + \int_{T_a}^{T_e} \frac{y_R}{v^2} \cdot \frac{\partial v}{\partial T} dT$$

so that, using 5.37, the lemma follows.

If we substitute the right hand side of (A5.17) for L'_i in (A5.14) and compare with (5.16), then using (5.2) and (5.4), (5.45) can be seen to be true. Similarly, from (5.2), (5.4), (A5.16), (A5.17) and (5.16); (5.44) follows¹.

1. The convention $\sum_{i=j}^{i=K} a_i = 0$ for $K < j$ is used.

Part II

We will prove equations 5.63a and b and the assertion about their connection with equations (5.18), (5.21).

The derivatives of $y_{e_N} = F_N(t_N, h_N, y_{a_N})$ with respect to the variables $h_1, h_2 \dots h_N; m_1, m_2 \dots m_N$ will be found, taking into account the following restraints:

$$\begin{aligned} y_{e_j} - F_j(t_j, h_j, y_{a_j}) &= 0, \quad j=1, 2 \dots N-1 \\ t_j - \frac{m_j}{w_j} &= 0, \quad j=1, 2 \dots N \\ w_j - w_N \left\{ \frac{h_N - h_m}{h_j - h_m} \right\} &= 0, \quad j=1, 2 \dots N-1 \end{aligned} \quad (A5.19)$$

$$w_{j+1}(y_{a_{j+1}} - y_m) - w_j(y_{e_j} - y_m) = 0, \quad j=1, 2 \dots N-1$$

To do this we will use Lagrange's method with multipliers p'_j, q'_j, r'_j, S'_j , and function Z :

$$\begin{aligned} Z = & F_N(t_N, h_N, y_{a_N}) - \sum_{j=1}^{N-1} p'_j (y_{e_j} - F_j) - \sum_{j=1}^N q'_j (t_j - \frac{m_j}{w_j}) \\ & - \sum_{j=1}^{N-1} r'_j (w_j - w_N \left\{ \frac{h_N - h_m}{h_j - h_m} \right\}) \\ & - \sum_{j=1}^{N-1} S'_j (w_{j+1} \{y_{a_{j+1}} - y_m\} - w_j \{y_{e_j} - y_m\}) \end{aligned} \quad (A5.20)$$

The multipliers may be determined by differentiating

Z partially with respect to the variables to be eliminated, i.e. y_{e_K} , y_{a_K} , w_K , and t_K , and equating to zero. (In differentiating (A.50) we may make use of some of the relations 5.66), we obtain:

$$0 = -p'_K + S'_K w_K \quad ; K=1,2 \dots N-1 ; \quad (A5.21)$$

$$0 = \frac{\delta_{KN} v_{e_N}}{v_{a_N}} + (1 - \delta_{KN}) p'_K \frac{v_{e_K}}{v_{a_K}} - S'_{K-1} w_K ; K=2 \dots N \quad (A5.22)$$

$$0 = -\frac{m_K q'_K}{\omega_K^2} - r'_K - S'_{K-1} (y_{a_K} - y_m) (1 - \delta_{K1}) + (y_{e_K} - y_m) S'_K ; \quad (A5.23)$$

$K=1,2, \dots, N-1.$

$$0 = \delta_{KN} v_{e_N} + p'_K v_{e_K} (1 - \delta_{KN}) - q'_K ; K=1,2 \dots N ; (A5.24)$$

These four sets of equations are easily solved, giving:

$$S'_K = \frac{1}{w_N} \prod_{j=K+1}^{j=N} \frac{v_{e_j}}{v_{a_j}} ; A5.25 ; \quad p'_K = \frac{w_K}{w_N} \prod_{j=K+1}^{j=N} \left\{ \frac{v_{e_j}}{v_{a_j}} \right\} \dots ; (A5.26)$$

$$q'_K = \frac{w_K}{w_N} v_{e_K} (1 - \delta_{KN}) \prod_{j=K+1}^{j=N} \left\{ \frac{v_{e_j}}{v_{a_j}} \right\} + \delta_{KN} v_{e_N} \quad ; (A5.27)$$

$$r'_K = \frac{1}{w_N} \prod_{j=K+1}^{j=N} \frac{v_{e_j}}{v_{a_j}} [y_{e_K} - y_m - \frac{m_K}{w_K} v_{e_K} (1 - \delta_{KN}) - (y_{a_K} - y_m) (1 - \delta_{1K}) \frac{v_{e_K}}{v_{a_K}}] ; \quad (A5.28)$$

If Z is differentiated partially with respect to h_K or m_K and the above expressions for the multipliers are used, we obtain the desired $\frac{\partial y_{e_N}}{\partial h_K}$, $\frac{\partial y_{e_N}}{\partial m_K}$:

$$\text{Now: } \frac{\partial Z}{\partial h_K} = \delta_{KN} V_{e_N} t'_N + (1 - \delta_{KN}) p'_K V_{e_K} t'_K + \omega_N \delta_{KN} \sum_{j=1}^{N-1} \frac{\tau'_j}{p_j - p_m} - \frac{\omega_K \tau'_K}{p_K - p_m} (1 - \delta_{KN}) \quad (\text{A.5.29})$$

Using (A5.26) and (A5.28), it is easy to see that for $K \neq N$, the above expression will vanish if and only if:

$$V_{e_K} t'_K - \frac{1}{p_K - p_m} \left\{ -t_K V_{e_K} - \frac{(y_{a_K} - y_m)(1 - \delta_{iK}) V_{e_K}}{V_{a_K}} + y_{e_K} - y_m \right\} = 0 \quad (\text{A.5.30})$$

Putting $K=i$ we get 5.63a.

$$\text{Similarly, } \frac{\partial Z}{\partial h_N} = V_{e_N} t'_N + \sum_{i=1}^{N-1} \frac{1}{(h_i - h_m)} \prod_{j=i+1}^{j=N} \frac{V_{e_j}}{V_{a_j}} \left\{ -t_i V_{e_i} - (y_{a_i} - y_m)(1 - \delta_{ii}) \frac{V_{e_i}}{V_{a_i}} + y_{e_i} - y_m \right\}$$

Equating to zero and using (A5.30) we get:

$$V_{e_N} t'_N + \sum_{i=1}^{N-1} \prod_{j=i+1}^{j=N} \left\{ \frac{V_{e_j}}{V_{a_j}} \right\} V_{e_i} t'_i = 0 \quad (5.63b)$$

For completeness we will also obtain the derivatives

with respect to m_K and consider the case $\sum m_i$ constant:

$$\frac{\partial Z}{\partial m_K} = \sum_{j=1}^N \frac{q'_j \delta_{jK}}{w_j} = \frac{q'_K}{w_K}$$

$$\therefore \frac{\partial Z}{\partial m_K} = \frac{1}{w_N} \left\{ v_{e_K} (1 - \delta_{KN}) \prod_{j=K+1}^N \left\{ \frac{v_{e_j}}{v_{a_j}} \right\} + \delta_{KN} v_{e_N} \right\} \quad (A5.31)$$

If $\sum_{i=1}^N m_i - M = 0$ where M is constant, we may obtain

the optimum condition equations by introducing another Lagrange multiplier, μ , and writing:

$$Z' = Z - \mu \left(\sum_{i=1}^N m_i - M \right)$$

Using (A5.31):

$$\therefore 0 = \frac{\partial Z'}{\partial m_N} = \frac{v_{e_N}}{w_N} - \mu \therefore \mu = \frac{v_{e_N}}{w_N}$$

so that for $K \neq N$,

$$0 = \frac{\partial Z'}{\partial m_K} = \frac{v_{e_K}}{w_N} \prod_{j=K+1}^N \frac{v_{e_j}}{v_{a_j}} - \frac{v_{e_N}}{w_N}$$

$$\therefore V_{e_{N-1}} = V_{a_N} ; V_{e_{N-2}} = V_{a_{N-1}}, \text{ etc.}$$

$$\text{so } V_{e_{K-1}} = V_{a_K} ; \quad K=2,3 \dots N.$$

(The remaining assertions follow immediately).

TABLE 5.1.

TWO STAGE DIRECTLY CONTROLLED ADIABATIC CASCADE

Note: $a, -b = a \times 10^{-b}$

COLD SHOT TEMPERATURE DEGREES KELVIN		T_{a1}	$\log\left(\frac{y_{e2}}{1-y_{e2}}\right)$	$\log M$	$\frac{w_1 t_1}{M}$	w_1	T_{e1}
600	FIRST	585	1.490, +0	8.415, -1	0.956	0.655	732
		590	1.438, +0	4.939, -1	0.800	0.333	742
		600	1.411, +0	2.634, -1	0.582	0.259	752
		800	5.917, -1	-2.644, +0	0.212	0.653	904
		1000	-2.166, -1	-4.942, +0	0.211	0.823	1040
		1150	-7.404, -1	-6.469, +0	0.194	0.864	1165
	SECOND	581	1.510, +0	7.458, -1	0.622	0.714	703
		589	1.439, +0	5.948, -1	0.442	0.423	727
		700	1.063, +0	-1.139, -1	0.180	0.446	830
		900	1.845, -1	-1.551, +0	0.217	0.714	965
		1100	-5.606, -1	-2.913, +0	0.208	0.816	1118
		1250	-1.046, +0	-3.853, +0	0.193	0.835	1256
300	THIRD	600	1.359, +0	7.523, -1	0.163	0.349	706
		800	6.246, -1	2.226, -2	0.165	0.539	889
		1000	-2.299, -1	-9.952, -1	0.214	0.746	1029
		1200	-9.410, -1	-1.988, +0	0.198	0.799	1206
	FIRST	625	2.061, +0	7.034, -1	0.141	0.697	775
		750	1.003, +0	-1.738, +0	0.178	0.790	871
		950	-6.629, -3	-4.370, +0	0.224	0.879	1005
		1200	-8.960, -1	-6.935, +0	0.201	0.910	1211
	SECOND	625	2.089, +0	1.009, +0	0.124	0.681	773
		750	1.038, +0	-2.977, -1	0.190	0.766	868
		950	1.651, -2	-1.868, +0	0.245	0.852	1000
		1200	-8.838, -1	-3.541, +0	0.213	0.883	1209
	THIRD	650	1.976, +0	1.066, +0	0.125	0.648	789
		775	9.122, -1	2.512, -1	0.203	0.745	878
		950	-3.281, -3	-7.155, -1	0.252	0.830	993
		1200	-9.298, -1	-1.975, +0	0.217	0.861	1207

TABLE 5.2.

THREE STAGE DIRECTLY CONTROLLED ADIABATIC CASCADE

Note: $a, -b = a \times 10^{-b}$

Note: $a_1 = 2 - 2X_1$										
		T _{a1}	$\log\left(\frac{y_{e3}}{1-y_{e3}}\right)$	logM	$\frac{w_1 t_1}{M}$	$\frac{w_2 t_2}{M}$	w ₁	w ₂	T _{e1}	T _{e2}
COLD SHOT TEMPERATURE DEGREES KELVIN	600	RATE FUNCTION PARAMETERS								
		FIRST								
		600	1.411, +0	4.242, -2	0.372	0.242	0.100	0.385	752	751
		700	1.192, +0	-1.068, +0	0.095	0.245	0.286	0.600	835	791
		800	7.554, -1	-2.315, +0	0.074	0.222	0.490	0.750	904	854
		900	3.165, -1	-3.498, +0	0.079	0.233	0.631	0.830	970	919
		1000	-7.519, -2	-4.581, +0	0.081	0.240	0.722	0.877	1040	986
		SECOND								
		600	1.402, +0	4.683, -1	0.164	0.198	0.155	0.465	742	738
		750	1.022, +0	-2.322, -1	0.066	0.186	0.333	0.625	866	808
		900	3.831, -1	-1.247, +0	0.084	0.214	0.555	0.778	965	902
		1000	-1.247, -2	-1.923, +0	0.088	0.230	0.652	0.836	1036	968
		THIRD								
		600	1.366, +0	7.561, -1	0.077	0.119	0.167	0.478	706	700
		800	8.830, -1	2.704, -1	0.055	0.141	0.317	0.588	889	813
		900	4.297, -1	-2.033, -1	0.077	0.181	0.481	0.718	955	881
		1000	7.472, -3	-7.008, -1	0.087	0.211	0.596	0.798	1029	948
		300	RATE FUNCTION PARAMETERS							
FIRST										
675	1.945, +0		2.277, -1	0.032	0.142	0.632	0.857	816	730	
800	9.390, -1		-2.034, +0	0.059	0.207	0.727	0.889	905	839	
900	3.827, -1		-3.395, +0	0.080	0.246	0.786	0.911	971	913	
1000	-4.763, -2		-4.537, +0	0.086	0.260	0.828	0.929	1041	983	
SECOND										
675	2.097, +0		9.487, -1	0.038	0.134	0.585	0.816	814	719	
775	1.245, +0		-8.879, -2	0.064	0.183	0.660	0.847	885	805	
875	6.052, -1		-9.609, -1	0.091	0.232	0.724	0.877	950	879	
975	1.297, -1		-1.706, +0	0.101	0.257	0.773	0.901	1018	948	
THIRD										
700	2.148, +0		1.157, +0	0.044	0.116	0.525	0.762	827	718	
825	1.025, +0		3.235, -1	0.081	0.185	0.639	0.824	910	824	
925	4.023, -1		-2.668, -1	0.105	0.234	0.710	0.865	975	895	
1000	5.059, -2		-6.649, -1	0.107	0.251	0.747	0.885	1030	945	

TABLE 5.3.

FOUR STAGE DIRECTLY CONTROLLED ADIABATIC CASCADE

Note: $a, -b = a \times 10^{-b}$

COLD SHOT TEMPERATURE DEGREES KELVIN														
600														
RATE FUNCTION PARAMETERS														
FIRST														
	T _{a1}	log($\frac{ye_4}{1-ye_4}$)	logM	$\frac{w_1 t_1}{M}$	$\frac{w_2 t_2}{M}$	$\frac{w_3 t_3}{M}$	w ₁	w ₂	w ₃	T _{e1}	T _{e2}	T _{e3}		
	600	1.411, +0	-1.014, -1	0.247	0.160	0.206	0.047	0.183	0.475	752	751	750		
	700	1.260, +0	-9.408, -1	0.048	0.122	0.231	0.191	0.402	0.669	835	791	773		
	800	8.643, -1	-2.071, +0	0.034	0.101	0.209	0.392	0.600	0.800	904	854	827		
	900	4.251, -1	-3.234, +0	0.037	0.110	0.216	0.546	0.718	0.865	970	919	891		
	1000	2.714, -2	-4.314, +0	0.039	0.117	0.224	0.652	0.792	0.903	1040	986	957		
SECOND														
	600	1.403, +0	4.492, -1	0.094	0.114	0.173	0.085	0.255	0.550	742	737	734		
	700	1.272, +0	1.583, -1	0.033	0.093	0.178	0.153	0.343	0.620	830	779	757		
	800	9.476, -1	-3.665, -1	0.033	0.090	0.172	0.304	0.502	0.731	899	839	806		
	900	5.295, -1	-1.022, +0	0.040	0.103	0.188	0.450	0.631	0.811	965	902	867		
	1000	1.272, -1	-1.689, +0	0.044	0.116	0.205	0.563	0.721	0.863	1036	968	930		
THIRD														
	600	1.370, +0	7.595, -1	0.043	0.066	0.104	0.094	0.268	0.560	706	700	695		
	700	1.294, +0	6.704, -1	0.017	0.053	0.113	0.079	0.226	0.515	816	747	720		
	900	6.217, -1	-1.618, -3	0.036	0.084	0.147	0.357	0.532	0.741	955	881	836		
	1000	1.873, -1	-4.870, -1	0.044	0.106	0.179	0.489	0.655	0.821	1029	948	903		
300														
RATE FUNCTION PARAMETERS														
FIRST														
	700	1.935, +0	-1.578, -1	0.012	0.051	0.147	0.594	0.786	0.910	835	753	714		
	825	9.511, -1	-2.048, +0	0.027	0.089	0.204	0.688	0.827	0.925	921	859	823		
	900	5.192, -1	-3.084, +0	0.036	0.112	0.230	0.735	0.851	0.934	971	913	881		
	1000	6.570, -2	-4.251, +0	0.042	0.128	0.246	0.783	0.879	0.946	1041	983	952		
SECOND														
	725	1.966, +0	7.735, -1	0.019	0.059	0.132	0.545	0.727	0.874	851	764	713		
	825	1.154, +0	-2.263, -1	0.034	0.090	0.177	0.620	0.771	0.893	917	844	798		
	975	2.968, -1	-1.448, +0	0.051	0.131	0.229	0.712	0.830	0.921	1018	948	907		
	1000	1.864, -1	-1.626, +0	0.052	0.133	0.233	0.724	0.837	0.925	1037	965	924		
THIRD														
	750	2.125, +0	1.133, +0	0.023	0.056	0.106	0.471	0.647	0.824	861	763	697		
	875	9.981, -1	2.917, -1	0.044	0.098	0.166	0.589	0.735	0.869	942	860	807		
	975	3.814, -1	-2.966, -1	0.056	0.128	0.208	0.662	0.791	0.899	1011	929	880		
	1050	4.178, -2	-6.814, -1	0.055	0.136	0.225	0.698	0.818	0.914	1071	980	930		

TABLE 5.4.

TWO STAGE INDIRECTLY CONTROLLED ADIABATIC CASCADE

Note: $a, -b = a \times 10^{-b}$

Note: $a_2 = 2.5 \times 10^{-3}$

RATE FUNCTION PARAMETERS		T_{a1}	$\log\left(\frac{y_{o2}}{1-y_{e2}}\right)$	$\log M$	t_1/M	T_{a2}	T_{e1}
FIRST	650	2.146, +0	4.986, -1	0.090	661.8	796	
	775	9.662, -1	-1.991, +0	0.172	772.1	888	
	950	2.651, -2	-4.324, +0	0.240	915.4	1005	
	1225	-9.615, -1	-7.147, +0	0.224	1145	1234	
SECOND	650	2.123, +0	8.255, -1	0.165	658.9	795	
	775	1.007, +0	-4.454, -1	0.234	756.0	886	
	950	5.753, -2	-1.830, +0	0.284	890.8	1002	
	1225	-9.410, -1	-3.666, +0	0.244	1115	1233	
THIRD	650	2.169, +0	1.052, +0	0.243	645.3	794	
	775	1.027, +0	2.813, -1	0.288	735.7	882	
	950	3.661, -2	-6.875, -1	0.316	868.7	995	
	1225	-9.791, -1	-2.055, +0	0.256	1089	1231	

TABLE 5.5.

THREE STAGE INDIRECTLY CONTROLLED ADIABATIC CASCADE

Note: $a, -b = a \times 10^{-b}$

NOTE: $a_2 = 0 = a_{\infty}$

RATE FUNCTION PARAMETERS		T_{a1}	$\log\left(\frac{y_{e3}}{1-y_{e3}}\right) / \log M$	t_1/M	t_2/M	T_{a2}	T_{a3}	T_{e1}	T_{e2}
1st.	700	1.992, +0	-1.440, -2	0.030	0.221	707.1	682.0	835	727
	825	9.109, -1	-2.265, +0	0.066	0.261	813.8	792.3	922	846
	925	3.297, -1	-3.618, +0	0.091	0.293	895.2	870.9	988	924
	1000	-8.969, -3	-4.486, +0	0.098	0.304	956.2	928.2	1041	978
2nd.	700	2.167, +0	7.548, -1	0.064	0.270	698.6	659.7	834	719
	825	1.059, +0	-4.650, -1	0.101	0.289	794.0	762.0	919	831
	925	4.370, -1	-1.284, +0	0.122	0.310	871.1	837.1	984	906
	1000	8.009, -2	-1.833, +0	0.124	0.319	930.7	892.5	1038	959
3rd.	725	2.130, +0	9.619, -1	0.112	0.305	699.7	651.9	849	729
	850	9.773, -1	1.980, -1	0.141	0.311	791.2	751.2	929	835
	925	4.854, -1	-2.299, -1	0.150	0.323	849.0	806.9	978	889
	1000	1.066, -1	-6.284, -1	0.146	0.331	908.6	861.4	1032	940

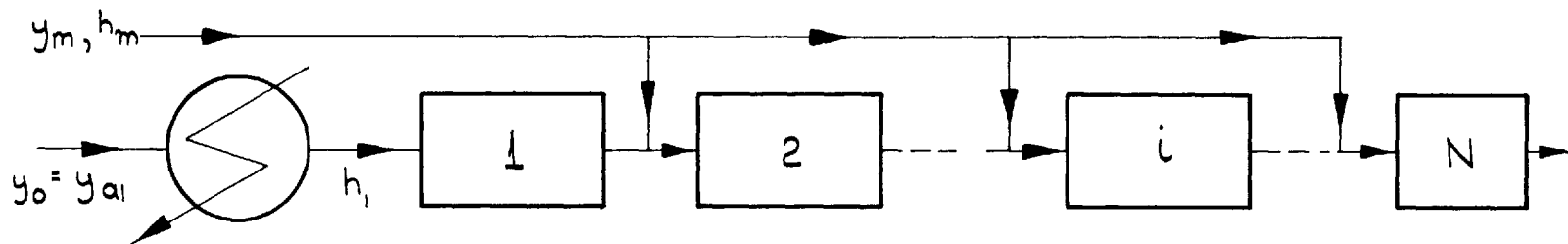
TABLE 5.6.

FOUR STAGE INDIRECTLY CONTROLLED ADIABATIC CASCADE

Note: $a, -b = a \times 10^{-b}$

Note: $a, -b = a \times 10^{-b}$

RATE FUNCTION PARAMETERS		T_{a1}	$\log\left(\frac{y_{e4}}{1-y_{e4}}\right)$	$\log M$	t_1/M	t_2/M	t_3/M	T_{a2}	T_{a3}	T_{a4}	T_{e1}	T_{e2}	T_{e3}
1st.	725	1.972, +0	-1.123, -1	0.014	0.087	0.283	729.2	705.5	682.8	853	753	709	
	850	9.278, -1	-2.277, +0	0.032	0.119	0.290	834.3	812.5	792.3	938	867	827	
	950	3.473, -1	-3.609, +0	0.046	0.146	0.299	915.4	890.0	870.5	1005	942	906	
	1050	-9.301, -2	-4.734, +0	0.050	0.156	0.305	997.4	966.5	945.0	1080	1015	979	
2nd.	750	2.035, +0	5.778, -1	0.035	0.125	0.295	737.0	702.1	669.3	870	766	708	
	825	1.361, +0	-1.468, -1	0.048	0.139	0.293	794.0	762.0	732.2	919	831	777	
	925	6.562, -1	-1.003, +0	0.064	0.162	0.297	871.1	837.1	810.5	984	906	859	
	1000	2.599, -1	-1.567, +0	0.068	0.173	0.302	930.7	892.5	865.3	1038	959	913	
3rd.	775	2.120, +0	9.308, -1	0.065	0.159	0.301	735.7	693.0	650.9	882	774	703	
	900	9.581, -1	1.659, -1	0.082	0.177	0.295	829.5	788.5	755.2	961	871	814	
	1000	3.387, -1	-3.881, -1	0.084	0.190	0.301	908.6	861.4	828.7	1032	940	887	



N stage adiabatic cascade with feed preheater and cold shot intercooling.

Fig. 5.1.

(For Fig. 5.2. please turn over.)

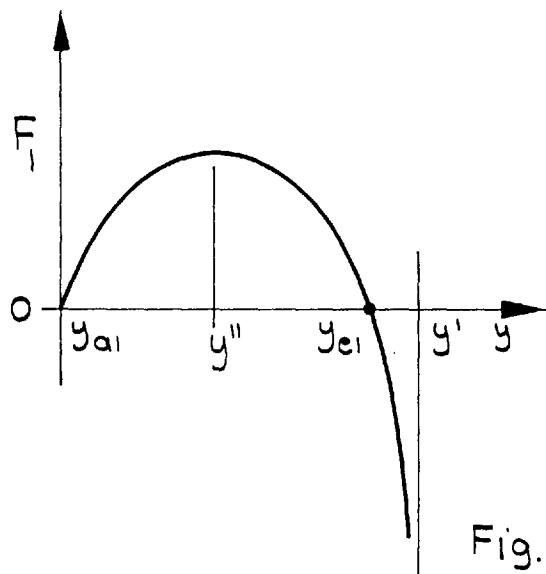


Fig. 5.3.

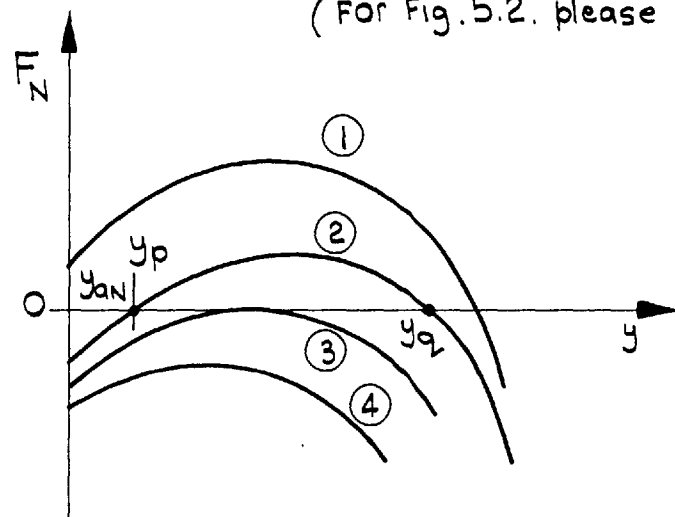
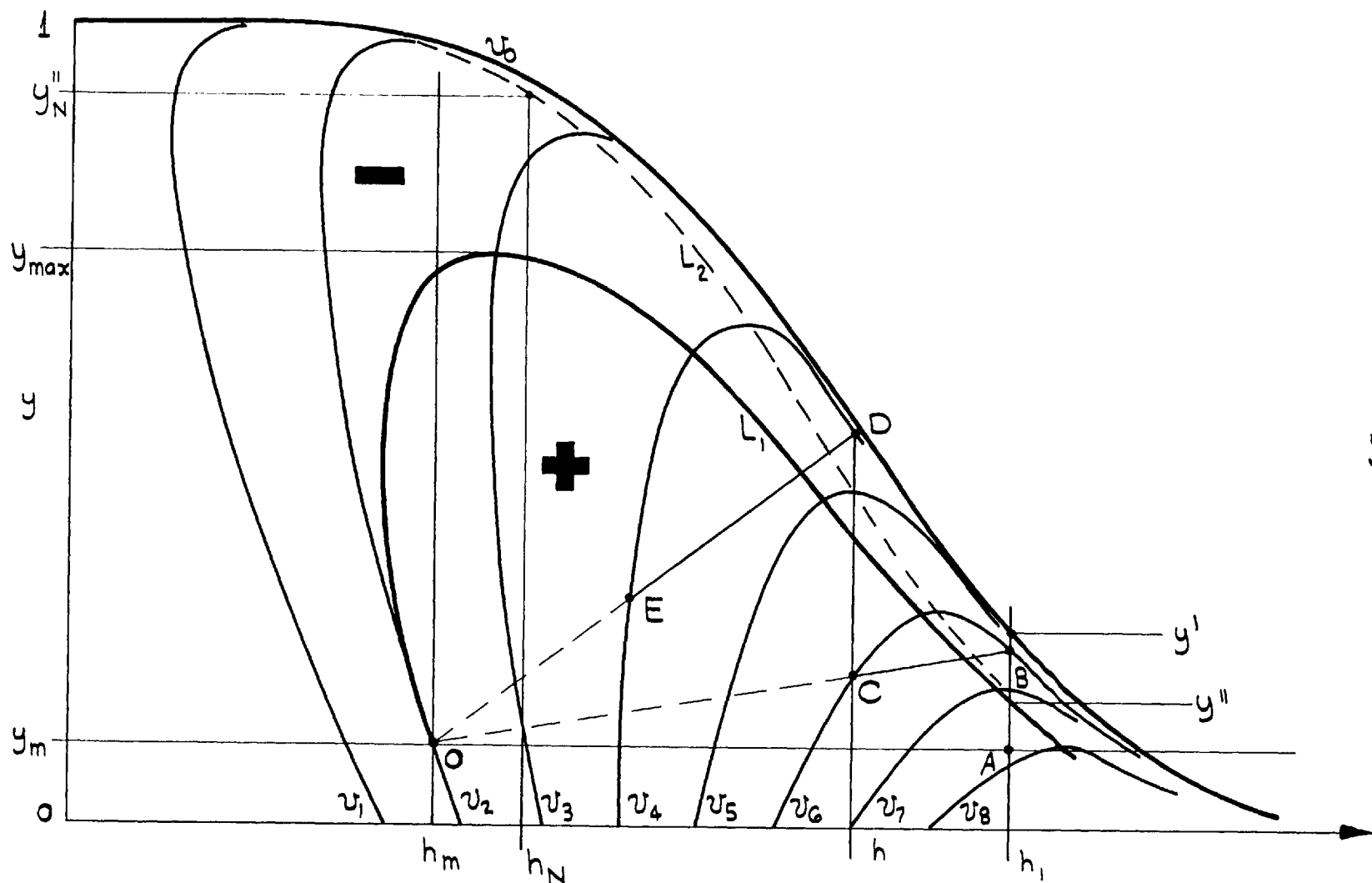


Fig. 5.4.



$$0 = v_0 < v_1 < v_2 < v_3 < v_4 < v_5 < v_6 < v_7 < v_8$$

Fig. 5.2.

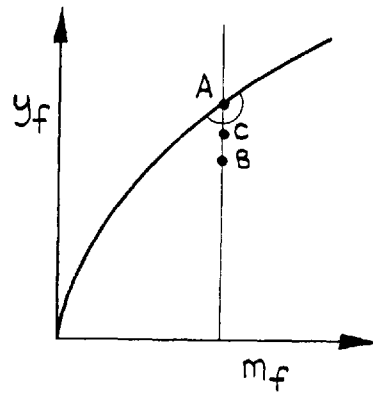


Fig. 5.5.

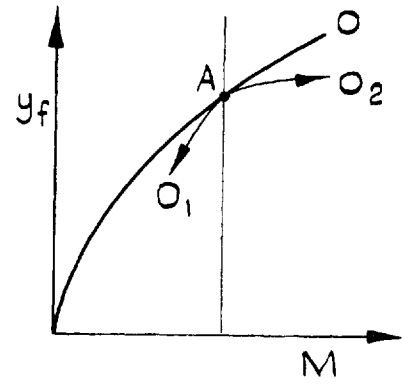


Fig. 5.6.

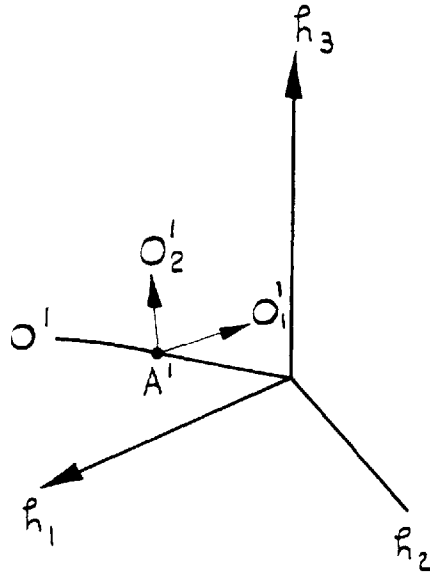


Fig. 5.7.

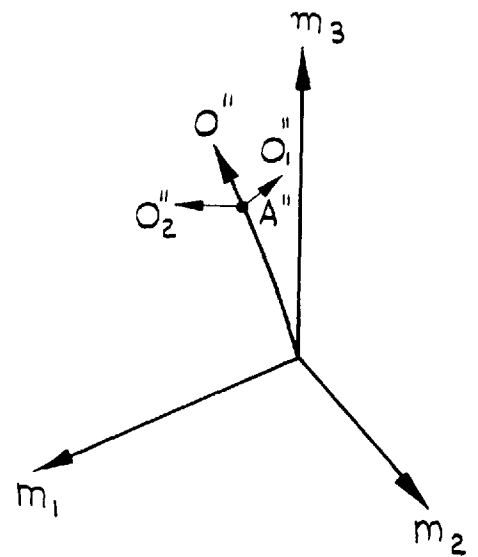


Fig. 5.8.

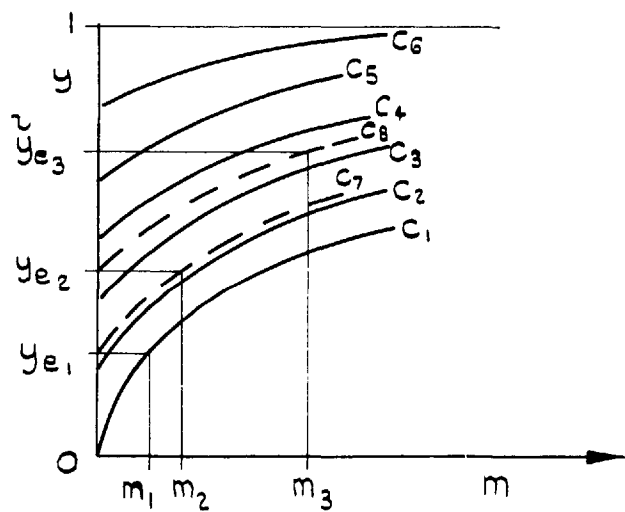


Fig. 5.9.

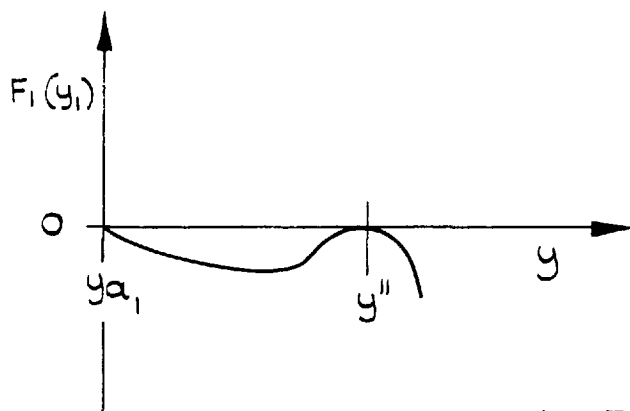


Fig. 5.10.

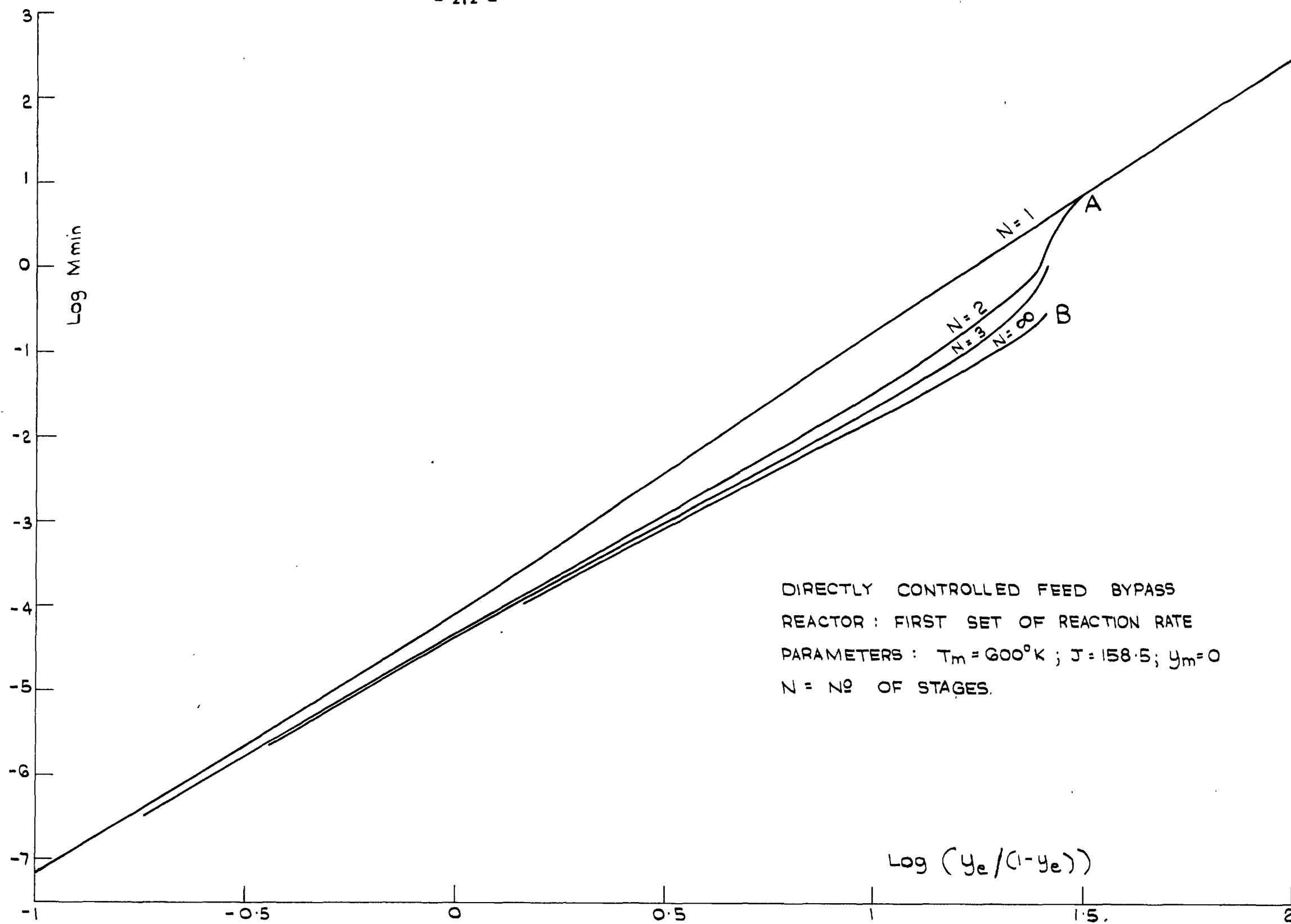


FIG. 5.11.

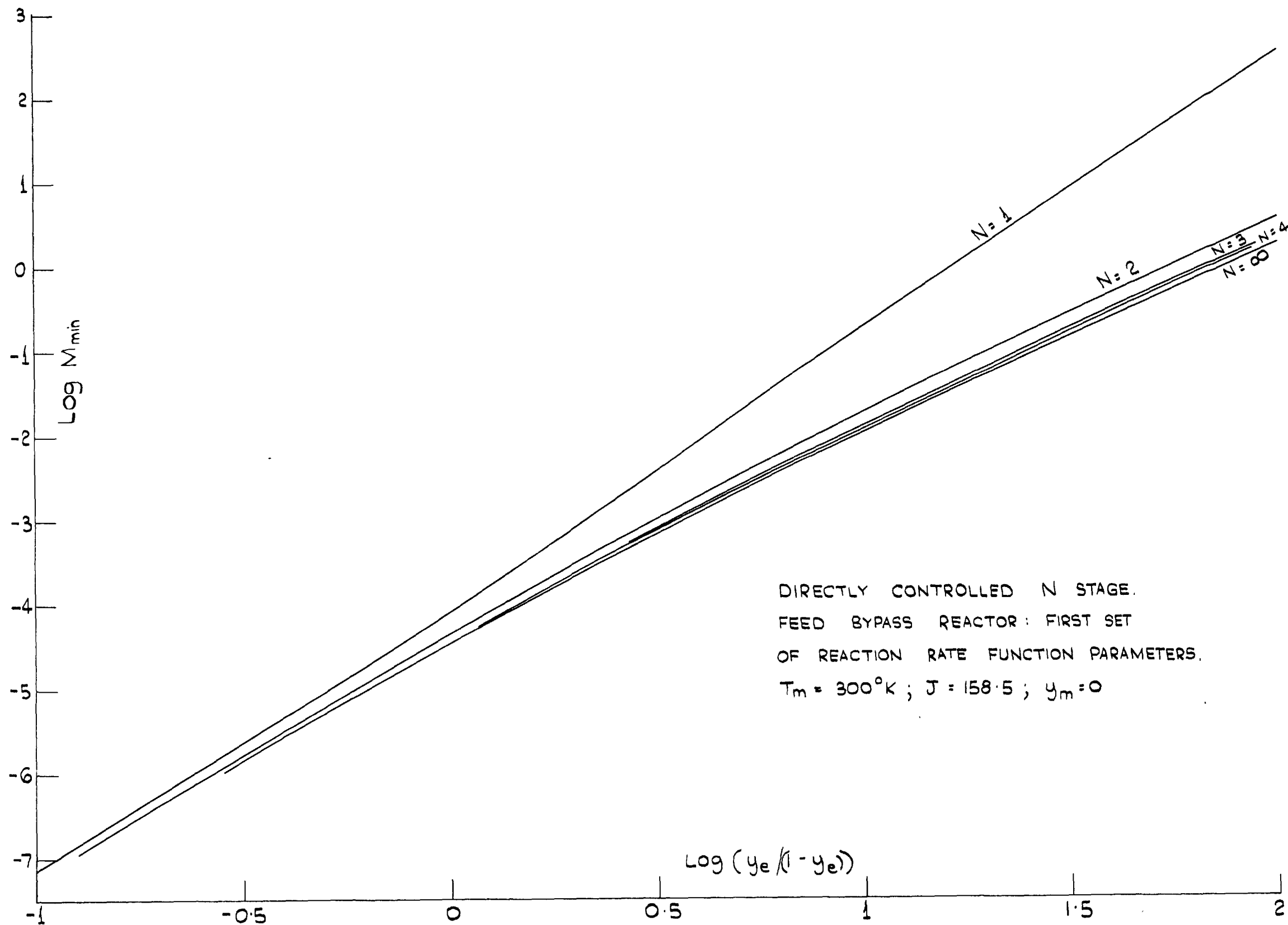


Fig. 5.12.

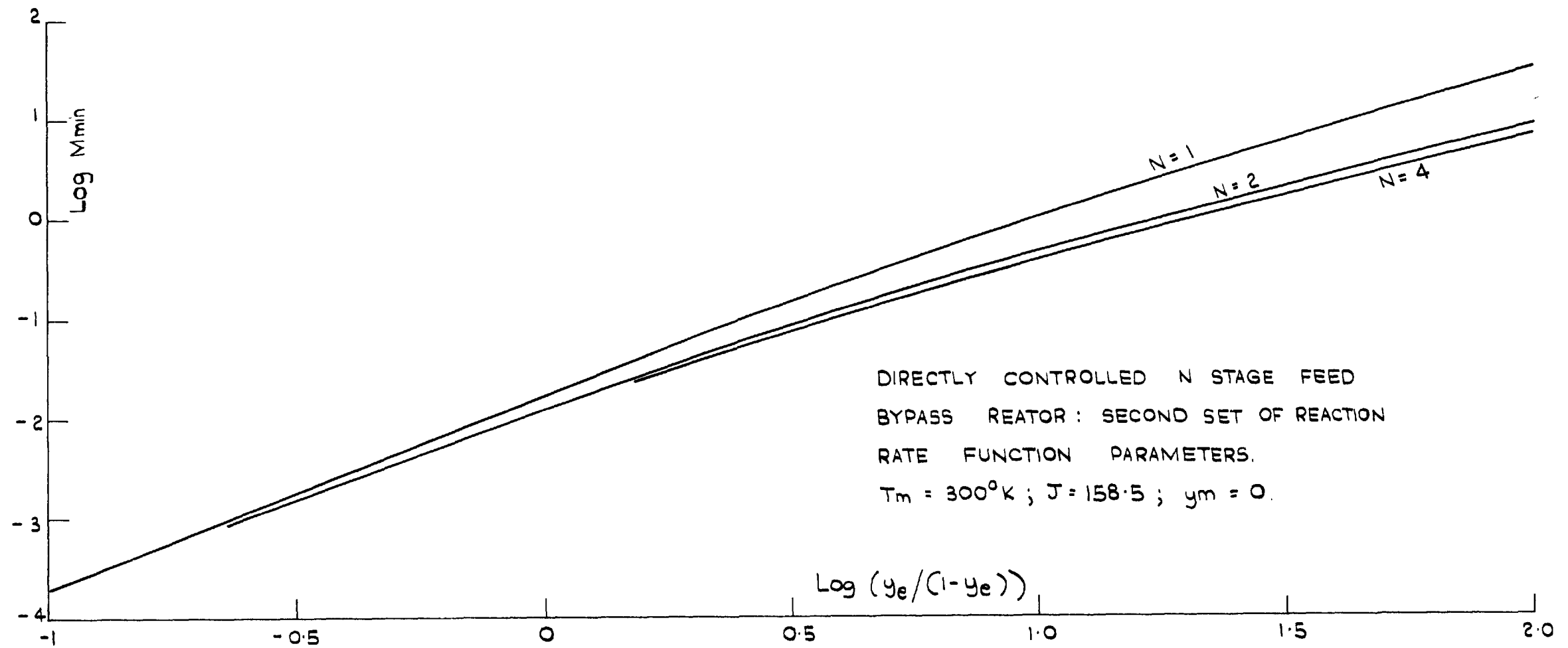


FIG. 5.13.

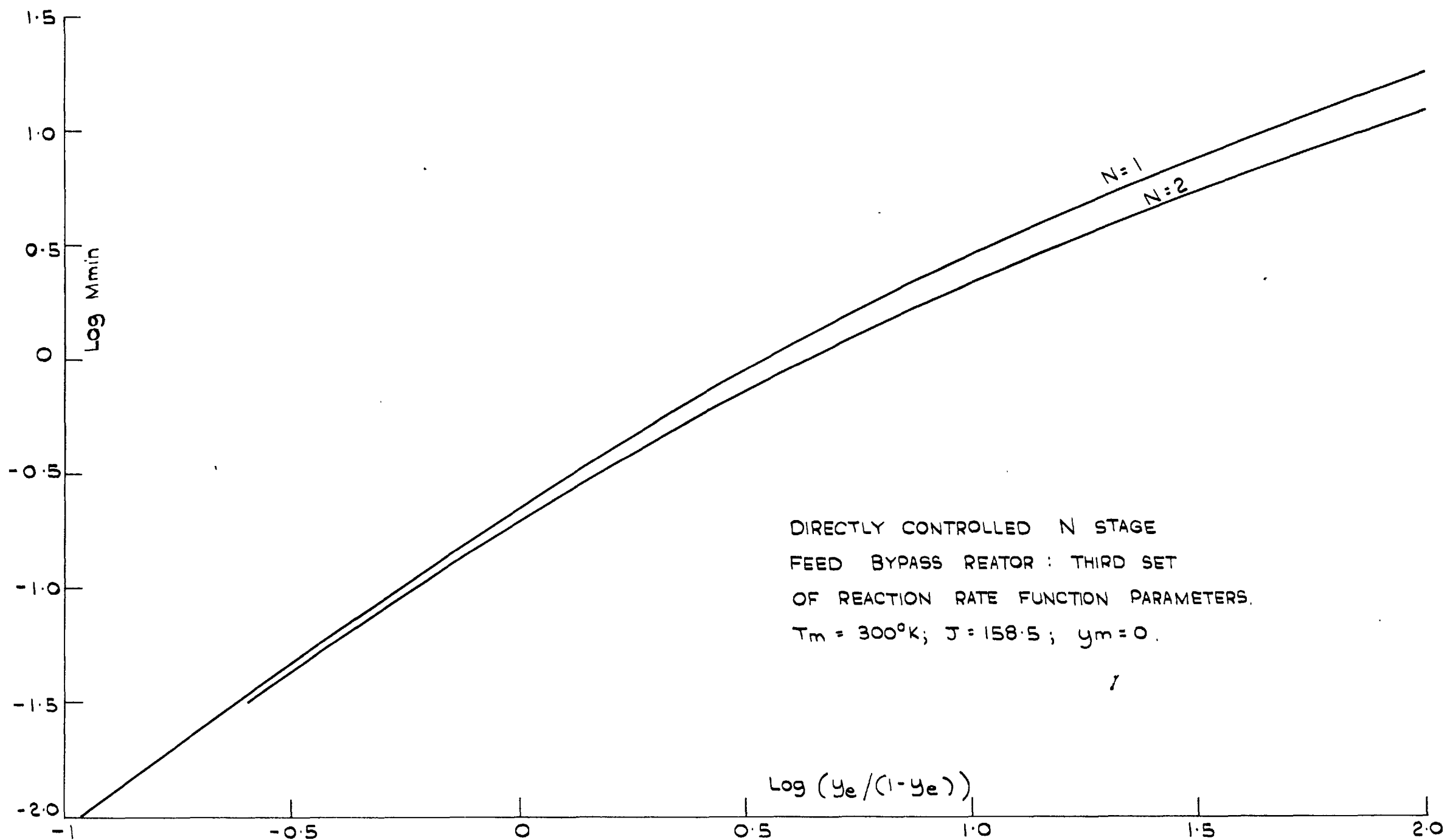


FIG. 5.14.

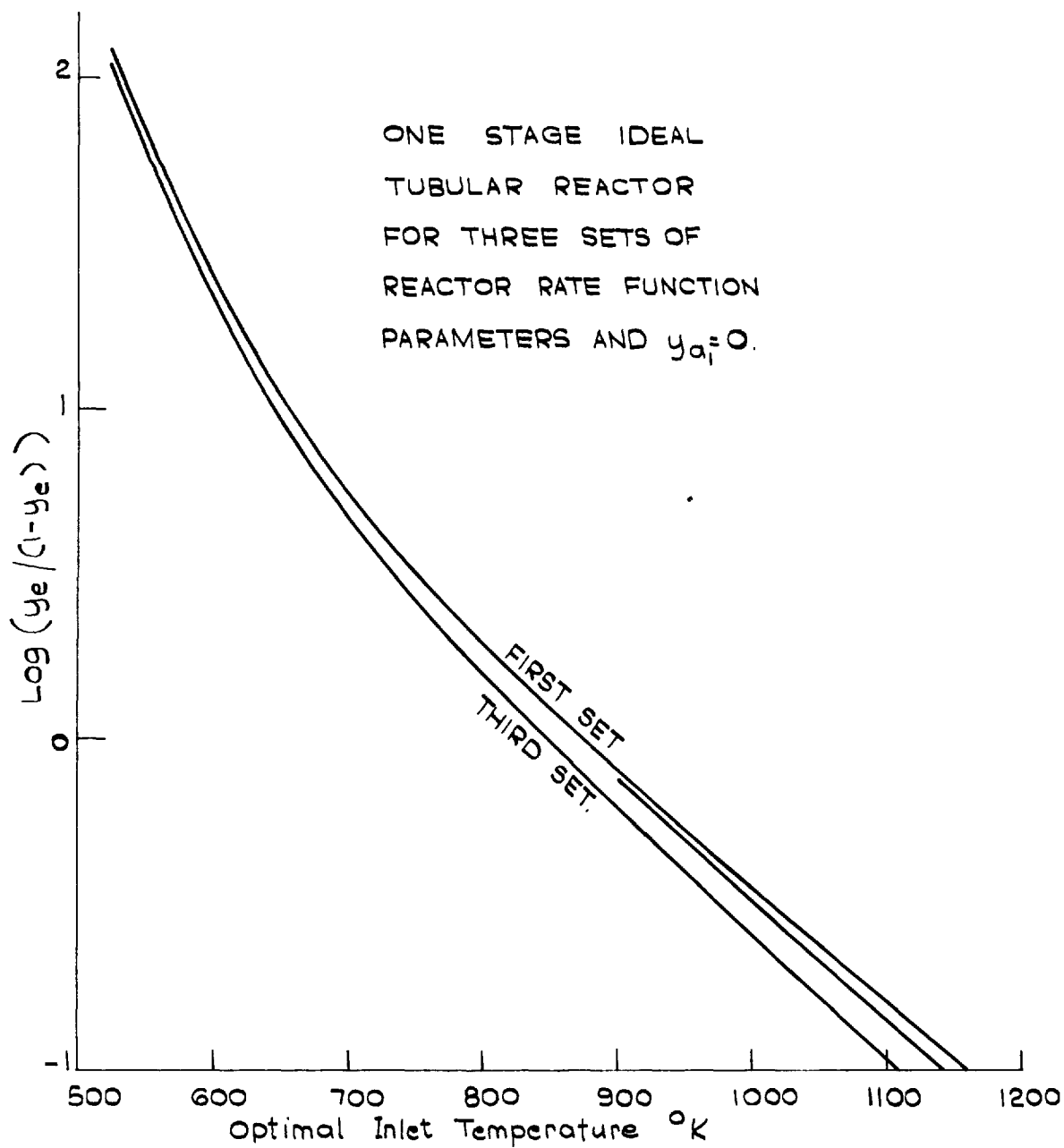


Fig. 5.15.

Chapter VI

Optimum Problems for U-Tube And Related Reactors.

In this chapter heat and material balance equations will be derived for the ideal distributed feed reactor represented in Fig. 6.1; specialisations of these equations will be shown to be applicable to the reactors represented in Figs. 6.2 and 2.10; methods for optimizing the reactors will be discussed.

VI. I. Heat and material balance equations:¹

Consider Fig. 6.1. The main feed enters at basic molal flowrate w_1 , conversion y_{a1} , and temperature T_{a1} , at the bottom end of the left hand tube, flows up the tube (in which reaction may or may not take place), emerging at the top where it is mixed with a stream of basic molal flowrate $w_2 - w_1$, conversion y_m and temperature T_m ; the resulting stream flows down the right hand tube, in which reaction takes place, emerging at

1. We will make use of some elementary results derived in Chapter 2.

the bottom with basic molal flowrate w_2 , conversion y_{e2} and temperature T_{e2} .

Indirect heat transfer may take place only orthogonal to the flow axis, across the dividing¹ wall.

The specific heat C based on one mole of reference substance and J the adiabatic temperature rise coefficient are both assumed to be constant.

To fix ideas consider first a homogeneous reaction taking place at a rate $v(y,T)$ in each tube, and let m be the volume of the right hand tube from the bottom end to the reference plane in Fig. 6.1., and K the (constant) ratio of the sectional area of the right hand tube to the left hand tube: a differential mass balance on each tube, a differential heat balance on the right hand tube, and an overall heat balance across the broken line in Fig. 6.1. give:

1. Since the ideal distributed feed reactor model is being used it is understood that within the fluid phase there is perfect heat transfer orthogonal to the flow axis. Whether the resistance to heat transfer is at the wall alone, or includes infinitesimally thin films on either side of the wall, is irrelevant.

$$\dot{y}_0 = -b_1 ((b_2-1)y_0 - b_3 + J(y_1 - y_2)) \quad (6.1)$$

$$K y_1 = b_2 v(y_1, b_2 y_0 - b_3 + J y_1) \quad (6.2)$$

$$\dot{y}_2 = -v(y_2, y_0 + J y_2) \quad (6.3)$$

where the dot denotes differentiation with respect to t and the variables t and y_0 (i.e. θ in Chapter II), and the parameters b_i are defined as follows:

$$t = m/w_2 \quad (6.4)$$

$$y_0 = T_2 - J y_2 \quad (6.5)$$

$$b_1 = \frac{\text{overall heat transfer coeff.} \times \text{area of contact}}{C \times \text{volume of right hand tube}} \quad (6.6)$$

$$b_2 = w_2/w_1 \quad (6.7)$$

$$b_3 = (b_2-1)(T_m - J y_m) \quad (6.8)$$

(The temperatures T_1 and T_2 are given by the right hand arguments of the rate function v in 6.2 and 6.3 respectively).

The initial conditions for 6.1, 6.2, and 6.3, are:

$$\text{At } t=0, y_0=b_0, y_1=y_{a1}, y_2=y_{e2} \quad (6.9)$$

And if the final value of t is given by the equation:

$$\bar{A}(F) = 0 \quad (6.10)$$

$$\text{where } \bar{A}(t) \equiv y_1 + (b_2-1)y_m - b_2 y_2 \quad (6.11)$$

Specializations of heat and mass balance equations:

1. Equal Branched U-Tube Reactor: The Push-Pull Reactor

If in the above equations we put:

$$b_2 = 1, b_3 = 0, K = 1 \quad (6.12)$$

we get the equations for the U-Tube reactor with no "cold shot" at the top, and equal branches. These equations also correspond to each of the two reactors represented in Fig. 6.3, and hence to the two straight tube counterflow reactors in thermal contact (Fig. 6.2). To prove the latter it is sufficient to observe that equations 6.1, 6.2, 6.3 together with 6.12 are invariant against the transformation:

replace t by $-t$ and interchange y_1 and y_2 .

These equations may also be used to describe a homogeneous reaction taking place in a pebble heat exchanger (Fig. 2.10) where flow is alternately from left to right and from right to left during each half cycle if a quasi-steady state is stable and the cycling can be so arranged to be neither so rapid that back-mixing is serious, nor so slow that the pebble surface temperatures are not fairly constant. This type of

reactor will be called a PUSH-PULL reactor.

The reaction may be solid catalysed: If so the catalyst is assumed to be in thermal contact only with the fluid.¹

2. The Empty-Full U-tube reactor.

If the right hand branch of the U tube in Fig. 6.1 is packed with catalyst and the left hand branch is not (such as the ammonia synthesis reactor²) then we

1. Another simple model may be used where it is assumed that the solid catalyst is all at the wall (or pebble) temperature and that the heat of reaction liberated in the catalyst is transferred to the fluids (the catalyst temperature minus fluid temperature providing the driving force). In this case it is no longer reasonable to base the reaction rate on the fluid temperature, but one must use the catalyst temperature. This model leads to three differential equations as before, but the wall temperature must be eliminated by solving a simultaneous nonlinear equation.

2. See references 47 and 57 for a similar treatment which however requires one more differential equation because two differential heat balances were carried out and the resulting integral of the equations was not used to eliminate a differential equation.

need use only two differential equations; 6.2 disappears on putting:

$$b_2 = 1, b_3 = 0, b_2/K = 0 \quad (6.13)$$

3. Adiabatic stages with intercooling

Equations 6.1 to 6.11 represent a two stage adiabatic reactor with "cold shot" intercooling if we put:

$$b_1 = 0 \quad (6.14)$$

If the cooling is indirect then in addition, one may put:

$$b_2 = 1 \quad (6.15)$$

$$- b_3 = \text{temperature drop across interstage exchanger.} \quad (6.16)$$

Hence a one stage adiabatic reactor may be included by making b_3 zero.

One may make use of these results in checking numerical integrations of the equations in Chapter V for adiabatic cascades; also the sensitivity of a two

stage adiabatic cascade to maldistribution of volume (catalyst) could be investigated, since K , the ratio of the two volumes (masses of catalyst) is a parameter in the equations.

The above specializations are summarised in table 6.1:

Table 6.1.

Parameter Reactor Type		b_1	b_2	b_3	$1/K$
1	Equal branched U		1	0	1
2	Push-Pull Reactor		1	0	1
3	Empty-Full U		1	0	0
4	One stage adiabatic	0	1	0	
5	Two stage adiabatic with cold shot intercooling	0			
6	Two stage adiabatic with indirect intercooling	0	1		

VI. II. The Basic problems for the U-Tube¹ and Push-Pull reactors.

For a given reaction rate expression and inlet

1. i.e. those listed 1, 2, and 3 in table 6.1. It would not be unreasonable (although outside our scope) to consider the more general problem where b_2 and or b_3 are also adjustable.

conversion y_{a1} the basic problems are:

- (i) For given y_{e2} find b_0 and b_1 such that F is minimum.
- (ii) For given F find b_0 and b_1 such that y_{e2} is maximum.

For the reaction rate expressions used in this work, problems (i) and (ii) have invariably turned out to be equivalent¹. Anyway we will suppose that they will always be equivalent in situations of practical importance, so that we may solve whichever is most convenient.

VI. III. Integration of mass and heat balance equations.

Evidently we must integrate the equations 6.1, 6.2, and 6.3 in order to calculate the objective functions. These equations will have to be integrated numerically in general, of course. There are two possibilities:

- (a) Forward integration; i.e. from $t=0$ to $t=F$.
- (b) Backward integration²

1. See discussion about equivalence in Chapter III.
2. If backward integration were to be used, then one would define b_0 (instead of by 6.9) by $b_0 = y_0$ at $t=F$.

It will be shown in what follows that in order to avoid wasting information it is best to solve problem (i), integrating forwards (except if only the empty-full case were of interest).

Let us first consider in Fig. 6.4 some trajectories in the y, T plane obtained by forward integration in the push-pull case for $y_{a1} = 0$, $y_{e2} = 0.9$, $b_0 = 630$, $J = 158.5$ and the second set of reaction rate parameters¹. For all values of b_1 the two branches of the trajectories start out at points A_1 and A_2 on the line $y_0 = 630$, labelled (1) in Fig. 6.4. For $b_1 = 0$ both branches lie entirely in this line, and terminate at P_0 . For $b_1 = 2.97$ we get trajectory (2) terminating at P_1 . (At P_1 both trajectories are parallel to the $y_0 = \text{constant}$ line).

For $b_1 = 29.7$ however the two branches (3) do not connect. (The top branch crosses the equilibrium line. For an arbitrary² reaction rate expression this implies

1. See Chapter I. equation 1.1 and table 1.1.

2. The system is assumed to have the property that along $v = 0$ contour $\frac{dy}{dT} < 0$ and also, $(\frac{\partial T}{\partial y_h}) > 0$ everywhere. c.f. footnote in section II, Chapter V.

that the branches cannot connect for any t however large¹; (note that corresponding points on each branch lie on the same constant enthalpy line, that the rate is negative above the equilibrium line, that T_1 and T_2 are monotonic increasing functions of t and that y_1 and y_2 both lie between 0 and 1). Such a trajectory will be termed endless and the corresponding point in the (b_0, b_1) plane an inadequate point.

It is clear that for any rate expression which describes a reversible exothermic reaction and for any b_0 , by making b_1 large enough one can get an inadequate point, since for b_1 infinite both branches are horizontal lines in the y, T diagram. Also, it seems highly plausible² that the following is true for reasonable reacting systems:

(for given y_{a1}, y_{e2}) there exists a curve which divides the first quadrant of the b_0, b_1 plane into two regions, the region below the curve containing no inadequate points, the region above it only inadequate points,

1. i.e. the boundary condition 6.10 cannot be satisfied.

2. No evidence to the contrary has been found yet.

whilst for points on this curve F is infinite.

In Fig. 6.5 points (b_0, b_1) are plotted: circles if inadequate, otherwise dots with the corresponding F values written adjacent to them (for the case discussed above). The inferred border of the inadequate region is also sketched (full curve), and the broken curve represents approximately the locus of the minima of F along constant b_0 lines¹. The inferred border has the shape one would expect: the higher b_0 the lower the corresponding value of b_1 until at $b_0 \approx 666^\circ\text{K}$ (which corresponds to the point A_2 in Fig. 6.4 lying on the equilibrium line), b_1 is zero, while for low values of b_0 , b_1 is approximately constant, because, at all these low values of b_0 the initial reaction rates are practically zero for all conversions.

We have seen that the forward integration procedure used to calculate the objective function for the basic problem (i) has the disadvantage that one has no a priori knowledge of whether a point (b_0, b_1) will be inadequate

1. Not much information additional to that supplied by the dots and crosses was used in drawing these curves, so they may be slightly out of place here and there.

or not, and, to judge by Fig. 6.5, this disadvantage appears to be serious¹. (examples which are much worse than the one represented in Fig. 6.5 will be given later). Basic problem (ii) together with forward integration is obviously unreasonable. Basic problem (ii) with backward integration should be satisfactory² for the empty-full reactor since y_1 and y_2 are both zero at $t = F$ (and for the backward integration we make $b_0 = y_0(F)$ rather than $y_0(0)$). For the push-pull and equivalent reactor however we still must specify $y_1(F)$ in order to start the integration, and only for certain values of $y_1(F)$ will the boundary condition $y_1(0) = y_{a1}$ be satisfied, so information will be wasted. Further, for certain values of $b_1, y_0(F)$ and $y_1(F)$ the boundary condition $y_1(0) = y_{a1}$ cannot be satisfied for any F as can easily be seen by considering the case b_1 infinite. Basic problem (i) together with backward integration should also be suitable for the empty-full reactor.

Since we set out intending to solve the basic problem for the two types of reactor attention was

-
1. The same trouble occurs with the empty-full reactor, of course.
 2. The difficulty with crossing the equilibrium line which occurs for the forward integration procedure cannot occur here provided that the initial reaction rate is positive.

concentrated on problem (i) and forward integration.

VI. IV. Numerical Procedures Used for the Basic Problem:

a) Preliminary Investigation:

A programme was written to evaluate F by forward integration of equations 6.1, 6.2, 6.3, using the Runge Kutta Merson variable step length procedure¹. The sign of y_2^* was tested at the beginning of each step, and if negative, integration continued. At the end of each step $\bar{A}$ was determined, and if negative, integration continued, otherwise F satisfying 6.10 to a specified accuracy was determined by the rule of false position.

If y_2^* became non negative somewhere indicating an endless trajectory, this information was dealt with suitably, and integration was terminated.

The method turned out to be very satisfactory. It was found that if the error tolerances on y_0 , y_1 , y_2 for each step were set at 0.1, 0.00001, and 0.00001 respectively F would be determined to a precision of about 1 part in 1 million, 5 to 40 steps being required even if the initial interval were made unreasonably

1. This programme used a library machine code Merson routine. Only the programme outline will be given, such details as loop counters etc. being omitted. See Ref. 8.

small, except with the first set of reaction rate parameters¹ when the precision was about 1 in 10000 and slightly more steps were required. It turned out that (except for the first few steps in some cases) the steplength remained fairly constant throughout an integration.

In each of the 36 cases² investigated the above programme was used in a preliminary search in the (b_0, b_1) plane.

A master programme, using the above programme for function evaluation, was written to carry out a simple search along lines of constant b_0 .

A value for b_0 was specified (in the data for the programme) as well as an initial non-zero value for b_1 which would guarantee a value for F . b_1 was then increased in a geometric sequence until either the corresponding value of F was larger than the smallest previous value (in which case the search along the line was terminated), or the point b_0, b_1 became inadequate.

1. Equation and table 1.1.

2. See Tables 6.2 and 6.3.

After each inadequate point the value of b_1 was made the harmonic mean of the largest value of b_1 known to correspond to a value of F , and the smallest value of b_1 known to be inadequate.

The programme was quite satisfactory, not more than ten attempted function evaluations being required, as a rule. Most of the points in Fig. 6.5 were obtained in this way. From this and other information it was concluded that the minimum value of F corresponded to a point in a trough lying close to the inadequate region.¹ It appeared also that the minimum along a line of constant b_0 was not very sensitive to b_0 .

It soon became clear that a powerful hill climbing procedure would be required in order to determine the

1. Of the 36 cases studied, in 4 cases the b_0, b_1 plane was explored in some detail, and in all cases the situation was found to be similar to that represented in Fig. 6.5. The coordinates $(\hat{b}_0, \hat{b}_1)$ of the minimum approached the inadequate region more closely (on a relative basis) as γ_{e2} became larger and as the ratio of the activation energies decreased. In one case both b_0 and b_1 were within one part in 20,000,000 of the respective coordinates of an inadequate point.

coordinates of the minimum in Fig. 6.5., so the problem of how best to find the derivatives of F with respect to b_0 and b_1 was considered¹.

b) Determination of derivatives of F with respect to b_0 and b_1 :

The equations for the push-pull and empty-full

1. Hill-climbing methods which do not require derivative evaluation are being developed by many workers; at the present time methods with quadratic convergence are available (Ref. 73); at the time this work was in progress however no such methods were known to the author. The utility of the derivatives should not be overlooked; to get a reasonable indication of what point to try next the derivatives at a point (plus accumulated information about curvatures) even if they are known with a relative precision of $\pm 10\%$ may well be far more useful than two or three function evaluations made in a small region (plus the same information about curvature. (Over a small interval $[\alpha, \beta]$ on some given line rounding errors may easily

be such that while $\frac{dF}{dz} < 0$ for all z in $[\alpha, \beta]$, $F(\alpha) - F(\beta)$ appears to be negative).

reactors are of the form:

$$y_i' = f_i(y_j, a) \quad (6.17)$$

$$y_i(0) = x_i \quad (6.18)$$

$$g(z_i) = 0 \quad (6.19)$$

$$z_i = y_i(F) \quad (6.20)$$

Where a is the parameter b_1 (equation 6.6), the y_i are as before (equation 6.1 to 6.3) the x_i are the initial values of the y_i , and F , the final value of t is determined by 6.19 and 6.20.

We wish to find $\frac{\partial F}{\partial x_0}$ and $\frac{\partial F}{\partial a}$. It would also be useful to know $\frac{\partial F}{\partial x_2}$, since for the optimum choice of a and y_1 this will give us the slope of the $F_{\min}$, y_{e_2} relation.

There are different ways of obtaining these derivatives.

First, let us consider F given, and z_i defined by 6.17, 6.18, 6.20, and suppose we have determined the derivatives:

$$\frac{\partial z_i}{\partial x_j} \text{ and } \frac{\partial z_i}{\partial a} \quad (6.21)$$

Then, it follows that the derivatives we want are:

$$\frac{\partial F}{\partial x_j} = - \frac{\frac{\partial g}{\partial z_i} \frac{\partial z_i}{\partial x_j}}{\frac{\partial g}{\partial z_r} f_r(z_k, a)} \quad (6.22)$$

$$\frac{\partial F}{\partial a} = - \left[\frac{\frac{\partial g}{\partial z_i} \frac{\partial z_i}{\partial a}}{\frac{\partial g}{\partial z_k} f_k(z_j, a)} \right] \quad (6.23)$$

(Where summation over the repeated suffices is understood, and the functions and derivatives are evaluated at the point which satisfies 6.19).

It is well known that the quantities 6.21 may be obtained by integrating the variational equations, i.e. that they are given by:

$$\frac{\partial z_i}{\partial x_j} = u_{ij}(F) \quad (6.24)$$

$$\frac{\partial z_i}{\partial a} = p_i(F) \quad (6.25)$$

$$u_{ij} = \frac{\partial f_i}{\partial y_r} u_{rj} \quad ; \quad u_{ij}(0) = \delta_{ij} \quad (6.26)$$

$$p_i = \frac{\partial f_i}{\partial y_r} p_r + \frac{\partial f_i}{\partial a} \quad ; \quad p_i(0) = 0 \quad (6.27)$$

$$\left. \begin{aligned} \delta_{ij} &= 0 \quad \text{for } i \neq j \\ \delta_{ij} &= 1 \quad \text{for } i = j \end{aligned} \right\} \quad (6.28)$$

We could obtain all derivatives by integrating the above equations together with 6.1, 6.2 and 6.3, forward, i.e. 15 equations¹ all together; or 12 if we note that $\frac{\partial F}{\partial x_1}$ is not required, or 9 if we relinquish our interest in $\frac{\partial F}{\partial x_2}$ as well. In this way we would have no intermediate storage problem and could use a variable steplength method, so that not knowing F before the integration starts would not be a drawback: on the other hand, there are many² equations to integrate.

Consider the equations (6.26): if we were interested in a linear combination of the $u_{ij}(F)$ of the form:

$$q_j u_{ij}(F) \quad (6.29)$$

1. For the push-pull case: less for the empty-full reactor.

2. There may also be problems with numerical instability.

where the q_j are parameters known at $t=0$, then we could reduce 6.26 to a set of three equations by multiplying by q_j and summing over the index j . What we require however¹ is a linear combination of the form

$$q_i u_{ij}(F) \quad (6.30)$$

where the other suffix is summed and the q_i are defined at $t=F$, so there is no reduction of the equations 6.26; with the adjoint equations however we have the dual situation.

Consider a set of adjoint variables G_{ki} defined for all t by:

$$G_{ki} u_{ij} = u_{kj}(F) \quad (6.31)$$

Differentiating 6.31 with respect to t (noting that its right hand side is independent of t , and relettering dummy suffices), using 6.26, and cancelling the (assumed nonsingular) matrix u_{ij} , we obtain:

$$\dot{G}_{ki} = - G_{kj} \frac{\partial f_j}{\partial y_i} \quad (6.32)$$

1. See equation 6.22.

If we put $t=F$ and $t=0$ respectively in 6.31, we get; using 6.24:

$$G_{ki}(F) = \delta_{ki} \quad (6.33)$$

$$G_{kj}(0) = \frac{\partial z_k}{\partial x_j} \quad (6.34)$$

These adjoint equations are of the right form to be reduced. The inhomogeneous equations 6.27 may also be dealt with in the same way. The relation

$$p_i(F) = \int_0^F G_{ij} \frac{\partial f_j}{\partial a} dt \quad (6.35)$$

may easily be verified.

Let us introduce reduced adjoint variables W_i :

$$W_i = q_k G_{ki} \quad ; \quad i = 0, 1, 2 \quad (6.36)$$

$$W_3 = q_k p_k \quad ; \quad k = 0, 1, 2 \quad (6.37)$$

where the parameters q_k , i are given by:

$$q_k = \frac{-\frac{\partial g}{\partial z_k}}{\frac{\partial g}{\partial z_i} f_i(z_j, a)} \quad ; \quad i, j, k = 0, 1, 2 \quad (6.38)$$

It follows from 6.32, 6.35 to 6.38 that if we write:

$$L_{ji} = \frac{\partial f_j}{\partial y_i} ; \quad i, j = 0, 1, 2 \quad (6.39)$$

$$L_{3i} = 0 ; \quad i = 0, 1, 2, 3 \quad (6.40)$$

$$L_{j3} = \frac{\partial f_j}{\partial a} ; \quad j = 0, 1, 2 \quad (6.41)$$

then the quantities W_i defined by 6.36 and 6.37 satisfy the equations:

$$W_i' = - W_j L_{ji} ; \quad i, j = 0, 1, 2, 3 \quad (6.42)$$

and so we see that if these equations are integrated backwards with the starting condition:

$$W_i(F) = q_i ; \quad W_3(F) = 0 ; \quad (6.43)$$

$$\text{Then: } W_i(0) = \frac{\partial F}{\partial x_i} \text{ for } i=0,1,2 ; \quad W_3(0) = \frac{\partial F}{\partial a} ; \quad (6.44)$$

Thus, in order to get F and the derivatives required we may integrate 6.1, 6.2, and 6.3 forward, (storing at each step information suitable for the

calculation of the L_{ij}) and equations 6.42 backwards.

This forward-backward method was the only method we used for the evaluation of the derivatives of F .

It is convenient to use the ordinary Runge Kutta¹ method with coefficients (1, 2, 2, 1) for the integrations; for each step of the backward integration it is necessary to have stored information which will enable the elements of L_{ij} to be computed at the beginning, mid-point, and end. A complication arises because it is not known before the forward integration has been completed whether the number of steps will be even or odd. The method illustrated in Fig. 6.6 was used to overcome this difficulty. (The first two steps were made half the "normal" step length, and an additional step was inserted at the end, as shown).

In (on the average) half the cases the information stored at the beginning of the second step would not have been required, but as several hundred steps were often used, this wastage was trivial.

Some care is required in programming to ensure

1. Also known as Kutta-Simpson. See for example reference 77.

that values of the elements of L_{ij} corresponding to the correct values of t are used at each step in the backward integration. If those corresponding to neighbouring values of t are used the mistake may easily go undetected but the accuracy achieved with a given number of steps will in general suffer.

A routine based on the above forward backward method was written. The routine was supplied on call with $\bar{k}$ the "normal" forward integration steplength, the parameters b_0, b_1 , etc. and n the maximum allowable number of steps for the forward integration; apart from fault exits of various kinds which we need not bother with there were three possible exits:

- 1) function and derivatives evaluated satisfactorily.
- 2) integration stopped because $v(y_0 + Jy_2, y_2)$ became non positive.
- 3) step count exceeded n .

Reasonable values for $\bar{k}$ were determined by precision trials in which 20 to 2000 forward integration steps were used. From 100 to 500 forward integration

steps were sufficient to determine the function F and derivatives with adequate precision for the hill-climbing methods to be described below (the number depending on y_{e_2} and the rate function parameters) in the cases where the hill-climbing was successful; where it was abandoned 500 steps ensured a relative precision of 0.001 in each derivative. On an I.C.T. Atlas approximately 5 seconds was required to evaluate the function and derivatives using 500 steps forwards (and 1000 backwards) for the push-pull reactor, and approximately 3 seconds for the empty-full reactor..

c) Hill Climbing using derivatives evaluated by the forward backward integration procedure.

The minimization of F was attempted in all cases listed in Tables 6.2 and 6.3, and was successful except in the three cases marked with queries.

The problem of minimising $F(b_0, b_1)$ is unconventional in that the set of points (b_0, b_1) for which F is defined is not known in advance. The methods used for treating this problem were based on the following assumption: suppose P_1 and P_2 are two interior points

of the first quadrant of the (b_0, b_1) plane, and P_2 is inadequate while F at P_1 is F_1 . Then it is assumed that there exists a point P_3 between, and on the line joining P_1 and P_2 such that only points between P_3 and P_2 are inadequate.

The first strategy used was to bracket together the exits (2) and (3) above from the function evaluation routine and assign to F some fictitious value (such as $2\bar{k}n$) and also to the derivatives with respect to b_0 and b_1 , and start hill-climbing with values (b_0, b_1) known to be reasonable: this procedure was used with a programme based on a simplification of Davidon's¹ method, kindly furnished by Dr. M.J.D. Powell, and was quite satisfactory² except for the first set of reaction rate

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1. A powerful iterative gradient method with quadratic convergence which starts with a given symmetric positive definite matrix Y_0 which is modified step by step generating $Y_1, Y_2 \dots Y_i \dots$, in such a way that Y_∞ , the inverse Hessian matrix at the minimum is (in general) rapidly approximated. For points (b_0, b_1) not unreasonably far from the coordinates of the minimum, the hill-climbing step is $- Y_i \text{ grad } F$. See References 7 and 80.
 2. About 10 to 40 function evaluations being required to go from a crude estimate to an extremely precise one.

parameters (for conversions $y_{e2} > 0.25$), and for the second set of reaction rate parameters for $y_{e2} \geq 0.9$). The method might have succeeded in finding the minimum in all the cases where it was subsequently found if allowed enough function evaluations but, because it was obviously inefficient, some modifications were made. (This was the sort of trouble which occurred with the "fictitious values" method: suppose F was evaluated at a point P_1 , (relatively far from the point corresponding to the minimum F) at some stage of the process, and the next point produced by the hill climbing routine was P_2 , which turned out to be relatively far from P_1 and also inadequate - then it commonly occurred that many subsequent points were either very close to P_1 or very close to P_2).

A modified procedure used was in essence as follows:

If the first point turns out to be inadequate¹ then a fault exit is taken. Otherwise the procedure is essentially the same as Powell's except if an inadequate point P_2 should turn up subsequently, in which case the next point to be tried is P_3 , the mid-point of the line

1. Or to give rise to an excessive step count.

joining P_2 to P_1 . (P_1 corresponds to the lowest value of F so far computed). If this point (P_3) is inadequate the bisection process is repeated. Counts are kept of the number of function evaluations since the last inadequate point in each of the two stages of the hill climbing procedure¹, and these may be used to limit movement in an effort to reduce unproductive excursions into the inadequate region.

The computer accessibility was not good enough to enable the two methods to be compared in a reasonable period of time; the latter method was used to carry on from points at which the former method had been abandoned.

Both hill-climbing methods produced a sequence of points corresponding to decreasing values of F . The trajectories generally consisted of a few points to get to the trough (see Fig. 6.5) followed by a number of points lying close to the bottom of the trough. A method which naturally follows trough is desirable because if there are local minima of interest they will lie in the trough so the hypothesis of unimodality can

1. In Powell's method the function F is in general evaluated either at a point obtained by cubic interpolation along a line (on which F and its derivatives is known at two points) or at a point which together with the previous best point defines a new line.

be tested by using two widely separated starting points, each close to the trough. Such a verification was only attempted in one case and proved exceedingly time-consuming; based on the preliminary investigations carried out it seemed reasonable to assume however that the function F had only one local minimum for all values of problem parameters used, and this was done.

In the three cases marked with a query in Tables 6.2 and 6.3 the function $F(b_0, b_1)$ was very badly behaved: in fact, even for the case shown in the fifth row of Figure 6.3, where we are fairly confident to have found $\hat{b}_0$ and $\hat{b}_1$, if $\hat{b}_0$ is multiplied by 1.000,000,05 (and $\hat{b}_1$ left unchanged) an inadequate point¹ is obtained! Except in these four cases, the behaviour Powell's method close to the point $(\hat{b}_0, \hat{b}_1)$ was excellent, the magnitude of each derivative being reduced by a factor of 1,000 to 100,000 in a few steps, each so close together that the first six significant figures or so of both b_0 and b_1 remained constant, F itself only

1. The figures $\hat{b}_0, \hat{b}_1$ in Table 6.3 are of course rounded. Closer figures are 610.26148864 and 110.18130553.

changing by a factor of 0.999 or so.

The reason for bothering to locate the minimum so precisely is that one wants to be sure that one has a minimum and is not stopping perhaps far from the minimum at a place where the derivatives appear to be small. Besides, it is only at the minimum that one can make use of $\frac{\partial F}{\partial x_2}$ which is obtained as a bonus, and (even in moderately well-behaved cases) this quantity fluctuates wildly (even taking on negative values) for all but the last few hill-climbing steps.

VI.V. The Optimal Controls and the impossible region.

The results of the minimizations are shown in Tables 6.2 and 6.3 and Figures 7.1 to 7.3 (in which the $\frac{\partial F}{\partial x_2}$ information is utilised so that not only the points but the tangents (long lines) are plotted as well).

It is clear from Tables 6.2 and 3 that $\hat{b}_0$ and $\hat{b}_1$ are both decreasing functions of y_{e2} - as one would expect. The variation of b_1 with y_{e2} is very marked and of course reflects the variation of

$$\max_T v(y, T)$$

with y (if a trajectory in the y, T plane is to depart

much from an adiabatic then b_1 must be much larger for small y_{e2} than for large).

What is the practical significance of the impossible region? Suppose for example that we were interested in a reactor with $y_{e2} = 0.9$ corresponding to row 11 in Table 6.2 and that this exit conversion were essential. To overdesign on heat exchange making $b_1 = 8$ say at the design flowrate would appear from Fig. 6.5 to prevent a conversion of 0.9 being attained at any flowrate and with any inlet temperature if b_1 were independent of flowrate. In general however b_1 will be an increasing function of the flowrate so that the the design conversion could be achieved but only at a reduced flowrate. Thus the penalty for overdesign on internal heat exchange is far more serious than the penalty for underdesign, an unusual situation in engineering.

What can we say about the proximity of $\hat{b}_0, \hat{b}_1$ to the impossible region? It appears that this is connected with the mathematical formulation of the problem where y_{e2} is specified. It is clear from

Fig. 6.5 and Table 6.2, that a reactor with values b_0 , b_1 both slightly larger than the figures in row 11, but with the same values of y_{a_1} and F would have a y_{e2} slightly lower than 0.9.

The performance of these reactors is compared with other indirectly controlled reactors in Chapter VII.

V.VI. The Stability of U-Tube reactors.

We have considered above only a steady state (or quasi steady state) of the U-tube reactors. The question of the stability of this steady state (with or without control devices) is of course important.

Much work has been done on reactor stability and control: see for example References 47, 48, 50, 51, 52, 53, 58.

V.VII. Optimum heat transfer distribution.

Suppose a in 6.17 is not a parameter, but a function $a(t)$, and the function $a^*(t)$ which minimizes F is sought. For the empty-full reactor (if a is unrestrained) the solution is simply to assign a in such a way that the rate is everywhere maximum. For

the push-pull reactor the situation is more complicated. As a first step, consider the variation in F produced by changing a by da over an interval dt . It can easily be shown that:

$$dF = - W_3^* da |dt|$$

Now W_3^* is shown in Fig. 6.7. (for a given set of problem parameters). From the shape of this curve it can be deduced that by decreasing b_1 (from $\hat{b}_1$) for $0 < t < 0.1072$ and increasing it for $t > 0.1072$, one can decrease F .

V.VIII. Accounting for heat exchange cost.

In a practical case a cost function which includes the cost of heat exchange can always be constructed in such a way that we remain with a hill climbing problem in the two variables b_0 and b_1 .

TABLE 6.2.

PUSH - PULL REACTOR RESULTS

(Note: 1.5,3 means 1.5×10^3 ; 6,-2 = 0.06 etc.)

		$\hat{b}_0$	$\hat{b}_1$	y_{e2}	$\log(y_{e2}/1-y_{e2})$	$\log(2F)_{\min}$
SET OF REACTION RATE FUNCTION PARAMETERS	1st. i.e. ($A'/A=1.5$)	1134.7	1.531,8	0.090909	-1	-7.1646
		983.4	2.341,6	0.240254	-0.5	-5.6787
		833.2	5.412,4	0.5	0	-4.2336
		701.5	1979	0.76149	0.5	-2.8933
		614.1 ?	146.1 ?	0.9	0.9542	-1.7966 ?
		533.5 ?	8.166 ?	0.96963	1.5	-0.5479 ?
	2nd. i.e. ($A'/A=2$)	1117.3	4.972,4	0.090909	-1	-3.7191
		970.8	2699	0.240254	-0.5	-2.7453
		822.7	226.3	0.5	0	-1.8148
		690.5	26.58	0.76149	0.5	-0.9774
		603.7	5.332	0.90000	0.9542	-0.3384
		528.8	1.002	0.96963	1.5	0.3426
	3rd. i.e. ($A'/A=3$)	1089.8	817.7	0.090909	-1	-2.0492
		951	88.37	0.240254	-0.5	-1.3322
		810.2	14.87	0.5	0	-0.6639
		681.8	3.403	0.76149	0.5	-0.0815
		588.6	1.052	0.90909	1	0.3845
		521.3	0.3993	0.96963	1.5	0.7742

TABLE 6.3.

EMPTY - FULL U - TUBE REACTOR RESULTS

(Note: 1.567,3 means 1.567×10^3 ; 2,-1=0.2 etc.)

		$\hat{b}_0$	$\hat{b}_1$	y_{e2}	$\log(y_{e2}/1-y_{e2})$	$\log F_{\min}$
SET OF REACTION RATE FUNCTION PARAMETERS	1st. i.e. ($A'/A=1.5$)	1100.5	2.1777,8	0.090909	-1	-7.2675
		960.2	2.7639,6	0.240254	-0.5	-5.8153
		820.2	5.8889,4	0.5	0	-4.4257
		693.6	2098.77	0.76149	0.5	-3.1142
		610.26	110.18	0.90909	1	-1.9186
		530.34?	8.292?	0.96963	1.5	-0.7774 ?
	2nd. i.e. ($A'/A=2$)	1059.7	1.0335,5	0.090909	-1	-3.7831
		927.2	4065.3	0.240254	-0.5	-2.8312
		793.3	264.43	0.5	0	-1.9465
		671.99	28.952	0.76149	0.5	-1.1585
		590.42	5.7438	0.9	0.9542	-0.5447
		518.99	1.06839	0.96963	1.5	0.1225
	3rd. i.e. ($A'/A=3$)	1011.2	2625.7	0.090909	-1	-2.0857
		887.7	182.158	0.240254	-0.5	-1.3815
		760.6	20.634	0.5	0	-0.7423
		644.7	3.9162	0.76149	0.5	-0.1997
		560.5	1.1388	0.90909	1	0.2335
		499.8	0.42223	0.96963	1.5	0.5991

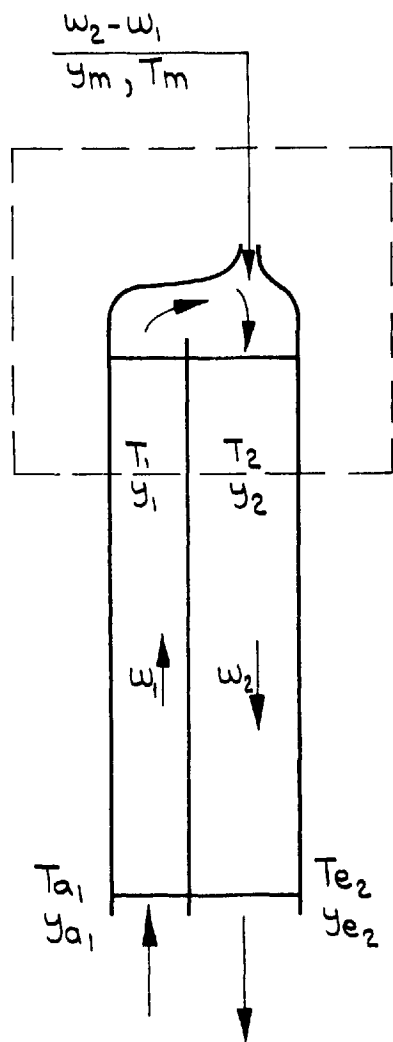


Fig. G.1.

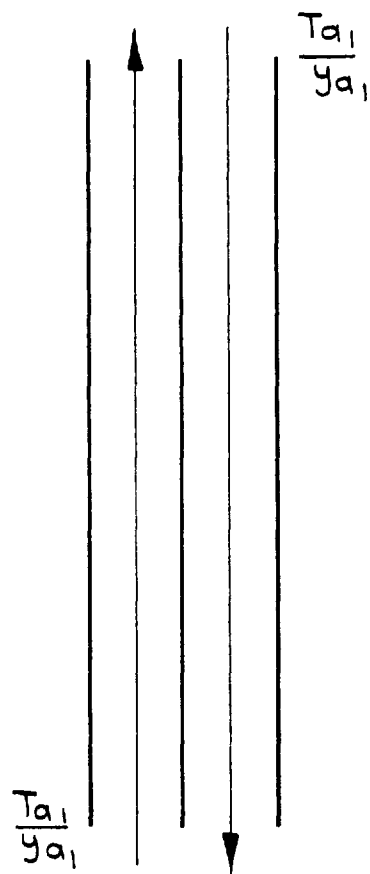


Fig. G.2.

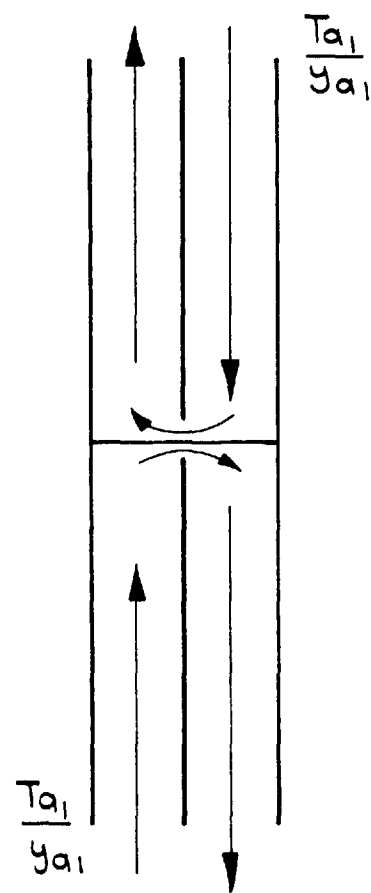


Fig. G.3.

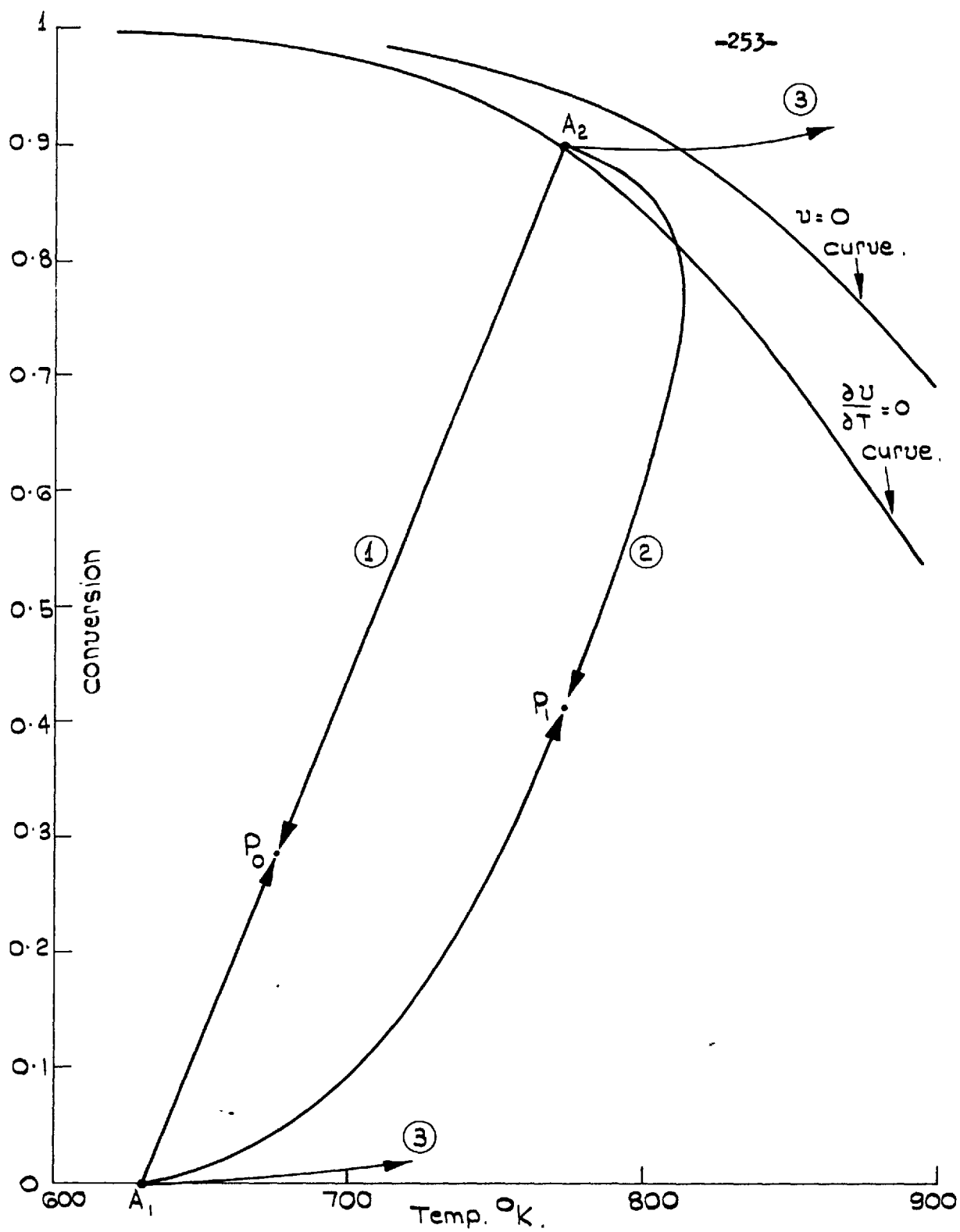


Fig. G.4.

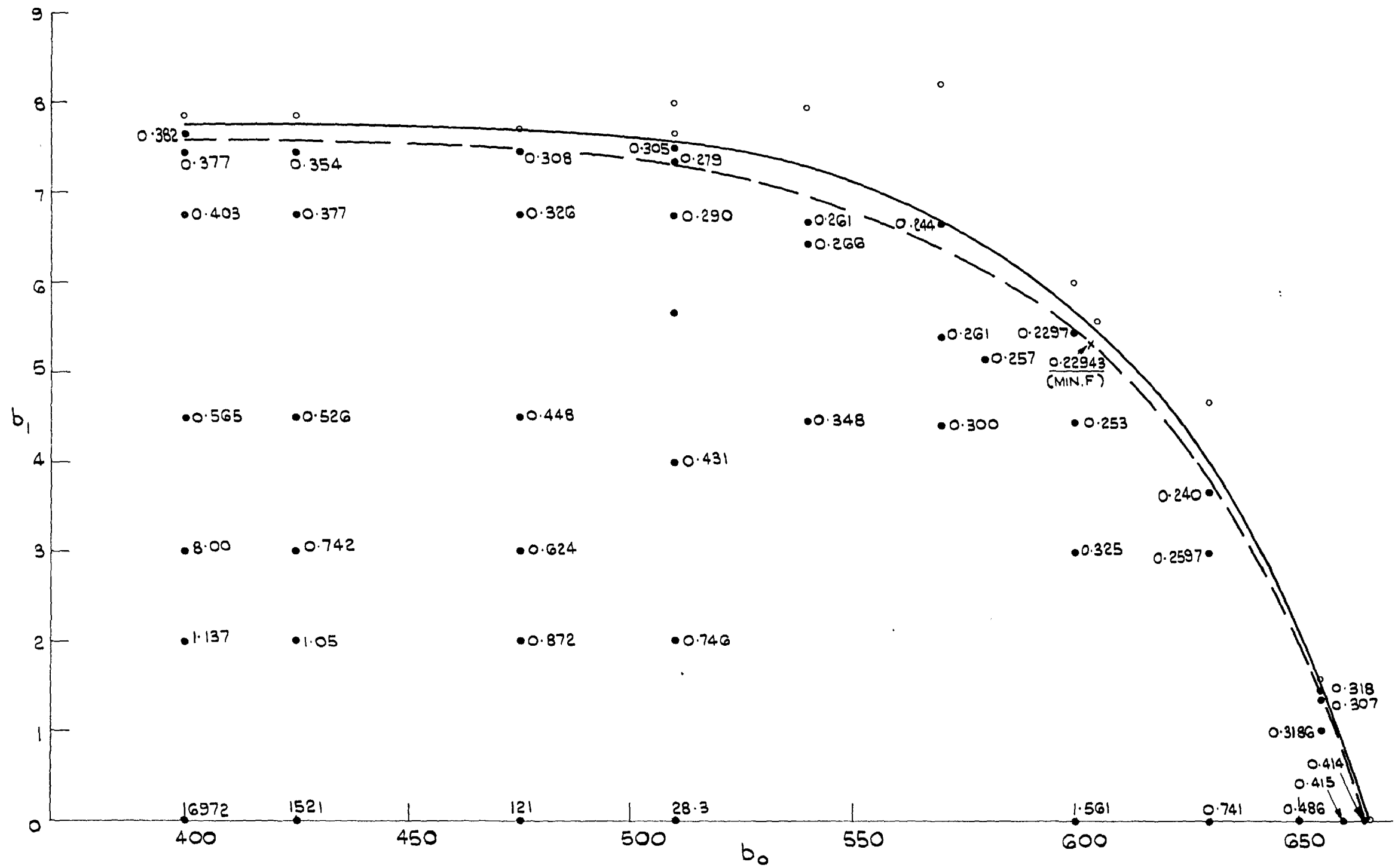


Fig. 6.5.

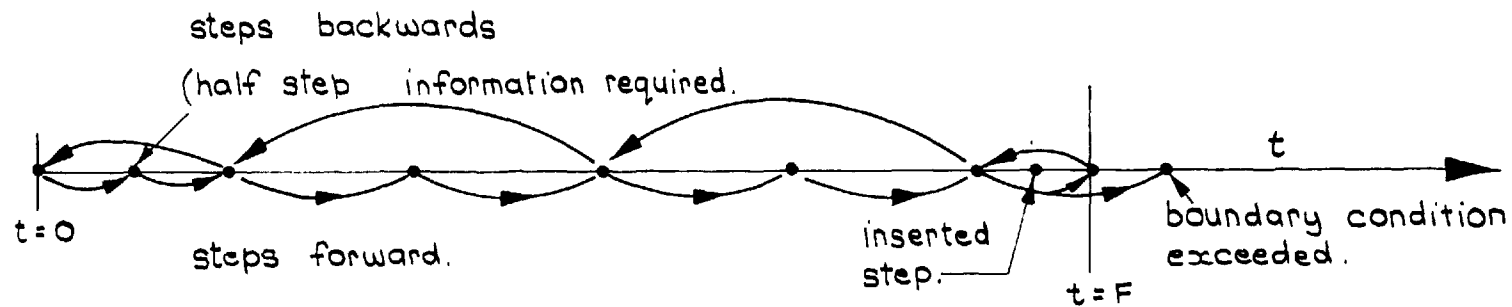
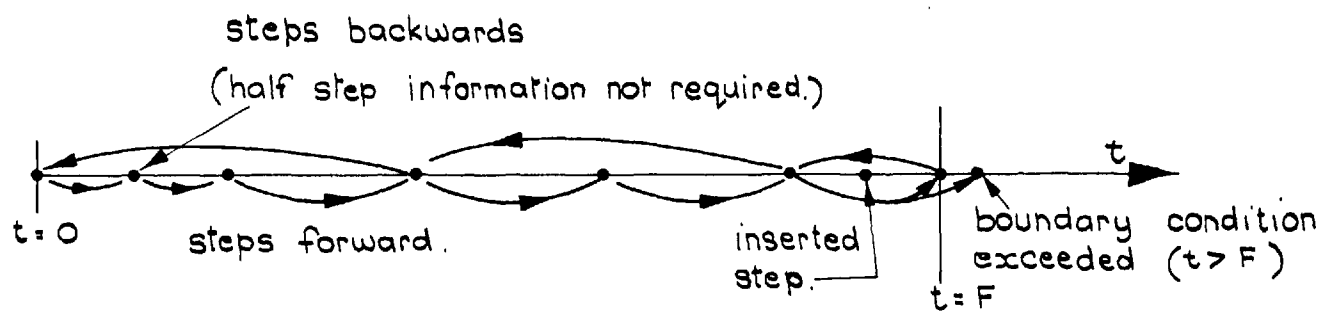


Fig. 6.6.

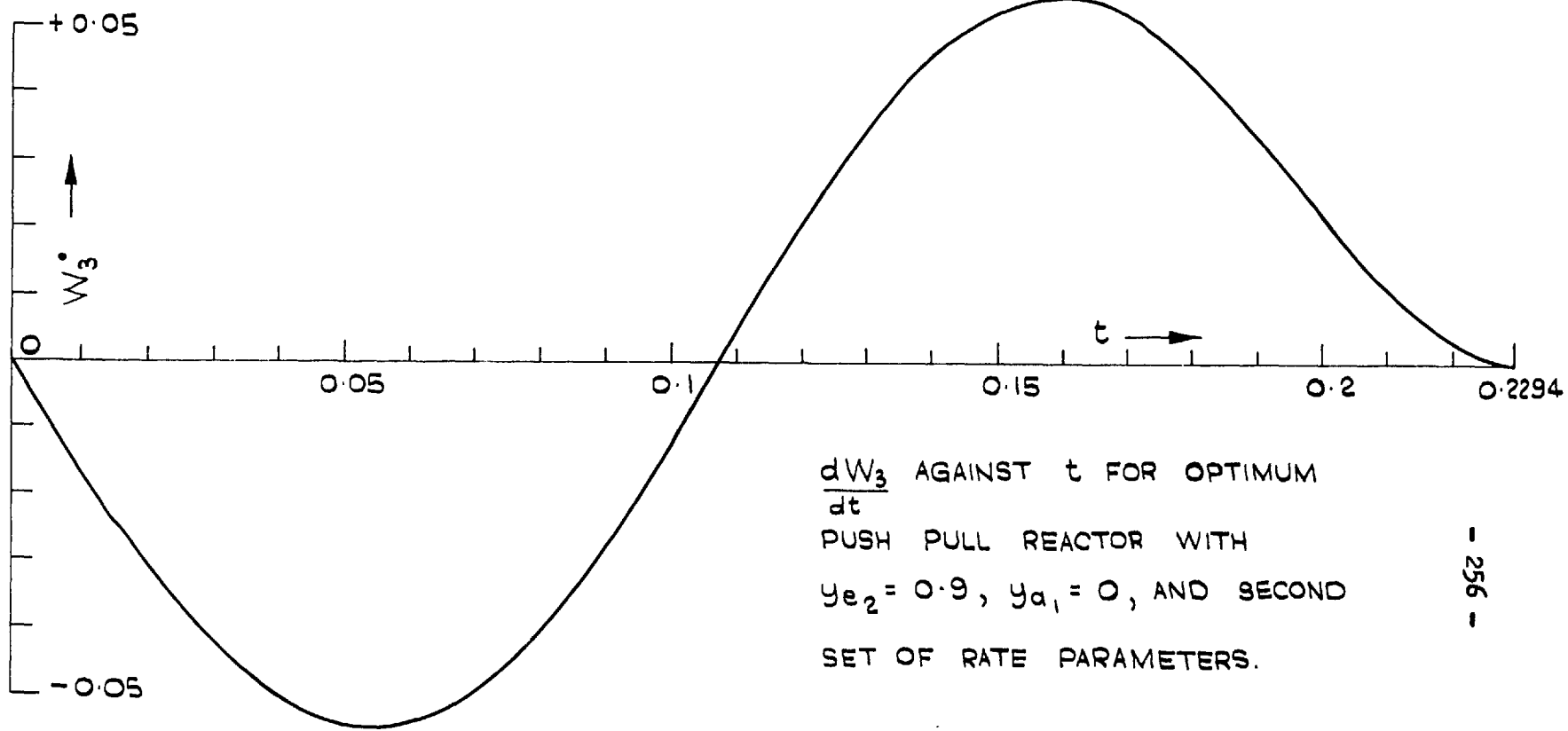


FIG. G.7.

CHAPTER VII

COMPARISON OF REACTORS

The $y_f, (m_f)_{\min}$ results (for $w=1$) for the 1,2,3,4 and ∞ staged indirectly controlled adiabatic cascades, the single stage continuous stirred tank reactor, the empty-full, and push-pull reactors¹ are shown in Figs. 7.1 to 7.3. In general the empty-full and push-pull results are shown as point and slope (the long line in the empty-full case). Let us start with the case $N = \infty$. The curves in Figs. 7.1 and 2 were obtained both by using the programme for direct control described in Chapter IV, giving Θ_m the (fictitious) value -10^{20} degrees K, some points being verified by evaluating the elementary integrals obtained by putting $r = 1.5, 2$, and 3 in A3.1; the points for $N = \infty$ in Fig. 7.3 were obtained only by the latter method.

It is easy to show that for $N = \infty$ the asymptotic slopes:

$$\frac{d \log(m_f)}{d \log(y_f/(1-y_f))}$$

as $y_f \rightarrow 0$ should be $A'/(A'-A)$, and as $y_f \rightarrow 1$ should

1. The points marked with a query in Fig. 7.1 have the correct abscissa but the ordinate may conceivably be lower. See discussion in Chapter VI.

be $A/(A'-A)$. The slopes at either end of the $N = \infty$ curves in the figures are close to these numbers. For the tank reactor the entire curves are straight lines of slope $A'/(A'-A)$, while as $y_f \rightarrow 0$ the asymptotic separation from the corresponding $N = \infty$ curves, i.e.

$$\log(m_f)_{\min(\text{tank})} - \log(m_f)_{\min(N=\infty)}$$

may easily be shown to be $\log(A'/(A'-A))$, i.e. 0.4771, 0.3010, 0.1761 for A'/A 1.5, 2, and 3 respectively; the corresponding figures taken from the left hand ends of Figs. 7.1 to 7.3 are 0.5, 0.3, and 0.2 respectively which seem reasonably close.

In the following discussion it will be assumed that for a given reactor type the cost of reactor control (for $w_f=1$) depends on the number of control devices only.

The single tank, single tube results are interesting. For the second and third set of rate function parameters, where the activation energies are moderate, the tank is inferior to the tube for all y_f in the ranges investigated, and it would seem that the larger y_f the worse it is. For the first set of rate function parameters, however, the tank is worse for y_f below

about 0.85 and better for higher conversions. In this comparison the inlet temperatures to the adiabatic tube and tank were of course separately adjustable, (the optimum inlet temperature for the tank being always lower than that for the tube); R. Aris (Ref. 33) carried out a comparison of a tank with a tube for a given inlet temperature which was the same for both.

The empty-full U-tube reactor (for which m_f is the volume of the packed tube only) has two heat exchangers (feed preheater and internal exchanger) and can be seen to require from about 0.9 - 1.1 times as much catalyst as the two stage tube (which also has two heat exchangers).

The push-pull (or full-full U-tube reactor) appears to be practically no improvement (it cannot be worse) over the single tube for small y_f but the improvement increases with y_f : for $y_f = 0.9$, for example, the push-pull reactor requires for the 1st, 2nd, 3rd set of rate function parameters; 3.0, 2.1, and 1.7 times as much catalyst respectively as the perfect indirectly controlled reactor, whereas the one stage reactor requires 22, 3.7, and 2.0 times as much as the perfectly controlled reactor. The push-pull reactor has internal

heat exchange it is true, but this might well be provided more cheaply than the conventional interstage heat exchanger for a two stage reactor. The full-full U-tube reactor is not very attractive, but at any rate the catalyst required is never as much as twice that required by the empty-full reactor so if we consider the case where the reaction takes place at high pressure, (such as a T.V.A. ammonia reactor) where it is the high pressure volume that one wishes to reduce (the catalyst is cheap), then it would appear that one could improve the converter by using less tubes of a larger diameter packed with catalyst.

The directly controlled adiabatic cascades for $T_m = 300^\circ\text{K}$ (Figs. 5.12 - 5.14) may also be compared with the push-pull and empty-full reactors. The push-pull reactor requires at most about 1.4 times as much catalyst as the two stage reactor; for $y_f = 0.97$ however, for the first set of parameters the catalyst requirement is about the same for both whereas for the second and third sets the push-pull reactor requires about 10 and 13 per cent more catalyst. The empty-full reactor almost always requires less catalyst than the

two stage directly controlled reactor.

A complete parametric investigation for a first order/Arrhenius reaction rate expression and constant adiabatic temperature rise coefficient has not been carried out (although for perfect indirect control and for the tank all cases for which $A'/A=1.5, 2,$ and 3 - in the y_f range examined - can easily be deduced from the results¹) but those who might wish to carry out such an investigation should of course transform our equations, introducing dimensionless variables so as to avoid wasteful computation; for example, for the push-pull reactor the six parameters H, H', A, A', J and b_1 can be combined into four by replacing the enthalpy function Θ by a new variable Θ/J , and t by a new variable Ht .

We have examined the performance of a large number of reactors from a broad point of view. In a practical design case the field would be narrower and the objective function more complicated. Much has been written on the balance which must be made between describing the economics accurately and reducing the computational effort. See for example Refs. 30, 31.

1. This information is not new of course.

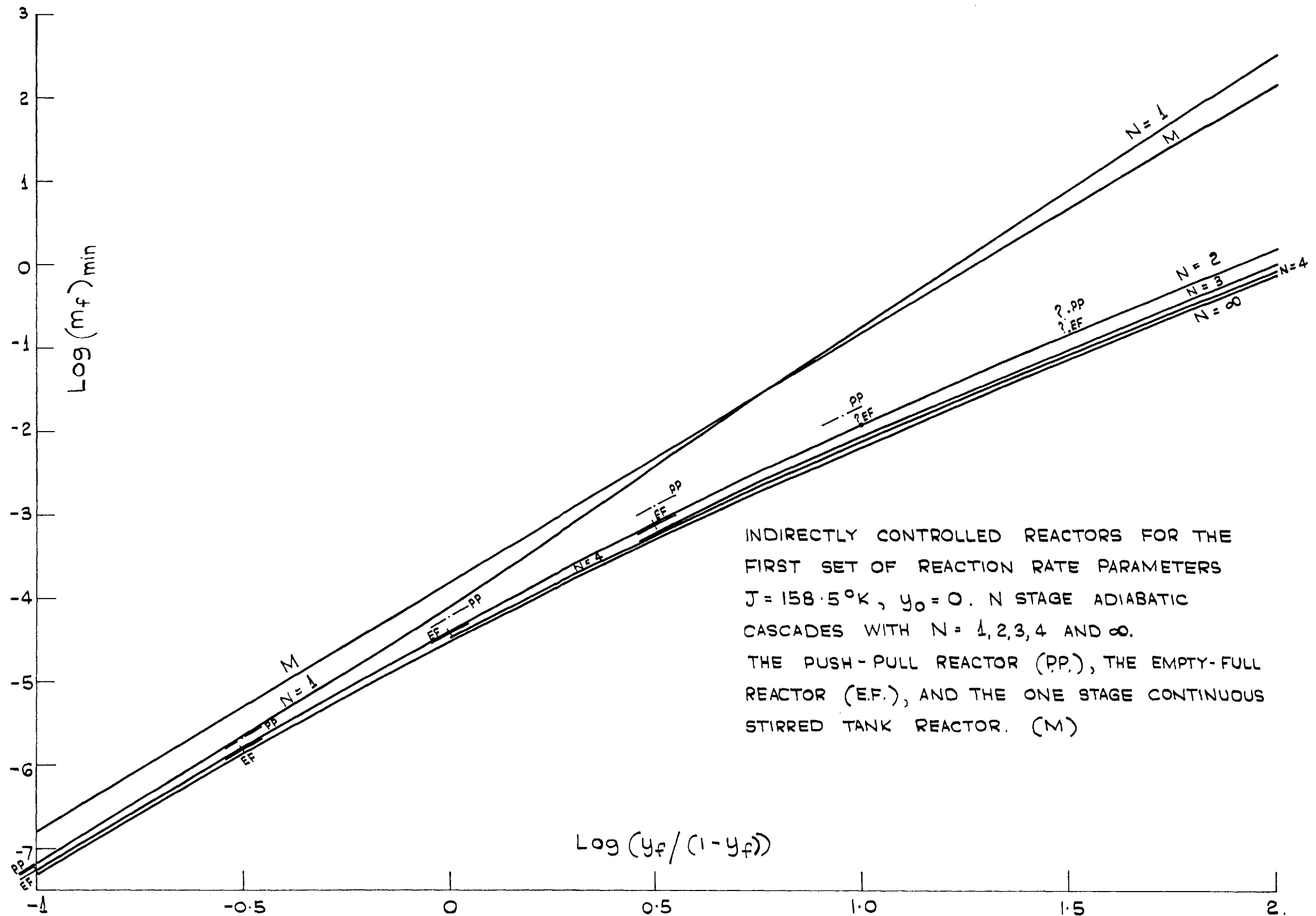
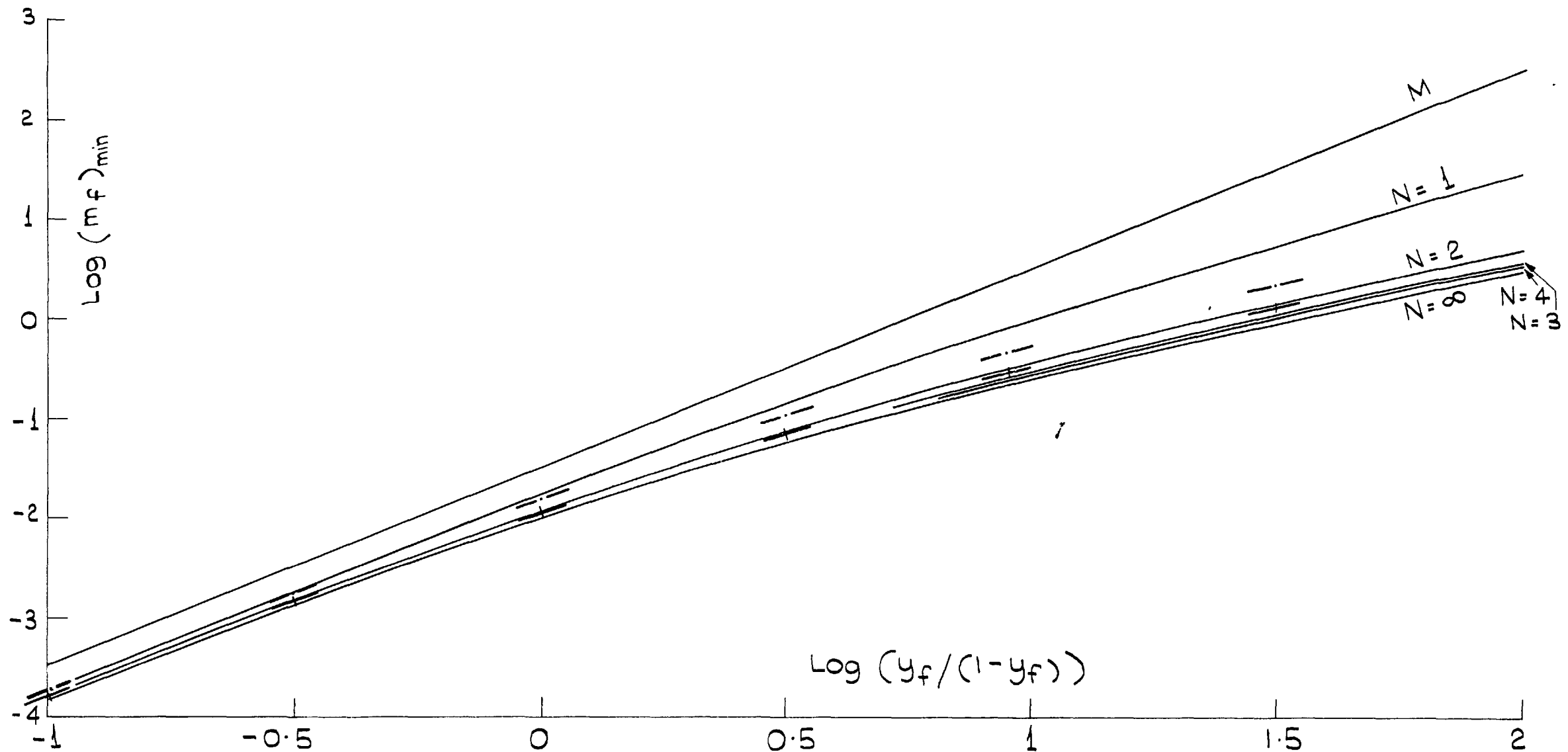


Fig. 7. 1.



INDIRECTLY CONTROLLED REACTORS FOR THE SECOND SET OF RATE PARAMETERS. $y_0=0$, N STAGE ADIABATIC CASCADES WITH $N=1, 2, 3, 4, \infty$. THE PUSH-PULL REACTOR ($- \cdot -$), THE EMPTY FULL REACTOR ($- + -$) AND THE ONE STAGE CONTINUOUS STIRRED TANK REACTOR (M).

Fig. 7. 2.

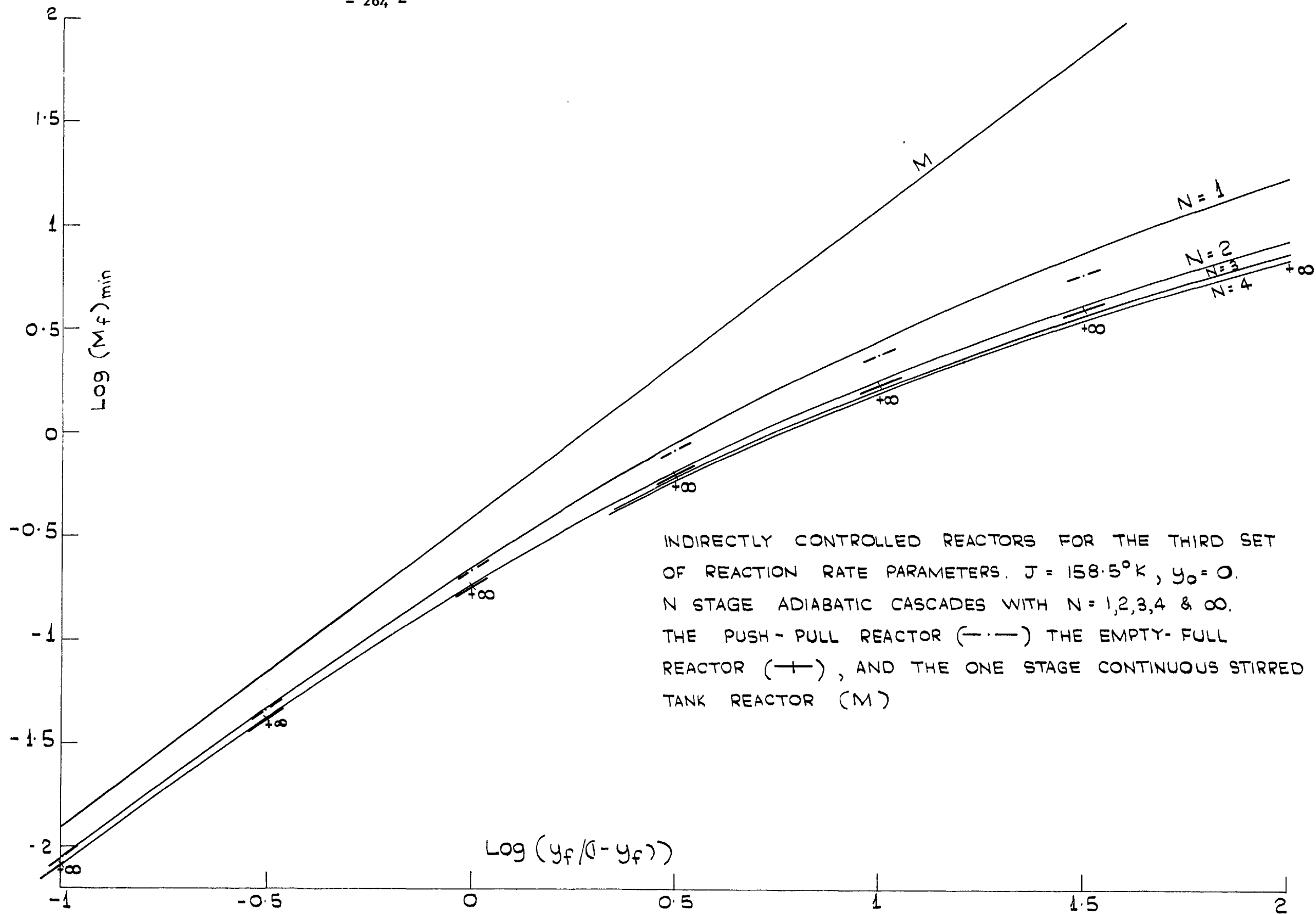


Fig. 7.3.

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