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BY
BOUNDARY CONTROL IN TEMPERATURE
OF REACTORS WITH
DECAYING CATALYST

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by

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A Thesis
Submitted to the School of Graduate Studies
in Partial Fulfilment of the Requirements
For the Degree
Master of Engineering

McMaster University
April 1973

MASTER OF ENGINEERING (1973)
(Chemical Engineering)

McMaster University
Hamilton, Ontario

TITLE: Optimization by Boundary Control in Temperature of Reactors with Decaying Catalyst.

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NUMBER OF PAGES: xi, 193.

SCOPE AND CONTENTS:

A quasi-steady state optimization of an adiabatic, fixed bed tubular reactor, with catalyst decay, is considered.

The optimal inlet temperature (distribution) $T_0(t)$, is sought, so as to maximize the total amount of reaction in a fixed given period of time. Upper and lower bounds are placed on the inlet temperature.

A single irreversible reaction is considered with a reaction rate expressible as separable functions of inlet temperature, conversion and catalyst activity.

The rate of catalyst decay is expressed in an analogous manner and in particular, the conversion dependence is maintained.

The optimal policy of choosing the temperature so as to maintain the exit conversion constant in time when catalyst decay is independent of conversion, is examined.

The extension of this constant conversion policy to the present system is discounted.

New optimum seeking methods are developed and numerical calculations presented to illustrate the optimal profiles.

ACKNOWLEDGEMENTS

I would like to express my sincere gratitude to my supervisor Dr. C.M. Crowe for his guidance and encouragement throughout the course of this study.

I extend my appreciation to Mrs. Sheelagh Courtney and Mrs. Lynn Smith for their conscientious typing.

I express appreciation also, for the financial assistance received through McMaster University.

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CHAPTER 1

INTRODUCTION

Many examples in the chemical industry are to be found where a fixed bed catalytic reactor forms the basis of the process. The catalyst may take several forms - one common form being small solid porous pellets, which are packed into a tubular reactor. The reaction fluid flows through and around the pellets and reacts to form the products.

In the process of product formation, the catalyst begins to "age" and its activity begins to fall off in time, until it reaches a point where its catalytic properties have so deteriorated that it must be either regenerated or exchanged for fresh catalyst.

This aging process is caused by several factors and can usually be expressed as a function of the conversion in the reactor as well as the temperature. Many reactors are controlled using the temperature and it is of great interest to determine that temperature profile which maximises some profit function, such as the integrated exit conversion over time.

In practice it is usually not possible or economically feasible to control the temperature at every point along the length of the reactor, as well as at each point in time. In these instances, one may have to be content with a uniform temperature control instead of a distributed control, i.e. we maintain the temperature in the reactor uniform along its length and change this value (in some optimal fashion) continuously in time as the reaction proceeds.

An alternative is boundary control of the reactor. Here one would control only the inlet temperature to the reactor. This type of control is encountered frequently in adiabatic reactors. The temperature is often bounded between two limits.

Another area of boundary control is the determination of the optimal initial catalyst activity distribution for an adiabatic reactor.

It is, of course, possible to combine these problems and determine the optimal inlet temperature and initial catalyst distribution in the reactor.

In the above examples the control is a function of the one variable (time or distance) only, as opposed to distributed control, where the temperature is controlled at each point along the reactor as well as in time. This restricted form of control can be loosely referred to as boundary control or uniform control.

A common practice in industry has been to control the reactor temperature in such a way as to maintain the exit conversion constant in time. It has been shown [Crowe (1970) and Thérien (1971)] that, for the class of reactions in a plug flow, fixed bed, tubular reactor with catalyst decay (whose reaction rate equations may be expressed as a single, separable function of conversion, catalyst activity and temperature) this is indeed the optimal policy in that it maximises the integrated exit conversion. However, these workers in order to simplify the analysis, considered the decay rate or aging of the catalyst to be independent of the conversion. This assumption serves to decouple the system equations and greatly simplifies the mathematical analysis of the optimal system.

No analytical or numerical work has been reported for the more general case where catalyst decay depends on the conversion in the reactor. The introduction of conversion dependence, couples the decay rate equation with the reaction rate, seriously complicates the analysis of the optimal profile and serves also, to introduce instability into the numerical optimal seeking methods and integration methods of the system equations. To date, no general or specific proof exists, establishing the validity of the constant conversion policy, when the catalyst decay depends on conversion, irrespective of whether distributed or boundary control is used.

Furthermore, no generally established proof of a strong maximum principle for boundary control of distributed systems exists. Pontryagins maximum principle (1962), which is a strong maximum principle (as described in Chapter 4), is not applicable to systems described by partial differential equations. Other workers Sirazetdinov and Degtyarev (1967) and Jackson (1965)] have developed maximum principles using first order perturbation methods: however, both these formulations are weak forms (as explained in Chapter 4) for boundary control of non linear systems and thus serve to introduce into the analysis a large class of possible policies, called 'Pontryagin Policies', which may or may not be optimal, but among which, the optimal policy (if it exists) will be. The engineer then usually has to turn to the physical system to ensure the existence of an optimum and to distinguish between the possible policies.

In the present study, special cases of the more general forms of catalyst decay are investigated analytically, to determine whether the common principle of maintaining exit conversion constant, can be extended to boundary (or uniform) control of tubular reactors, where the catalyst decay is conversion dependent.

A new Fixed Point algorithm is developed for the optimum search and combined with existing gradient search methods to obtain the optimum.

A brief literature survey of past and current developments is given in Chapter 2.

In Chapter 3, the mathematical model for the reactor is developed and a mathematical statement of the optimal problem is presented.

Chapter 4 deals with the optimal system itself and formulates the necessary condition for optimality.

Analytical properties of the optimal system are derived in Chapter 5 and some properties of the optimal exit conversion are proved.

In Chapter 6 new algorithms are developed and used to investigate properties of the optimal profiles.

Chapter 7 presents a summary of the main conclusions and points to further work in this area.

CHAPTER 2

LITERATURE SURVEY

2.1 Distributed Systems

The well known maximum principle of Pontryagin (1962) was developed for lumped parameter systems, that is, for systems which may be adequately described by variation in one dimension only, thus leading to a set of ordinary differential equations.

For the present system, it is necessary to consider both the spatial and time variation of the system variables and thus our system is governed by partial differential equations and is referred to as a distributed system.

Extension of Pontryagin's work to include distributed systems has been partially successful but one notable area of deficiency is the lack of a strong form for the boundary control of these systems.

The strong form of the maximum principle is discussed in Chapter 4.

2.2. Early Work

Most of the early work is to be found in the Russian literature; a comprehensive survey has been given by Butkovskiy, Egorov and Lurie (1968).

Katz (1964) formulated a very general maximum principle using a functional analysis approach. His approach, though sound, has not been adopted widely in the engineering fields; probably due to the difficulties encountered in applying his general approach to specific problems. However, there seems to be evidence that this functional analysis approach is becoming more popular and recently there has been both analytical [Yang (1972)] and computational efforts [Chang (1970)] in this direction.

2.3 Recent Work

2.3.1 Analytical

One of the most comprehensive papers brought out in this area is due to Sirazetdinov and Degtyarev (1967). Sirazetdinov (1964) initially derived a maximum principle for processes described by a quasilinear, first order partial differential equation. A serious disadvantage was that only one dependent variable was allowed. He, along with Degtyarev, extended this treatment in 1967, to cover systems described by simultaneous sets of quasilinear equations of the following form

$$\text{Maximise } I = \int_0^\tau \int_0^L G_1(\underline{X},\underline{u})\,dz\,dt + \int_0^\tau G_2(\underline{X}(L,t),\underline{u}^0(t))\,dt + \int_0^L G_3[\underline{X}(\tau,z)]\,dz \tag{2-1}$$

subject to

$$\frac{\partial X_i}{\partial t} + \sum_{j=1}^{N} A_{ij}(z,t,\underline{X})\,\frac{\partial X_j}{\partial z} = F_i\,(z,t,\underline{X},\underline{u}) \qquad i=1\ldots.n \tag{2-2}$$

where

$X_i(z,t)$ $i = 1,n$ are the dependent variables of the system, varying spatially (z) and in time (t)

$A_{ij}\ (z,t,\underline{X})$ are the generally non linear coefficients

$F_i(z,t,\underline{X},\underline{u})$ are the inhomogeneous terms

I is the objective function which is to be maximized subject to the system (2-2)

G_i are the integrands of the objective function and are functions of the dependent variables and the controls $\underline{u}$

However, there is still the question of sufficiency to be dealt with, for even though we have an admissible control which causes the Hamiltonian to have its largest value, we are not assured that this control is indeed the optimal control, since the maximum principle provides only a necessary condition for optimal control.

The establishment of general sufficiency conditions in a maximum principle is extremely complex. If both the system equations (2-2) and the objective function are linear, second order perturbations become zero and Sirazetdinov and Degtyarev's (1967) theorem becomes a necessary and sufficient condition for the optimum.

Of course, one still has to consider the question of uniqueness,for there may be more than one admissible control which maximizes the Hamiltonian. In these cases the engineer (and often the mathematician too) has to rely on his knowledge of the physical system.

Thérien (1971) has applied Sirazetdinov and Degtyarev's theorem to a fixed bed catalytic reactor system.

2.3.2 Boundary Control

In Sirazetdinov and Degtyarev's (1967) treatment of boundary control, they defined a separate Hamiltonian function which due to their first order perturbation analysis, provides them with a statement concerning only the stationarity of the objective function and not its extremum. Although this point is not emphasized in their paper, it is quite clear if one examines the form of their optimal condition and the perturbation analysis accompanying them. However, for the special case where both the objective function and the system equations (2-2) are linear, their boundary Hamiltonian is of the strong form.

Ogunye and Ray (1971) following Jackson's (1966) methods, derive a generalized weak maximum principle which applies to both distributed and boundary control. It turns out that, if the control is distinct from a state variable, the boundary Hamiltonians are functions integrated along the dimension which is uncontrolled. For example, in the present study, where control is sought at each point in time only, the Hamiltonian is an integral over the length of the reactor. In the case of initial activity control the control is in fact a boundary condition on a state variable. Here the Hamiltonian condition, although derived analogously, turns out to be in the form such that the adjoint variable (defined in Chapter 4 below) is constant.

2.4 Computation

2.4.1 Method of Characteristics

The method of characteristics has been used by Acrivos (1966) with great success in semilinear systems and proved to be superior to other methods in the case where the characteristics are of constant slope; when this is not the case the method can be used, but may cause difficulties [Lapidus (1962)].

In this present study the characteristic lines are parallel to the z (length) and t (time) axes, making for an extremely convenient application of this method.

2.4.2 Gradient Methods in Function Space

An early, reliable paper by Denn (1966) makes use of a gradient method in function space, or method of steep descent to compute the optimum. He uses a second order diffusion equation and via the method of Greens functions, obtains a necessary condition which forms the basis of a steep descent algorithm to compute the optimal profile.

A comprehensive description is given by Chang and Bankoff (1969) of the general algorithmic procedure for gradient methods.

As with gradient methods in lumped parameter systems,this method suffers from the disadvantage that in the neighbourhood of the optimum, the method slows down and in fact may fail to reach the true optimum within a reasonable number of iterations.

In an attempt to speed up the method Zone and Chang (1972) developed a second order gradient method which is designed to take over from the usual gradient method (which is a first order method) in the neighbourhood of the optimum.

Using a second order expansion of the objective function, a second order estimate of the improved control is obtained. A disadvantage of the method is that this second order estimate is not obtained directly from the Hamiltonian but appears as the solution to a series of simultaneous, partial, two point boundary value equations, which must be solved at each iteration. It appears too, from the results, that the method may suffer from serious instabilities and in fact a smoothing routine is incorporated so as to smooth the second order estimate before it is used to provide a correction in the direction of the optimal profile.

A functional analysis approach to computation has been taken by Chang (1970). He used a steep descent method in Hilbert space. He expresses the solution to the system equations in terms of an integral equation. The objective function is expressed in terms of linear operators and inner products in a Hilbert space. The solution to the optimal control appears in an operator equation of the form

$$A^* u = W \tag{2-3}$$

where

A^* is a self adjoint, positive operator formed from the system, and

W an integral expression.

The steepest descent method is obtained directly from this operator equation and takes the form

$$u^{(1)} = u^{(o)} - d^{(o)}[|| d^o ||^2/<A^* d^{(o)}, d^o>] \tag{2-4}$$

where

$$d^o = A^* u^{(o)} - W \tag{2-5}$$

and $u^{(o)}$ is an initial estimate of the optimal profile

$|| \quad ||$ is the norm for this Hilbert space, and

$<\cdot,\cdot>$ is the inner product for the space

2.5 Fixed Bed Reactors with Catalyst Decay

Much of the early literature on catalyst decay tended to describe the catalyst activity as a function of time on stream, of the reactor. This form gave an averaged description of the decay along the length of the reactor whereas equations describing local decay were avoided.

Anderson and Whitehouse (1961) showed that local characterization of the catalyst activity can be expressed as a function of the local concentration. Szepe (1966) used a deactivation equation to describe the catalyst decay, with a form analogous to a reaction rate equation. He showed that many of the recognised recent forms of catalyst decay are special cases of his general rate of deactivation equation:

$$\text{rate of deactivation} = k(T)\cdot g[\psi]\cdot f(X) \tag{2-6}$$

Crowe (1970) has given a comprehensive treatment of this class of problem, based on Pontryagin's Maximum Principle. He considered a simplified form of (2-6) where decay rate does not depend on conversion. He obtained an analytical characterization of the optimum policy and showed that the constant conversion policy holds at the optimum. Crowe and Lee (1971) extended the results of the single reactor bed case to include several beds in series, each with uniform temperature and catalyst activity.

Thérien (1971) studied this class of problems in the context of Sirazetdinov's and Degtyarev's (1967) maximum principle. He sought to choose the best temperature at each point along the reactor length, as well as at each point in time, $T(z,t)$, so as to maximize the integrated exit conversion over time. He, as well, considered the simplified decay form of (2-6) where conversion dependence is absent. Upper and lower bounds were placed on the temperature and a single, irreversible reaction was considered. His system was described then, by the two equations:

$$\text{rate of reaction} = K(T)F(X)\psi \qquad (2\text{-}7)$$

$$\text{rate of deactivation} = k(T)g(\psi) \qquad (2\text{-}8)$$

Thérien's study showed the strong influence of the parameter, p (p = ratio of the reaction activation energy to the deactivation energy for the catalyst) on the optimal policy. Using this parameter, p,he eliminates the possibility when $p > 1$,of an unconstrained temperature profile forming part of the optimum profile.

He obtains analytical forms for the exit conversion at the optimum and shows, provided that temperature is unconstrained and inlet conversion constant in time, that the policy of constant conversion at the optimum, holds. Thérien considers briefly the influence of the critical catalyst distribution on the optimal policy. He shows that, for a first order catalyst decay, the extremal control T(z,t) is uniform along the length of the reactor irrespective of the uniformity or continuity of the catalyst activity distribution along the reactor length. Nevertheless, for a second order decay form, the extremal control T(z,t) is dependent on the uniformity and continuity of the catalyst profile.

Crowe and Lee (1970b) have considered the general catalyst decay form (2-6) in a batch reactor system. They showed that Levenspiel's and Szepe's (1968) optimal result, which required that the unconstrained temperature be chosen so as to maintain the product of $K(T)\psi$ constant, cannot be extended to the case where catalyst decay is a function of the conversion, as in (2-6).

Ogunye and Ray (1971) derived a generalized weak maximum principle using a first order perturbation analysis. They obtain three Hamiltonian functions, one for distributed control and the remaining two for boundary control of the inlet temperature in time, and initial catalyst activity along the length of the reactor. They consider the quasi-steady state system for r reactions and q catalyst activities of the form

$$\frac{\partial \varepsilon_i}{\partial z} = Q(\varepsilon_j \ \psi_k) \qquad i = 1,\ r \tag{2-9}$$

$$\frac{\partial \psi_k}{\partial t} = g_k(\varepsilon_i \ \psi_j) \qquad k = 1,q \tag{2-10}$$

$$\text{Max } I = \int_0^1 \int_0^1 G(\underline{\varepsilon},\ \underline{\psi},\ \underline{u},\ \underline{v},\ \underline{w})\, dzdt \tag{2-11}$$

where

ε_i is the extent of reaction i,

ψ_k is the k^{th} catalyst activity,

$\underline{u}$ is the distributed control vector, and

$\underline{v}$ and $\underline{w}$ are boundary control vectors in z and t respectively.

Based on their Hamiltonian forms, they develop an efficient gradient method to solve for the optimum profile. For instances where unconstrained policy was optimal they made use of a Conjugate gradient method developed by Lasdon (1967).

All their computations were based on the simplified form of catalyst decay, where no conversion dependence exists. Detailed numerical examples are worked for isothermal and adiabatic reactors, with irreversible and reversible reactions. All their results confirm the constant conversion policy.

For the case of an irreversible reaction in an adiabatic reactor they do a parametric study, the basic results of which may be summarized as follows:

(i) Increasing the heat of reaction, increases the constant conversion portion of the optimal profile for both exothermic and endothermic reactions.

(ii) Increasing the operating life of the reactor decreases both the constant conversion level and the fraction of time spent at the upper constraint.

(iii) Decreasing the reactor length increases the average temperature in the reactor and reduces the fraction of time at constant conversion.

(iv) Increasing the parameter p (see 2.5 above) increases the constant conversion level, increases the average temperature in the reactor, and decreases the fraction of time spent at constant conversion.

(v) Decreasing the maximum allowable inlet temperature for both exothermic and endothermic reactions decreases the constant conversion level, as well as the fraction of time spent at constant conversion.

Ogunye and Ray also consider the catalyst distribution problem, that is, to choose the initial (time) catalyst distribution so as to maximize an objective function which takes into account the average catalyst cost over the lifetime of operation, offset against the exit conversion.

The authors then combine the problems to choose best temperature and initial catalyst activity and require approximately 8 minutes of computing time on an IBM 360/75. For the single problem of choosing best distributed temperature in an adiabatic reactor 3-5 minutes of computing time was required.

CHAPTER 3

THE REACTOR SYSTEM

3.1 Industrial Fixed Bed Catalytic Reactors

In the petrochemical industry a common use of the solid catalyst is the selective inhibition of unwanted side reactions, as well as lowering the ignition point of the reaction. The forms which the solid catalyst can take are many. Usually an important design factor is the total surface area, and as a result, small porous spherical pellets are often encountered.

It is not uncommon to find that, in the design of the reactor, the catalyst is the most economically significant and as a result, much importance is placed on careful control of catalytic reactors, to ensure maximum catalyst life or selectivity. In many processes, the catalyst can be regenerated and optimum regeneration cycle studies has received some attention in the literature.

For non-regenerative catalysts, it is usually economically unfeasible to simply operate the reactor until the catalyst activity is zero and little or no product is formed. In practice, there is often some total time of operation (economically, legally or practically determined) within which, we wish to obtain maximum production (conversion).

Of course, there is some optimal total operation time which can be determined using a simple one dimensional search technique, over a series of optimal policies with different operation times.

In the present study the total operation time is given as fixed.

3.2 Mathematical Model

3.2.1 Introduction

Froment (1970) has given an extensive review of the analysis and design of fixed bed catalytic reactors. His models have been grouped into two broad sections:

(i) Pseudo homogeneous models
(ii) Heterogeneous models

The first class of models do not account explicitly for the presence of the catalyst, whereas the heterogeneous models describe the system as two distinct phases, with separate equations for each.

Within each category, there are three subdivisions, each taking more effects into account and so increasing the complexity of the model.

3.2.2 Pseudo Homogeneous Model

Froment's basic model in this category assumes that concentration and temperature gradients occur only in an axial direction. The only transport mechanism operating in the axial direction,is the overall flow itself, which is assumed to be plug flow.

He states, that in most cases, pressure drop in the reactor is relatively small and it is common to use a mean constant value for the calculations.

The non-steady state reaction equation describing this system, is a first order partial differential equation in z (length) and t (time). The variation of the catalyst activity is incorporated into reaction equation to give an effective reaction rate constant.

To increase the complexity of the model, Froment successively introduces axial mixing to give rise to a second order differential equation, in the steady state, using the concept of effective diffusivity. He comments, saying it has been shown [Carberry (1963)] several times, that for flow velocities often encountered in industry, the effect of axial dispersion of heat and mass is negligible, when the bed depth exceeds about 100 times the catalyst particle diameter.

3.2.3 Heterogeneous Model

For very rapid reactions which are highly exothermic or endothermic or for large catalyst particles it may be necessary to distinguish between conditions in the fluid and the solid catalyst phase.

Froment introduces three levels of complexity for this class of reactors, the basic model here having the same assumptions as the basic pseudo homogeneous model, except that mass and heat transfer are described in separate sets of equations for solid and fluid respectively.

To increase the complexity of the model, Froment adds equations to the basic model, which account for interfacial and intraparticle gradients, when, for the above mentioned case, these properties cannot be assumed to be uniform. To simplify the integrations the concept of an effectiveness factor is introduced. This factor essentially corrects the surface catalyst conditions for the non-uniform conditions within the pellet.

3.2.4 Present Reactor System

The model adopted here lies somewhat closer to Froment's (1970) pseudo homogeneous model. Unlike Froment's basic pseudo homogeneous model, the catalyst decay is explicitly accounted for in a decay rate equation; nevertheless, this equation does not view the catalyst as a distinct phase, as does Froment's heterogeneous model, but considers the catalyst deactivation to be a homogeneous effect, analogous to, and simultaneous with, the reaction rate equation, [Szepe (1966)]. The catalyst decay rate is dependent on the conversion, the temperature and the catalyst activity itself.

A physical picture of the model may be obtained if one visualizes a high velocity, fixed bed reactor, perfectly mixed with stationary catalyst particles of the same size as the reaction molecules themselves.

3.3. Generalized Reactor Equation

The generalized mass balance for the j^{th} species in a tubular reactor with a homogeneous bulk flow in all directions may be written as:

$$\frac{\partial C_j}{\partial t} + \frac{\partial v_r C_j}{\partial r} + \frac{1}{r}\frac{\partial v_\Theta C_j}{\partial \Theta} + \frac{\partial v_z C_j}{\partial z} = \frac{1}{r}\frac{\partial}{\partial r}\left(D_j r \frac{\partial C_j}{\partial r}\right) + \frac{1}{r^2}\frac{\partial^2 D C_j}{\partial \Theta^2} + \frac{\partial^2 D_j C_j}{\partial z^2} + R_j \qquad (3\text{-}1)$$

where

C_j = molar concentration of species j

v_z, v_Θ, v_r = bulk flow velocities in 3 coordinate directions

R_j = reaction rate for species j (positive for production)

R_j is taken, for an irreversible reaction of the form A → B, to be a separable function of concentration activity and temperature

$$R_j = K_j(T)\ F_j(C)\psi \tag{3-2}$$

K is of the Arrhenius form

$$K = K_+^{\bullet} \exp[-E_R/T] \tag{3-3}$$

where $K_+^{\bullet}$ is a constant and E_R is activation energy for the reaction divided by the gas constant. $T(z,t)$ is distributed temperature.

In accordance with 3.2.2 above, we assume that

(i) Bulk flow is along length of reactor only (z direction) and is assumed constant

(ii) Axial diffusion is negligible

(iii) Radial diffusion is negligible

(iv) Density of reacting fluid is constant

(3-1) then reduces to

$$\frac{\partial C_j}{\partial t} + v\,\frac{\partial C_j}{\partial z} = R_j \tag{3-4}$$

3.4 Catalyst Decay

3.4.1 Causes of Decay

There are commonly three major causes for loss of activity in catalysts, viz., sintering, poisoning and fouling.

Sintering or melting of the catalyst particles often happens when uncontrolled hot spots or runaway temperatures occur in a reactor. This is a recurring problem in highly exothermic reactions with insufficient heat transfer. The catalyst material, in the vicinity of the hot spot, melts or undergoes an irreversible loss of activity.

Poisoning of the catalyst refers to the process whereby impurities in the reactant feed, deposit on the catalyst or react with the catalyst surface and reduce its active area. This may or may not be an irreversible process.

Fouling is analogous to the poisoning process and is caused by deposition of unwanted side products on the catalyst surface, causing loss of active surface area, blocking of pores, etc.

3.4.2 Catalyst Decay Rate

Mechanisms for all three types of decay referred to above, are to be found in the literature. [The key papers are Maath and Mascov (1965); Froment and Bischoff (1962)]. However, what is required is the additive effect of all these decay mechanisms. Experimentally four types of equations expressing decay rate are encountered:

(i) linear [Eley and Rideal (1941)]

(ii) exponential [Herington and Rideal (1945)]

(iii) hyperbolic [Pozzi and Rase (1958)]

(iv) reciprocal power [Prater and Lago (1956)]

Szepe (1966) proposed a general equation of the form:

$$\phi \;=\; \text{rate of deactivation} = -k(T)\cdot g(\psi)\cdot f(X) \qquad (3\text{-}5)$$

where

$$g(\psi) = \psi^{m} \qquad (3\text{-}6)$$

He showed that the four experimental forms are all special cases of (3-5) and (3-6).

k(T) is a decay rate constant of Arrhenius form

$$k(T) = k_{+}^{\bullet} \exp[-E_C/T] \qquad (3\text{-}7)$$

where E_C is catalyst deactivation energy divided by the gas constant and T is distributed temperature. $k_{+}^{\bullet}$ is a constant.

ψ is defined precisely as the relative activity and is written

$$\psi(z,t) = \frac{\text{rate of reaction with catalyst in a given condition}}{\text{rate of reaction with fresh (or reference) catalyst}} \qquad (3\text{-}8)$$

f(X) is the conversion dependence term for catalyst decay.

So we may write the catalyst decay equation as:

$$\frac{\partial\psi}{\partial t} \;=\; \phi(T,\psi,\, X) \qquad (3\text{-}9)$$

3.5 Quasi-Steady State

In practice, one often finds that the contact time of a reactor, that is, the time to process one void reactor volume at inlet conditions, is small (seconds or minutes) compared to the total time of operation (hours or days), then, it has been shown [Ogunye and Ray (1969a)] that:

$$\frac{\partial C}{\partial t} << v\,\frac{\partial C}{\partial z} \tag{3-10}$$

and that (3-10) holds, except for very long tubes and very rapidly decaying catalyst. The quasi-steady state form of (3-4) is written then as:

$$v\,\frac{\partial C_j}{\partial z} = R_j \tag{3-11}$$

3.6 Normalized Equations

Using a primed and barred set of variables we can write (3-9) and (3-11) in terms of conversion X(z,t) as:

$$v\,\frac{\partial X}{\partial z'} = \bar{K}(T)\bar{F}(X)\psi \tag{3-12}$$

$$\frac{\partial \psi}{\partial t'} = -\,\bar{k}(T)g(\psi)\bar{f}(X) \tag{3-13}$$

if we have a total time of operation τ and length of reactor L and we define dimensionless variables:

$$t = \frac{t'}{\tau} \qquad 0 \leq t \leq 1 \tag{3-14}$$

$$z = \frac{z'}{L} \qquad 0 \leq z \leq 1 \tag{3-15}$$

$$K(T) = \tau\,\bar{K}(T) \tag{3-16}$$

$$k(T) = \tau\,\bar{k}(T) \tag{3-17}$$

$$t_\theta = L/v \tag{3-18}$$

Then we may write (3-12) and (3-13)

$$\frac{\partial X}{\partial z} = \frac{t_\theta}{\tau}\,K(T)\psi\bar{F}(X) \tag{3-19}$$

$$\frac{\partial\psi}{\partial t} = -k(T)\, g(\psi)\, \bar{f}(X) \tag{3-20}$$

Natural boundary conditions on (3-19) and (3-20) on inlet conversion is:

$$\boxed{X(0,t) = X_o(t)} \tag{3-21}$$

and for initial catalyst activity

$$\boxed{\psi(z,0) = \psi_i(z)} \tag{3-22}$$

From (3-3) and (3-7) we may express K(T) as a function of k(T) as follows (incorporating the constants t_θ and τ into K_+ and k_+) in (3-19) and (3-20)

$$K(T) = K_+ \exp[-E_R/T] \tag{3-23}$$

$$k(T) = k_+ \exp[-E_C/T] \tag{3-24}$$

where

$$K_+ = K^{\bullet}_+ t_\theta/\tau \quad \text{and } k_+ = k^{\bullet}_+ \tag{3-24a}$$

$$K = a\, k^p \quad \text{(see also (3-51a) below)} \tag{3-25}$$

$$a = K_+/(k_+)^p \tag{3-26}$$

$$p = E_R/E_C \tag{3-27}$$

The general properties of the various functions may be summarized as follows:

Conversion $X(z,t)$	Continuous or piecewise continuous,non negative function of z and t; solution to (3-19) $X \in [0,1]$ all z,t (3-28)
$X_o(t)$	Continuous or piecewise continuous, function of t with continuous or piecewise continuous first derivatives.

Activity	$\psi(z,t)$	Continuous or piecewise continuous, non negative function of z and t; solution to (3-20) $\psi \in [0,1]$ all z,t (3-29)
	$\psi_i(z)$	Continuous or piecewise continuous or uniform function of z with continuous or piecewise continuous first derivatives.
	$\bar{F}(X)$	Continuous, non negative, monotonic, non increasing function of X and twice continuously differentiable with respect to X such that for $0 \leq X \leq 1$ (3-30) we have $0 \leq \bar{F}(X) \leq 1$ (3-31)
	$g(\psi)$	Continuous, non negative, monotonic, non decreasing function of ψ such that for $0 \leq \psi \leq 1$ (3-32) we have $0 \leq g(\psi) \leq 1$ (3-33)
	$\bar{f}(X)$	Continuous, non negative, monotonic, twice continuously differentiable function of X

$T(z,t)$ Positive, piecewise continuous distributed control variable, with finite number of discontinuous lines, bounded between two given finite limits

$$T_* \leq T \leq T^* \tag{3-34}$$

$k(T)$ Continuous, positive, strictly monotonic, increasing function of T. Likewise for K(T). Because of this strict monotonicity, k[T] is used to replace T as the control variable and we write the equation corresponding to (3-34) as

$$k_* = k[T_*] \leq k[T] \leq k[T^*] = k^* \tag{3-35}$$

For a single irreversible reaction we use $\bar{F}$ of the form

$$\bar{F} = (1 - X)^n \tag{3-36}$$

$g(\psi)$ is of the form

$$g(\psi) = \psi^m \tag{3-37}$$

where

n is order of the reaction

m is the order of decay

3.7 Adiabatic Reactor

With the values of t_θ and τ absorbed into the Arrhenius constants as in (3-23) and (3-24) we may write (3-19) and (3-20) as

$$\frac{\partial X}{\partial z} = K(T)\psi\bar{F}(X) \tag{3-38}$$

$$\frac{\partial \psi}{\partial t} = -k(T)g(\psi)\bar{f}(X) \tag{3-39}$$

For an adiabatic reactor with all the usual simplifying assumptions (constant pressure, heat of reaction mildly dependent on temperature, etc.) we may write the well known adiabatic relationship for a reaction of the form

$$A \rightarrow B \tag{3-40}$$

as

$$X - X_o = J_1^{\bullet}(T - T_o) \tag{3-41}$$

$$J_1^{\bullet} = -C_p/\Delta H^{\circ} \tag{3-42}$$

where

C_p is the specific heat of the reaction (3-40), and

ΔH° is heat of reaction for (3-40) (negative for exothermic reaction)

$T_o(t)$ is the inlet temperature to the reactor and is the boundary control variable.

Dividing (3-41) by $T\,T_o$ we obtain

$$X - X_o = T\,T_o\,J_1^{\bullet}\left(\frac{1}{T_o} - \frac{1}{T}\right) \tag{3-43}$$

Now if we make the assumption that the change in our boundary control is sufficiently limited so that

$$T\,T_o \simeq T_o^2 \tag{3-44}$$

and also that

$$J^{\bullet} = T_o^2\,J_1^{\bullet} \tag{3-45}$$

is approximately constant in z and t, then we may write, remembering that $J^{\bullet}$ is positive for exothermic reactions

$$X - X_o = J^{\bullet}\left(\frac{1}{T_o} - \frac{1}{T}\right) \tag{3-46}$$

From another viewpoint the alternate expressions (3-41) and (3-46) are seen to be direct consequences of the energy equations

$$\frac{dT}{dX} = -\frac{\Delta H^{\circ}(T)}{C_p(T)} \approx \frac{1}{J_1^{\bullet}} \qquad (3\text{-}46a)$$

and

$$\frac{d(\frac{1}{T})}{dX} = \frac{\Delta H^{\circ}(T)}{T^2 C_p(T)} \approx -\frac{1}{J^{\bullet}} \qquad (3\text{-}46b)$$

Assuming $J_1^{\bullet}$ constant leads directly to (3-41) and assuming $J^{\bullet}$constant leads directly to (3-46). It may well be that if $\Delta H^{\circ}(T)$ is a faster rising function of temperature, the division by T^2 serves to make the assumption that $J^{\bullet}$is constant better than the more common assumption that $J_1^{\bullet}$ is constant. In any case, assuming that T is constant with X is little different from assuming $\frac{1}{T}$ is constant with X, as is called for here.

Thus using (3-46) we write the distributed control (3-35) in terms of a boundary control k_o:

$$k_* = k_o[T_{o*}] \leq k_o(t) \leq k_o[T_o^*] = k^* \qquad (3\text{-}47)$$

using (3-23), (3-24) and (3-46) we have

$$k[T] = k_o[T_o]\exp[(X - X_o)E_C/J^{\bullet}] \qquad (3\text{-}48)$$

$$K[T] = K_o[T_o]\exp[(X - X_o)E_R/J^{\bullet}] \qquad (3\text{-}49)$$

where

$$k_o(t) = k_+ \exp[-E_C/T_o(t)] \qquad (3\text{-}50)$$

$$k_o(t) = K_+ \exp[-E_R/T_o(t)] \qquad (3\text{-}51)$$

(3-25) applies and we may write

$$K_o = a\, k_o^p \qquad (3\text{-}51a)$$

If we now define

$$F(X) = \bar{F}(X) \exp[(X - X_o)E_R/J^{\bullet}] \tag{3-52}$$

$$f(X) = \bar{f}(X) \exp[(X - X_o)E_C/J^{\bullet}] \tag{3-53}$$

We may write the final forms of the state equations (3-38) and (3-39) as:

$$\boxed{\frac{\partial X}{\partial z} = K_o[T_o(t)] \, \psi \, F(X)} \tag{3-54}$$

$$\boxed{\frac{\partial \psi}{\partial t} = - k_o[T_o(t)] \, g(\psi) f(X)} \tag{3-55}$$

Hence we have our distributed system on terms of the boundary control $k_o[T_o]$.

It can be seen that a reactor with uniform temperature (in z) is obtained in the limit as $J^{\bullet}$ (or $J_1^{\bullet}$) tends to infinity (zero heat of reaction), i.e. as $J_1^{\bullet} \rightarrow \infty$ from (3-41) $T_o(t) \rightarrow T(z,t)$ which states that we have a uniform temperature reactor.

For a uniform reactor we have from (3-52) and (3-53)

$$F(X) = \bar{F}(X) \tag{3-56}$$

and

$$f(X) = \bar{f}(X) \tag{3-57}$$

Thus the state equation forms for the adiabatic and uniform reactor are equivalent and differ only in the functional forms of F and f.

3.8 Statement of the Optimal Boundary Control Problem

The precise statement of the optimal boundary control problem is:

(i) Given state equations (3-54) and (3-55) with initial boundary conditions (3-21) and (3-22).

(ii) Given constraint on the boundary control (3-47).

Maximize, by choice of the boundary control k_0 (hence $T_0(t)$) at every instant in time, so as to maximize P, where P is the net integrated exit conversion, for a fixed reaction time

$$J = \underset{\{k_0[T_0(t)]\}}{\mathrm{Max}} \; P = \int_0^1 [X(1,t) - X_0(t)]dt \tag{3-58}$$

CHAPTER 4

THE OPTIMAL SYSTEM

4.1 The Weak Maximum Principle

The implications of the weak form of a maximum principle are best understood if they are contrasted with those of a strong form. Given the strong form of the maximum principle we are instructed unequivocally to choose our control from a given set of allowable functions so that at any z,t we obtain the largest value of the Hamiltonian with respect to any other admissible control. If there is a set of functions which give this largest value of the Hamiltonian, we then need only choose from this reduced set, that control function, which gives the largest value of the objective function. We can search for this global maximum such that

$$H(\underline{u}^+, \underline{x}\ \underline{\lambda}) \geq H(\underline{u}, \underline{x}\ \underline{\lambda}) \quad \text{for all } u \in U$$

where

$\underline{u} \in U$ the set of all admissible controls,

$\underline{x}$ and $\underline{\lambda}$ are state and adjoint variables respectively,

$\underline{u}^+ \in U$ maximizes the Hamiltonian.

Instead we search among all the local maximums such that $\underline{u}^+$ causes H to be maximum in local region or neighbourhood about $\underline{u}^+$. All these policies will satisfy the local maximum condition which requires the

Hessian matrix of second derivatives of the Hamiltonian with respect to the control to be non positive definite.

The set of all admissible policies which obey this local maximum condition may be called 'Pontryagin policies'. We search among these Pontryagin policies for our optimal policy and if it exists, it will be found among these policies. We must, of course, be prepared to assume from mathematical or physical reasoning, that an optimal solution to the problem indeed exists.

There is no general existence theorem for distributed systems, and even the special cases involve long and tedious proofs; so, often, intuitive reasoning or foreknowledge of the physical system has to be relied on.

Given the weak form of the maximum principle we are to select those controls from an allowable set which locally maximize the Hamiltonian only if the control is at a constraint[†], but otherwise, only cause the Hamiltonian to be stationary, that is, cause the 1st partial derivative of the Hamiltonian with respect to the control to vanish. This immediately introduces a potentially larger set of control functions which obey this necessary condition. This set of functions consists of all the functions which obey the necessary conditions for the strong form, as well as a larger set of functions which do not cause the Hamiltonian to have its largest value, but simply cause it to be stationary. One now has to choose from this potentially larger set of extremal policies, that one, which causes the objective function to have its greatest value.

[†] In exceptional circumstances the Hamiltonian may be stationary at the constraint in which case only the weak form applies at the constraint.

4.2 Perturbation Methods

A well known method for producing a weak form for a (local) maximum principle is by the method of a first order perturbation on the objective function; that is, all perturbations of the order of $(\delta u)^2$ (where δu represents a permissible variation in the control) are set to zero. This causes all second derivative terms to vanish leaving only the first derivatives to affect the sign of the perturbation of the objective function in the vicinity of the optimum. In order to ensure the necessary condition for an extremum in the objective function, these first derivatives are set to zero and provide the stationarity condition for the Hamiltonian.

Given that this necessary condition for an extremum in the objective function holds, that is, the first derivatives of the Hamiltonian with respect to unconstrained control are zero, it then becomes necessary to consider terms of the order of $(\delta u)^2$ and their corresponding second partial derivatives. We use these to determine whether this extremum is in fact a maximum, minimum or saddle point. Only at this stage can one make statements which identify the maximum (minimum) of the Hamiltonian with respect to the control, with the maximum (minimum) of the objective function, and give a strong maximum principle.

4.2.1 Existence of a Strong Maximum Principle for Boundary Control

Ogunye and Ray (1971), following the method of Jackson (1966) and using a first order perturbation method outlined in 4.2 above, obtained a weak form of a maximum principle for boundary as well as distributed control.

Possibly the most general and usable work in this area is that due to Sirazetdinov and Degtyarev (1967) who derive a strong maximum principle for a system described by first order partial differential equations. However, the strong form in their theorem applies only to distributed control and not where control exists in one dimension only, i.e., boundary control.*

There have been numerous claims of the existence of a strong form for boundary control (Chang (1967)) but to the authors knowledge no concrete, well established, proof exists.

4.3 Perturbation Analysis

Using a first order perturbation of the objective function (3-58) we obtain (see Appendix A) the following equations:

$$\delta P = \int_0^1 [\int_0^1 \frac{\partial H}{\partial k_0} dz] \partial k_0(t) dt \tag{4-1}$$

where

$$H = \lambda_1 \psi F K_0 - \lambda_2 g f k_0 \tag{4-2}$$

and

$$\bar{H} = \int_0^1 H \, dz \tag{4-3}$$

---

*except for the case where the system and objective function are linear.

$\bar{H}$ is the Hamiltonian function of the system. $\lambda_1(z,t)$ and $\lambda_2(z,t)$ are the adjoint variables of the system and are defined by the following partial differential equations

$$\frac{\partial\lambda_1}{\partial z} = \lambda_2\, k_o\, g\, f' - \lambda_1\, \psi\, K_o\, F' \tag{4-4}$$

Boundary Condition

$$\lambda_1\,(1,t) = 1 \tag{4-5}$$

where f' and F' denote the total derivatives with respect to the single argument X, i.e.

$$F' = \frac{dF(X)}{dX} \tag{4-6}$$

$$f' = \frac{df(X)}{dX} \tag{4-7}$$

Also

$$\frac{\partial\lambda_2}{\partial t} = \lambda_2\, k_o\, f\, g' - \lambda_1\, K_o\, F \tag{4-8}$$

Boundary Condition

$$\lambda_2\,(z,1) = 0 \tag{4-9}$$

where g' denotes the total derivative with respect to the single argument, ψ, i.e.

$$g' = \frac{dg(\psi)}{d\psi} \tag{4-10}$$

Now for a maximum it is necessary that any perturbation in the control be such that

$$\delta P \leq 0 \tag{4-11}$$

From (4-1) then, seeing we are free to perturb δk_o in either a positive or negative direction, it is necessary, in order that (4-11) be satisfied, that

$$\frac{\partial \bar{H}}{\partial k_0} = \int_0^1 \frac{\partial H}{\partial k_0} dz = 0 \qquad (4\text{-}12)$$

Differentiating (4-2) partially with respect to k_0 we obtain

$$\frac{\partial \bar{H}}{\partial k_0} = \int_0^1 \frac{\partial H}{\partial k_0} dz = \int_0^1 (p\lambda_1 \psi F K_0/k_0 - \lambda_2 g f)dz = 0 \qquad (4\text{-}13)$$

Seeing that the control $k_0(t)$ is a function of t only we may multiply through (4-13) by k_0 to obtain

$$\int_0^1 p \lambda_1 \psi F K_0 dz = \int_0^1 \lambda_2 k_0 g f dz \qquad (4\text{-}14)$$

Equation (4-14) is a necessary condition for the stationarity of the system where the control is unconstrained.

If the control $k_0(t)$ is at either of its boundaries k_* or k^*, then for k_0 at its upper boundary k^*, any perturbation in k_0 must be such that for $k_0 = k^*$,

$$\delta k_0 \leq 0 \qquad (4\text{-}15)$$

Thus from (4-11) and (4-1)

$$\frac{\partial \bar{H}}{\partial k_0} = \int_0^1 \frac{\partial H}{\partial k_0} dz \geq 0 \qquad (4\text{-}16)$$

Likewise for $k_0 = k_*$

$$\frac{\partial \bar{H}}{\partial k_0} = \int_0^1 \frac{\partial H}{\partial k_0} dz \leq 0 \qquad (4\text{-}17)$$

When k_0 is constrained at one of its boundaries, say k^*, then any perturbation in k_0 must decrease k_0. From the sign of $\frac{\partial \bar{H}}{\partial k_0}$ in (4-16) $\bar{H}$ will also decrease, (except for the special case where the strict equality holds and one has stationary condition coincident with the boundary (see 4.1 above)). Thus, since $\bar{H}$ decreases with respect to k_o at the upper boundary, it is a (local) maximum with respect to k_o, at the upper boundary and not simply stationary, as it is in the interior region for the weak maximum principle. Thus when the control is at a constraint the weak form reverts to the local strong form of the maximum principle.

4.3.1 Influence of p on the character of the Optimum Profile

If there were no doubt that the strong form of the maximum principle for boundary control existed, one would proceed to investigate the sign of the second derivative of the Hamiltonian with respect to k_o in order to distinguish between the possible stationary conditions.

From (4-13) differentiating again with respect to k_o remembering from (3-51a) that

$$dK_o = p\frac{K_o}{k_o}dk_o \tag{4-18}$$

$$\frac{\partial^2\bar{H}}{\partial k_o^2} = \int_o^1 \frac{\partial^2 H}{\partial k_o^2}dz = \int_o^1 [\frac{\lambda_1\psi F K_o}{k_o^2}p(p-1)]dz \tag{4-19}$$

Now assuming the existence of the strong form of the maximum principle a necessary condition for the unconstrained maximum (as opposed to stationarity) of the objective function would be

$$\frac{\partial^2\bar{H}}{\partial k_o^2} = \int_o^1 \frac{\partial^2 H}{\partial k_o^2}dz \leq 0 \tag{4-20}$$

From (4-14) provided $\frac{\lambda_1 \psi F K_0}{k_0^2}$ is positive (see Chapter 5 below) this would require

$$p \leq 1 \tag{4-21}$$

Thus (4-21) would be the condition for the existence of an unconstrained optimal profile, that is, an optimum profile for which

$$k_* < k_0 < k^* \tag{4-22}$$

where the strict inequalities are observed.

Likewise for $p > 1$, an unconstrained policy would be inadmissible and the optimal profile would consist only of constrained portions, with $k = k^*$ or $k = k_*$, or a mixture of these profiles.

This mixture of totally constrained profiles is often referred to as 'bang-bang' control and describes the situation where, for example, an optimum profile is constrained on a lower bound for some finite length of time and then switches, over an infinitely small time span, to the upper constraint, so that for no finite proportion of time is the optimum profile within the open interval (4-22).

The parameter p (3-27), because it enters directly into (4-19) plays a decisive role in the character of the extremal control policy and in the admissibility of certain control sub-policies to the extremal control policy.

If one considers the extreme values of p we have

(i) $p = 0$: From (3-54) and (3-23) it can be seen that the reaction rate is independent of temperature. For this case the obvious optimal policy is to maintain the temperature as low as possible so as to retain the highest possible catalyst activity in the reactor.

(ii) $p = \infty$: From (3-55) and (3-24) it can be seen that the catalyst decay rate is independent of temperature. Now the optimal policy is to maintain the temperature on its upper limit at all times to obtain the highest possible conversion.

The kinetic significance of the parameter p is that for $p < 1$ an increase of the operating temperature would increase the rate constant $k_0(T_0)$ for catalyst decay faster than the rate constant $K_0(T_0)$ for reaction. If the operating temperature were to be lowered a decrease in $k_0(T_0)$ would result and hence a higher catalyst activity would be maintained; however, this would, of course, cause a decrease in the reaction rate through K_0.

These conflicting choices of temperature indicate that somewhere between the two choices the 'best' choice lies, and it is this 'best' choice that represents the optimization problem at hand.

4.3.2 Singular and Bang-Bang Control

For $p = 1$ we have a degenerate case. From (4-3) it is seen that the Hamiltonian depends linearly on the control k_0; remembering from (3-51a) that for $p = 1$

$$K_0 = a\, k_0 \tag{4-23}$$

$$\bar{H} = \int_0^1 H\, dz = k_0(t)\left[\int_0^1 (ap\lambda_1\psi F - \lambda_2\, g\, f)dz\right] \tag{4-24}$$

$$\therefore \quad \bar{H} = k_0(t)A(t) \tag{4-25}$$

Now the stationary condition over a finite interval of t is:

$$\frac{\partial \bar{H}}{\partial k_o} = A(t) = 0 \tag{4-26}$$

where

$$A(t) = [\int_0^1 (ap\lambda_1\psi F - \lambda_2 \text{ g f})dz] \tag{4-27}$$

does not depend explicitly on k_o.

Now the only allowable form for $\bar{H}$, if it is to be stationary with respect to k_o, is for $\bar{H}$ to be a constant function of k_o. Comparing (4-25) and (4-26), we see that this constant must be zero.

There are in fact three possible cases for $\bar{H}$ (4-25) (see Figure 4-1).

If A(t) is zero, as it must be to satisfy the stationary condition for unconstrained profiles, then the Hamiltonian $\bar{H}$ is no longer a function of the control; it trivially obeys the necessary condition (4-13) and no longer provides us with information on the stationarity of the objective function. This situation is commonly called a singular policy. The conditions for the singular policy are:

(i) A(t) must vanish over a finite portion of the extremal policy. (4-28)

(ii) $$\frac{d^rA(t)}{dt^r} = 0 \qquad \text{for } r = 1,2,.... \tag{4-29}$$

It should be noted, however, that the existence of singular control policies, which satisfy (4-28) does not necessarily imply existence of singular sub arcs which form part of optimal control policy [Johnson (1965)].

The analysis of singular control policy for a distributed system, presents a major mathematical difficulty. There is still no general method for determining, a priori, whether control policies obeying the singular conditions stated above, actually form part of an optimal policy.

In the case of lumped parameter systems, Kelly (1964) derived a necessary condition for a candidate satisfying the singular policy, to be optimal with respect to an arbitrary piecewise continuous perturbation in the control. This result is now commonly known as the Generalized Legendre-Clebsch condition and is given as:

$$(-1)^r \frac{\partial}{\partial u_s} \left[\frac{\partial^{2r}}{\partial t^{2r}} \left(\frac{\partial H}{\partial u_s}\right)\right] \leq 0 \qquad r = 1,2, \ldots \qquad s \,\varepsilon [0,1,\ldots N] \tag{4-30}$$

where N is the number of control variables of the system.

Nevertheless, there has been no successful extension to the distributed system [Seinfeld (1967)].

Now if A(t) is non zero or contains only isolated zeros, then $\bar{H}$ cannot be stationary, and only constrained policies may exist at the optimum.

It was stated that the weak form of the maximum principle reverts to the local strong form when the control is at one of its constraints.[†] Hence if we now search in the set of all profiles such that

$$k_0 \notin \{k_0 : k_* < k_0 < k^*\} \tag{4-31}$$

then we may choose k_0, in order to maximize $\bar{H}$ at a boundary and not

---

[†] Except for the unusual case where one has stationarity exactly at the boundary.

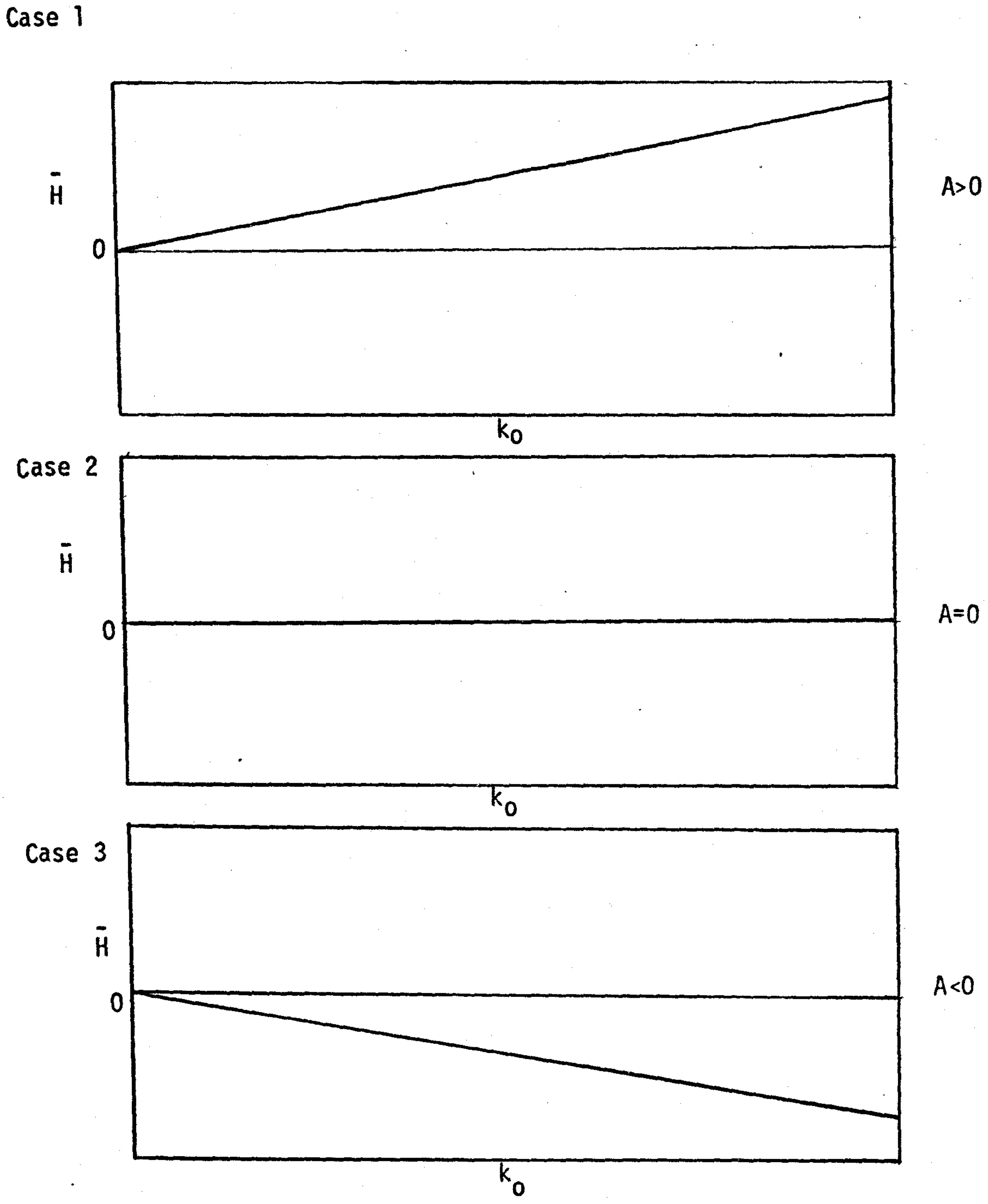

Figure 4-1 Three typical forms for the Hamiltonian as a function of the control k_o for the degenerate case of $p = 1$

simply to make it stationary. From Figure (4-1) it can be seen that the optimal profile will be governed by a 'bang-bang' policy where, for $A > 0$, k_o is chosen at its maximum value to maximize the Hamiltonian and vice versa, that is:

$$\text{Optimal profile for } A \neq 0: \quad \begin{aligned} k_o(t) &= k^* \quad A(t) > 0 \\ k_o(t) &= k_* \quad A(t) < 0 \end{aligned} \tag{4-32}$$

Computation for the bang-bang policy involves the determination of the switching points between upper and lower constraints and the function A(t) is commonly referred to as the <u>switching function</u>. However the computational methods are somewhat more involved than the standard gradient methods, and often involve the limit of a series of non-singular, non-bang-bang solutions. [Edgar and Lapidus (1972)].

4.4 Fixed Point Formulation of Necessary Condition

In spite of the appearance of integrals in the necessary condition (4-12) one can express the necessary condition in a functional form. The solution to the optimal problem then takes a fixed point formulation and opens the way to a new series of computational techniques, different from the standard gradient methods.

Expressing K_o as a function of k_o via (3-51a) and solving for k_o in (4-14), remembering that integration is with respect to z and k_o is a function of t only, we obtain:

$$k_o = G[k_o] \tag{4-33}$$

where

$$G[k_o(t)] = \left[\frac{a\ p \int_0^1 \lambda_1 \psi F\ dz}{\int_0^1 \lambda_2 g\ f\ dz}\right]^{\frac{1}{1-p}} \tag{4-34}$$

for $k_* < k_o(t) < k^*$ and $p \neq 1$.

(4-34) holds for unconstrained $k_o(t)$ and for the constrained regions we write

$$G[k_o(t)] = k^* \quad \text{when} \quad k_o(t) = k^* \tag{4-34a}$$

$$G[k_o(t)] = k_* \quad \text{when} \quad k_o(t) = k_* \tag{4-34b}$$

The equations (4-33) to (4-34b) define the functional G fully.

The profile which satisfies the necessary condition for stationarity of the Hamiltonian will be the fixed point of (4-33) in function space.

It can be seen from (4-33) that as $t \to 1$, $\lambda_2 \to 0$ (boundary condition) and $k_o \to \infty$ $(p < 1)$, and if k_o is constrained, then a necessary condition for a profile to be optimal, is that it end on the upper constraint k^*.

4.4.1 Fixed Point Methods

A solution to an equation of the form

$$x = T_f(x) \tag{4-35}$$

is said to be the fixed point of the transformation T_f, since T_f leaves x invariant. To find a fixed point by the method of successive approximations, we compute a sequence of vectors of the form:

$$x_{n+1} = T_f(x_n) \tag{4-36}$$

under appropriate conditions, the sequence $\{x_n\}$ converges to a solution of (4-35).

If we define S^* to be a closed subset of a Hilbert space X^* and let T_f be a transformation mapping of S^* into S^* then T_f is said to be a contraction mapping if there exists an α, $0 \leq \alpha < 1$ such that

$$|| T_f(x_1) - T_f(x_2) || \leq \alpha || x_1 - x_2 || \qquad . (4\text{-}37)$$

for all $x_1, x_2 \in S^*$.

$|| \ ||$ is a norm in X^*, which is induced by the inner product $<x,y>$ such that

$$|| x || = \sqrt{<x,x>} \qquad (4\text{-}38)$$

The inner product may take several forms, a common form being:

$$<x,y> = \int_0^1 x(t)\, y(t)\, dt \qquad x, y \in S^* \qquad (4\text{-}39)$$

<u>Theorem</u>: [Luenberger (1968)] Contraction Mapping

If T_f is a contraction mapping on a closed subset S^* of a Banach space, there is a unique vector $x_o \in S^*$ satisfying $x = T_f(x)$. Furthermore, x_o can be obtained by the method of successive approximation of the form (4-36), starting with an arbitrary initial vector in S^*.

Note that a Hilbert space is simply a Banach space equipped with an inner product which induces the norm (4-38).

Now provided we could prove that G was a contraction mapping according to (4-37) then k_o could be obtained by the method of successive approximation, and furthermore it would be unique. Thus it would be the only candidate satisfying the necessary condition for the unconstrained optimum and provided we were sure a maximum solution existed, k_o would be the required solution and would satisfy the necessary and sufficient conditions for the maximum of the objective function.

So, in a sense, one can strengthen the weaker maximum principle by casting the necessary condition into a fixed point problem; examine the mapping G which must leave the control invariant, and if one can prove that G is a contraction mapping, then the solution to the fixed point problem will be unique. Further, if a solution is known to exist, the solution obtained by successive approximation will be the required (unconstrained) optimal control, since it is the only solution satisfying the necessary condition.

CHAPTER 5

PROPERTIES OF THE OPTIMAL SYSTEM

5.1 Introduction

For many properties of the optimal system it is necessary to derive certain properties of the state variables X, ψ, as well as the adjoint variables λ_1, λ_2, including those boundary conditions not already specified. In some instances, formal solutions to these variables are required and these too are obtained.

Properties of the state variables are considered first, followed by the adjoint variables. Using these derived properties, several properties of the optimal system are derived in 5.4 below.

5.2 State Variables

We seek to derive the analytical expression for a first order decay rate, this will allow us to obtain an expression for the activity ψ, as a function of f(X).

5.2.1 First Order Reaction

If we set the order of the reaction n=1 in (3-36) and consider a uniform reactor (3-56) then we may write:

$$F = (1-X) \tag{5-1}$$

From the first state equation (3-54) we have

$$\frac{\partial X}{\partial z} = K_o\psi\,(1-X) \tag{5-2}$$

Separating variables and integrating formally we have

$$\int_{X_0}^{X} \frac{dX}{1-X} = K_0(t)\int_0^{z} \psi dz^{\bullet} \tag{5-3}$$

which gives

$$[1-X(z,t)] = [1-X_0(t)] \exp [-K_0(t)\int_0^{z} \psi dz^{\bullet}] \tag{5-4}$$

For the special case of zero initial conversion we have

$$X_0(t) = 0 \qquad\qquad 0 \le t \le 1 \tag{5-5}$$

and we may write (5-4) as

$$\boxed{X(z,t) = 1 - \exp [-K_0(t)\int_0^{z} \psi dz^{\bullet}]} \tag{5-6}$$

and exit conversion

$$\boxed{X_1(t) = 1 - \exp [-K_0\ \Phi(t)]} \tag{5-7}$$

where $\Phi(t) = \int_0^1 \psi dz$ is called average activity (5-8)

5.2.2 First Order Decay Rate

For a uniform temperature reactor in which case $F(X) = \overline{F}(X)$ [see(3-56)], an analytical expression for the conversion $X(z,t)$ at any point is easily obtained from the first state equation. This then leads to an expression for the exit conversion from the reactor which is seen to depend only on the average activity [see (5-8)] and not the activity at the exit alone. From this expression it can be seen later (Chapter 6) how K_0 is chosen to guard against an exit conversion greater than unity.

If we set the decay order m = 1 in (3-37) we may write (3-55) as

$$\frac{\partial\psi}{\partial t} = -k_o f\psi \tag{5-9}$$

proceeding as in 5.2.1 above we obtain

$$\psi(z,t) = \psi_i(z)\ \exp\left[-\int_0^t k_o(t^\bullet)f(X)dt^\bullet\right] \tag{5-10}$$

For the special case of fresh uniform catalyst initially

$$\psi_i(z) = 1 \qquad 0\lessgtr z\lessgtr 1 \tag{5-11}$$

and we write (5-8) as

$$\boxed{\psi(z,t) = \exp\left[-\int_0^t k_o(t^\bullet)f(X)dt^\bullet\right]} \tag{5-12}$$

5.2.3 n^{th} Order Reaction Rate

Under this section various analytical forms of the state variables X and ψ are derived. The forms are divided, for convenience, into a first order reaction system and first order decay rate, and the corresponding n^{th} order reaction systems for reaction and decay rates. The reaction schemes apply to a uniform temperature reactors, in which case $F(X) = \bar{F}(X)$ [see(3-56)].

For a uniform reactor F(X) takes the form

$$F = (1-X)^n \tag{5-13}$$

substituting (5-13) in (3-56) and integrating formally as in 5.2.1 we obtain

$$[1-X(z,t)]^{1-n} = [1-X_o(t)]^{1-n} - (1-n)K_o(t)\int_0^z \psi dz^\bullet \tag{5-14}$$

$$n \neq 1$$

For the case of zero initial conversion (5-5) applies and we write

$$\boxed{[1 - X(z,t)] = [1 - (1-n)\ K_0(t) \int_0^z \psi dz']^{\frac{1}{1-n}}} \qquad (5\text{-}15)$$

as in 5.2.1. The exit conversion may be obtained from (5-15) and is seen to depend only on the average activity $\Phi(t)$ in (5-8) and not the local activity $\psi(z,t)$.

$$\boxed{\begin{array}{r} X_1(t) = 1 - [1 - (1-n)\ K_0(t)\ \Phi(t)]^{\frac{1}{1-n}} \\ n \neq 1 \end{array}} \qquad (5\text{-}16)$$

5.2.4. m^{th} Order Decay Rate

One may obtain an analytical expression for the catalyst decay $\psi(z,t)$ at any point by making use of the second rate equation (3-55)

If one sets the decay order m as in (3-37) then (3-55) may be written

$$\frac{\partial\psi}{\psi^m} = -k_o(t)\ f(X)\ \partial t \tag{5-17}$$

Integrating formally one obtains

$$\psi(z,t)^{1-m} = \psi_i^{1-m}(z) - (1-m)\int_0^t k_o(t^\cdot)\ f(X)\ dt^\cdot \qquad m \neq 1 \tag{5-18}$$

If (5-11) applies we have

$$\boxed{\psi(z,t) = [1 - (1-m)\int_0^t k_o(t^\cdot)\ f(X)\ dt^\cdot]^{\frac{1}{1-m}}} \qquad m \neq 1 \tag{5-19}$$

5.2.5 Derivatives of State Variables

Derivatives of the state variables X and ψ are given in terms of z and t respectively. However, it is useful to have the corresponding derivatives along the opposite directions. What follows is a derivation of expressions for $\frac{\partial X}{\partial t}$ and $\frac{\partial\psi}{\partial z}$ respectively.

Using the first state equation (3-54) separating variables and integrating between X_o and X we have,

$$\int_{X_o(t)}^{X(z,t)} \frac{\partial X}{F(X)} = \int_0^z \psi K_o \, dz' \tag{5-20}$$

Differentiating both sides using Leibnitz's rule we have

$$\frac{1}{F}\frac{\partial X}{\partial t} - \frac{1}{F(X_o)}\frac{dX_o}{dt} = \int_0^z \frac{\partial \psi K_o}{\partial t} \, dz' \tag{5-21}$$

if we now specify constant initial conversion, i.e.,

$$X_o(t) = \text{constant} \quad \text{for all} \quad t \tag{5-22}$$

we have

$$\boxed{\frac{\partial X}{\partial t} = F(X) \int_0^z \frac{\partial \psi K_o}{\partial t} \, dz'} \tag{5-23}$$

Expressions for the activity derivative may be obtained likewise, using (3-55), separating variables and integrating:

$$\int_{\psi_i(z)}^{\psi(z,t)} \frac{\partial \psi}{g(\psi)} = -\int_0^t k_o \, f \, dt'$$

Differentiating with respect to z using Leibnitz's rule and specifying

$$\psi_i(z) = \text{constant or piecewise constant for all } z \tag{5-24}$$

we obtain, using (3-54)

$$\boxed{\frac{\partial \psi}{\partial z} = -g(\psi) \int_0^t k_o f' \, \psi K_o F \, dt'} \tag{5-25}$$

5.3 Adjoint Variables

The adjoint variables are extremely important in the characterization of the optimal profiles. Their derivatives in z and t, their signs and their magnitudes all feature strongly in the determination of properties of the optimal profiles. Various analytical properties and forms for the adjoints are derived.

5.3.1 Integrated Forms

Analytical expressions for the adjoints may be obtained using an integrating factor on the adjoint equations defined in chapter 4, above. From (4-4) and (4-8) we may write

$$\frac{\partial \lambda_1}{\partial z} = \lambda_2 \ell_1 - \lambda_1 \ell_2 \tag{5-26}$$

$$\frac{\partial \lambda_2}{\partial t} = \lambda_2 \ell_3 - \lambda_1 \ell_4 \tag{5-27}$$

where

$$\ell_1 = k_o g f' \tag{5-28}$$

$$\ell_2 = \psi K_o F' \tag{5-29}$$

$$\ell_3 = k_o g' f \tag{5-30}$$

$$\ell_4 = K_o F \tag{5-31}$$

Where, as usual, the primes denote total derivatives with respect to the particular arguments of the respective functions.

In (5-26) using an integrating factor of the form

$$\exp\left[-\int_z^1 \ell_2(z',t)dz'\right] \tag{5-32}$$

and using the boundary condition on $\lambda_1(1,t)=1$ (4-5), the solution to (5-26) may be written as

$$\boxed{\lambda_1(z,t) = \exp\left[\int_z^1 \ell_2(z',t)dz'\right] - \int_z^1 \exp\left[-\int_{z'}^{z} \ell_2(z'',t)dz''\right]\lambda_2\ell_1(z',t)dz' \qquad (5\text{-}33)}$$

Proceeding in the same manner, using the boundary condition on $\lambda_2(z,1)=0$ (4-9) and the integrating factor

$$\exp\left[\int_t^1 \ell_3(z,t')dt'\right] \tag{5-34}$$

the solution to (5-27) may be written as

$$\boxed{\lambda_2(z,t) = \int_t^1 \exp\left[-\int_t^{t'} \ell_3(z,t'')dt''\right] \ell_4\lambda_1(z,t')dt' \qquad (5\text{-}35)}$$

It should be noted that since ℓ_4 is non negative (3-31), λ_2 will be non negative, if λ_1 is non negative.

5.3.2 Adjoint Integral Equations

Certain statements regarding the sign of the adjoint variables may be made from their integral equation forms. In general though, these forms may be useful for any analytical endeavours in this area.

Substituting directly for λ_1 from (5-33) in (5-35) we obtain

$$\lambda_2(z,t) = I_1(z,t) + \int_t^1 \int_z^1 C(z,t,z',t')\, \lambda_2(z',t')\, dz'dt' \qquad (5\text{-}36)$$

where

$$I_1(z,t) = \int_t^1 \exp\left[-\int_t^{t'} \ell_3(z,t'')dt'' + \int_z^1 \ell_2(z'',t')dz''\right] \ell_4(z,t')\, dt' \qquad (5\text{-}37)$$

$$\geq 0$$

$$C(z,t,z',t') = -\left[\exp \int_z^{z'} \ell_2(z'',t')dz'' + \int_{t'}^{t} \ell_3(z,t'')dt''\right] \ell_1(z',t')\, \ell_4(z,t') \qquad (5\text{-}38)$$

It is seen that since ℓ_4 is non negative [see 3.6 above], $I_1 \geq 0$ and C has the opposite sign to ℓ_1 which depends on the sign of f' (X).

Similarly for λ_1, substituting for λ_2 in (5-33) from (5-35) we we obtain

$$\lambda_1(z,t) = I_2(z,t) - \int_z^1 \int_t^1 \overline{C}\,(z,t,z',t')\, dz'\, dt' \qquad (5\text{-}39)$$

where

$$I_2(z,t) = \exp\left[\int_z^1 \ell_2(z',t)\, dz'\right] > 0 \qquad (5\text{-}40)$$

and

$$\bar{C}(z,t,z^{\bullet},t^{\bullet}) = \exp\left[-\int_{z^{\bullet}}^{z} \ell_2(z'',t)dz'' - \int_{t}^{t^{\bullet}} \ell_3(z^{\bullet},t'')dt''\right]\ell_1(z^{\bullet},t)\ \ell_4(z^{\bullet},t^{\bullet}) \tag{5-41}$$

It can be seen from (5-40) that the sign of I_2 is such that $I_2>0$ and $\bar{C}$ from (5-41) has the same sign as ℓ_1, since ℓ_4 is non negative, [see 3.6 above].

5.3.3 Properties of the Adjoints

Combinations of certain adjoint variables and state variables occur together, for example in the Hamiltonian equation and the expression for the optimal exit conversion, (5.4) below. In order to make certain concrete statements concerning the optimal profiles it is necessary to know the derivatives of these groups of variables as well as their signs and relative magnitudes. Some of these groups are amenable to analytical analysis and some derivations of their properties are given below. Also derived, are the all important signs of the adjoint variables themselves. The signs of the various derivatives are treated below, as well.

Partial Derivative of $\lambda_1 F$ with respect to z

This particular derivative turns out to give an expression which is closely related to the expression for the optimal exit conversion. It forms the basis of a series of analytical proofs of constant exit conversion for specific forms of F and f to be treated in 5.5 below.

$$\frac{\partial \lambda_1 F}{\partial z} = F \frac{\partial \lambda_1}{\partial z} + \lambda_1 F' \frac{\partial X}{\partial z} \tag{5-42}$$

substitute for $\frac{\partial \lambda_1}{\partial z}$ from (4-4) and for $\frac{\partial X}{\partial z}$ from (3-56)

$$\frac{\partial \lambda_1 F}{\partial z} = F(\lambda_2 k_0 g f' - \lambda_1 \psi K_0 F') + \lambda_1 F' (\psi K_0 F)$$

$$\boxed{\frac{\partial \lambda_1 F}{\partial z} = \lambda_2 k_0 g F f'} \tag{5-43}$$

It can be seen that this derivative has the same sign as $f'(X)$, from (5-47) below and 3.6.

From (5.43) we may obtain an alternative expression for λ_1

as follows:

$$\frac{1}{\lambda_1 F}\frac{\partial \lambda_1 F}{\partial z} = \frac{\lambda_2 k_o g f'}{\lambda_1} = \frac{\partial \ln \lambda_1 F}{\partial z} \tag{5-44}$$

Integrating between 1 and z and remembering that $\lambda_1(1,t) = 1$,we obtain

$$\boxed{\lambda_1(z,t) = \frac{F[X_1(t)]}{F[X_{(z,t)}]} \exp\left[-\int_z^1 \frac{\lambda_2 k_o g f'}{\lambda_1} dz^{\bullet}\right]} \tag{5-45}$$

since F is non negative (3-31), for all z and t, the only values of λ_1 satisfying (5-45), are $\lambda_1 \geq 0$.

Sign of Adjoints

From (5-45), due to the sign of F and the exponential,we require that:

$$\boxed{\lambda_1(z,t) \geq 0} \qquad \text{for all z and t} \tag{5-46}$$

Refering to (5-35), due to the sign of ℓ_4, the presence of the exponential and (5-46), we require that the second adjoint be non negative, i.e.

$$\boxed{\lambda_2(z,t) \geq 0} \qquad \text{for all z and t} \tag{5-47}$$

Partial Derivative of $\lambda_2\psi$ with respect to t

If we choose a particular form for $g(\psi)$ with m=1 we have from (3-37)

$$g = \psi \tag{5-48}$$

Consider the derivative with respect to t

$$\frac{\partial \lambda_2\psi}{\partial t} = \psi \frac{\partial \lambda_2}{\partial t} + \lambda_2 \frac{\partial \psi}{\partial t} \qquad (5\text{-}49)$$

substituting from (3-55) for $\frac{\partial \psi}{\partial t}$ taking (5-46) into account and likewise for $\frac{\partial \lambda_2}{\partial t}$ from (4-8) we have

$$\frac{\partial \lambda_2\psi}{\partial t} = \psi\,(\lambda_2 k_o f - \lambda_1 K_o F) + \lambda_2\,(-k_o f\psi) \qquad (5\text{-}50)$$

$$\boxed{\frac{\partial \lambda_2\psi}{\partial t} = -\,\lambda_1\psi K_o F \quad \leq 0} \qquad \text{for } g = \psi \qquad (5\text{-}51)$$

This derivative is non positive for all z and t (from (5-46) and 3.6) From (5-51), we may obtain an alternative expression for λ_2 for the case $g = \psi$ by integrating between the limits $t \leq t \leq 1$ taking into account the boundary conditions (4-9) for λ_2 we have

$$\boxed{\lambda_2(z,t) = \frac{1}{\psi(z,t)} \int_t^1 \lambda_1\psi K_o F \;\; dt} \qquad (5\text{-}52)$$

Again it is seen that for λ_1 non negative we have λ_2 non negative.

See also 5.6 below to replace ψ by g

Partial Derivative of $\lambda_1 F$ with respect to t

This derivative occurs in an expression for the optimal exit conversion over the unconstrained region to be derived in 5.4 below. It is thus important that both its sign and magnitude are known. It turns out that this derivative, even though an expression can be derived for it, leads to an integral to which neither magnitude nor sign can be attached. The expression for the derivative and some of the difficulties encountered are given below

Differentiating (5-43) partially with respect to t, and changing the order of integration, since (see 3.6) $\lambda_1 F$ is twice continuously differentiable in z and t, we obtain

$$\frac{\partial}{\partial z}\left(\frac{\partial \lambda_1 F}{\partial t}\right) = \frac{\partial}{\partial t}\left(\lambda_2 k_0 g F f'\right) \tag{5-53}$$

Integrating between limits $z \leq z^{\cdot} \leq 1$ and remembering the boundary condition on $\lambda_1(1,t)=1$ (4-5) we obtain

$$\boxed{\frac{\partial \lambda_1 F}{\partial t} = -\int_z^1 \frac{\partial}{\partial t}\left(\lambda_2 k_0 g F f'\right) dz^{\cdot} + F'\left[X_1(t)\right]\frac{dX_1}{dt}} \tag{5-54}$$

Although it is important to determine the sign of this derivative, this not an easy task, especially because the sign of the integrand may change for only part of the distance along z, and because of the presence of the integral, the entire past history of the integral must be known up to the point at which the sign of the derivative is required. From 3.6 above $F' \leq 0$, but $\frac{dX_1}{dt}$ may be of either sign or a mixture. However, the sign alone of the first term is insufficient; the relative magnitude as well, is required, to set off against the second term, and then only can the sign of the derivative be determined.

For the case where decay does not depend on conversion and the term $f'=0$, the sign of this derivative is easily seen to be opposite to that of $\frac{dX_1}{dt}$ and we have, from (5-54), assuming that $F' \leq 0$ from 3.6 above,

$$\frac{\partial \lambda_1 F}{\partial t} = F'\left[X_1(t)\right]\frac{dX_1}{dt} \qquad \text{for } f' = 0 \tag{5-55}$$

Partial Derivative of $\lambda_2\psi$ with respect to z

The significance of this derivative in determining the character of the optimal conversion profile has been discussed in the paragraph following (5-47) above. As well, in 5.4.3 below this precise derivative occurs alone in an expression for the optimal exit conversion over the unconstrained region. Its properties are thus of great importance.

A convenient expression to this derivative may be obtained for the case $g = \psi$ directly from (5-51). If a more general expression is required it may be obtained by multiplying both sides of (5-35) by ψ or $g(\psi)$ and differentiating partially with respect to z. However, this produces a long involved expression which is virtually useless if one requires the sign of the derivative. Yet a further method is shown in 5.6 below.

Directly then, from (5-51), using the same assumptions as in (5-53) and remembering the boundary condition on $\lambda_2(z,1)=0$ (4-9), we have,

$$\frac{\partial}{\partial t}\left(\frac{\partial \lambda_2\psi}{\partial z}\right) = -\frac{\partial}{\partial z}(\lambda_1\psi K_0 F) \tag{5-56}$$

Integrating (5-56) between $t \leq t \leq 1$ we obtain

$$\boxed{\frac{\partial \lambda_2\psi}{\partial z} = \int_t^1 K_0 \frac{\partial(\lambda_1\psi F)}{\partial z}\, dt'} \qquad \text{for } g = \psi \tag{5-57}$$

To determine, (analytically) the sign of this derivative one experiences similar difficulties to those for $\frac{\partial \lambda_1 F}{\partial t}$ above. From section 3.6 above we can determine that

(i) $K_o > 0$ for all t

(ii) The sign of $\frac{\partial \lambda_1}{\partial z}$ cannot be determined in general,

however, if we specify certain conditions on f we see that if $f' \geq 0$ then $\frac{\partial \lambda_1}{\partial z} \geq 0$ since from (5-43)

$$F \frac{\partial \lambda_1}{\partial z} = \lambda_2 k_o g F f' - \lambda_1 F' \psi K_o F$$

thus since all variables are positive except $F' \leq 0$ [see section 3.6, (5-46) and (5-47)] if $f' \geq 0$, then $\frac{\partial \lambda_1}{\partial z} \geq 0$

If $f' < 0$, $\frac{\partial \lambda_1}{\partial z}$ may be of either sign, depending on the relative magnitudes of the two terms on the righthand side.

(iii) $\frac{\partial F}{\partial z} = F' \psi K_o F$ is non positive (all variables non negative except for F')

(iv) $\frac{\partial \psi}{\partial z}$ may be determined from (5-25) to be

$$\frac{\partial \psi}{\partial z} = - g(\psi) \int_0^t K_o k_o \psi F f' dt' \qquad (5\text{-}58)$$

It can be seen from (5-58) that the sign of the derivative is opposite to that of $f'(X)$.

Hence the integrand consists of two negative terms for $f' \geq 0$: (iii) and (iv), balanced off by one positive term (ii). The relative magnitudes cannot be obtained, except numerically, hence the difficulty of obtaining the sign of (5-57).

Alternatively one may use (5-43) and (5-25), leaving only two terms, whose relative magnitudes need be determined before the sign of (5-57) can be determined.

Boundary Conditions for Adjoints

With the aid of expressions developed for the adjoint variables and their derivatives above, the sign of these variables along the boundaries may be obtained:

From (5-33), using the boundary condition on $\lambda_2(0,1)=0$ in (4-9):

$$\boxed{\lambda_1(z,1) = \exp\left[\int_z^1 \psi K_0 F'(z',1)dz'\right] > 0} \tag{5-59}$$

Alternatively from (5-45) using the same boundary condition on λ_2 we have

$$\boxed{\lambda_1(z,1) = \frac{F[X_1(1)]}{F[X(z,1)]} > 0} \tag{5-60}$$

Consider for the second adjoint (5-35) and use the known boundary condition $\lambda_1(1,t)=1$ (4-5) to obtain

$$\boxed{\lambda_2(1,t) = \int_t^1 \exp\left[-\int_t^{t'} k_0 g' f(1,t'')dt''\right] K_0 F(1,t')dt' \geq 0} \tag{5-61}$$

Boundary Derivatives of the Adjoints

The significance of the properties of these derivatives is discussed in the few paragraphs preceding (5-59) above.

Using (4-4), with known boundary conditions (4-9) we have, using 3.6 and (5-60)

$$\left.\frac{\partial \lambda_1}{\partial z}\right|_{(z,1)} = -\lambda_1 F' \psi(z,1) K_0(1) \geq 0 \tag{5-62}$$

Similarly for λ_2 at final time using (4-8) and (4-9)

$$\frac{\partial \lambda_2}{\partial t}\bigg|_{(z,1)} = -\lambda_1 K_o F(z,1) \tag{5-63}$$

From (5-60) and using (3.6)

$$\boxed{\frac{\partial \lambda_2}{\partial t}\bigg|_{(z,1)} = -K_o(t)F[X_1(1)] \leq 0} \text{ independent of } z \tag{5-64}$$

Hence the slope of λ_2 with respect to t, at the final time, is non positive and remains so for all z.

5.4 Stationarity Conditions

Using the properties of the state and adjoint variables derived so far, properties concerning the necessary condition for stationarity of the system are derived. These properties eventually lead to two expressions for the derivative of the optimal exit conversion. The one expression applies over all time, whereas the second, applies only to the unconstrained temperature region $0 \leq t \leq \bar{t}$ ($\bar{t}$ defined in 5.4.1 below). These two expressions, combined with expressions for the adjoint λ_1, eventually lead to a proof for the constancy of conversion at the optimum for special forms of F(X) and f(X) [see section 5.5 below].

5.4.1 Exit Conversion for a Stationary System

A necessary condition for optimality of the system has been provided (see Appendix A) in the form of a stationary Hamiltonian which, from (4-14), may be written as

$$pK_o(t)\int_0^1 \lambda_1 \psi F \, dz = k_o(t)\int_0^1 \lambda_2 g f \, dz \tag{5-65}$$

Define $\phi = - k_o fg$ (5-66)

then $\dfrac{\partial \psi}{\partial t} = \phi$ (5-67)

Consider the derivative $\dfrac{\partial (\lambda_2 \phi)}{\partial t}$

From (5-66)

$$\frac{\partial \lambda_2 \phi}{\partial t} = \phi \frac{\partial \lambda_2}{\partial t} + \lambda_2 \left[\frac{\partial \phi}{\partial \psi} \phi + \frac{\phi}{k_o} \frac{dk_o}{dt} + \frac{\phi f'}{f} \frac{\partial X}{\partial t}\right] \tag{5-68}$$

substituting for $\dfrac{\partial \lambda_2}{\partial t}$ from (4-8).

$$\frac{\partial \lambda_2 \phi}{\partial t} = \phi \left[-\lambda_1 K_o F - \frac{\lambda_2 \phi g'}{g}\right] + \lambda_2 \left[\frac{g\phi}{g'} \phi + \frac{\phi}{k_o} \frac{dk_o}{dt} + \frac{\phi f'}{f} \frac{\partial X}{\partial t}\right]$$

From (5-43) $$= - \phi \lambda_1 K_o F + \frac{\lambda_2 \phi}{k_o} \frac{dk_o}{dt} - \frac{1}{F} \frac{\partial \lambda_1 F}{\partial z} \frac{\partial X}{\partial t} \tag{5-69}$$

writing $\phi \lambda_1 K_o F = \lambda_1 F \dfrac{\partial \psi K_o}{\partial t} - \lambda_1 F \psi \dfrac{dK_o}{dt}$ (5-70)

and using $\dfrac{1}{K_o} \dfrac{dK_o}{dt} = \dfrac{p}{k_o} \dfrac{dk_o}{dt}$ from (3-51a) (5-70a)

$$\frac{\partial \lambda_2 \phi}{\partial t} = - \lambda_1 F \frac{\partial \psi K_o}{\partial t} + \left[\frac{p \psi \lambda_1 F K_o}{k_o} + \frac{\lambda_2 \phi}{k_o}\right] \frac{dk_o}{dt} - \frac{1}{F} \frac{\partial \lambda_1 F}{\partial z} \frac{\partial X}{\partial t}$$

$$\boxed{\frac{\partial \lambda_2 \phi}{\partial t} = - \lambda_1 F \frac{\partial \psi K_o}{\partial t} + \frac{\partial H}{\partial k_o} \cdot \frac{dk_o}{dt} - \frac{1}{F} \frac{\partial \lambda_1 F}{\partial z} \cdot \frac{\partial X}{\partial t}} \tag{5-71}$$

(5-71) when integrated leads directly (see below) to an expression for the optimal exit conversion

Optimum Exit Conversion

Crowe (1972) has shown that (5-71) leads directly to an expression for the derivative of the exit conversion at the optimum (point of stationarity). He proceeded as follows:

Integrate (5-71) over z to give

$$\int_0^1 \frac{\partial \lambda_2\phi}{\partial t}\, dz = \int_0^1 [-\lambda_1 F\frac{\partial \psi K_o}{\partial t} + \frac{\partial H}{\partial k_o}\,\frac{dk_o}{dt} - \frac{1}{F}\,\frac{\partial \lambda_1 F}{\partial z}\cdot\frac{\partial X}{\partial t}]dz \tag{5-72}$$

Now the term $\int_0^1 \frac{\partial H}{\partial k_o}\cdot\frac{dk_o}{dt}\, dz$ is zero at the optimum irrespective of whether k_o is constrained or not (since for k_o constrained $\frac{dk_o}{dt}=0$ and for k_o unconstrained, the Hamiltonian condition (4-12) applies).

Hence we may write (5-72) at the optimum as

$$\int_0^1 \frac{\partial \lambda_2\phi}{\partial t}\, dz = \int_0^1 [-\lambda_1 F\frac{\partial \psi K_o}{\partial t} - \frac{1}{F}\,\frac{\partial \lambda_1 F}{\partial z}\cdot\frac{\partial X}{\partial t}]dz \tag{5-73}$$

Integrating the second integral on the right hand side by parts we obtain

$$\int_0^1 \frac{\partial \lambda_2\psi}{\partial t}\, dz = -\int_0^1 (\lambda_1 F\frac{\partial \psi K_o}{\partial t})dz - \lambda_1 F\,(\frac{1}{F}\,\frac{\partial X}{\partial t})\Big|_{z=0}^{z=1} + \int_0^1 \lambda_1 F\,\frac{\partial}{\partial z}(\frac{1}{F}\,\frac{\partial X}{\partial t})dz \tag{5-74}$$

(5-74) holds for all $0 \le t \le 1$ at the optimum, irrespective of whether k_o is unconstrained or not.

Using the boundary condition on λ_1 (4-5) and the condition that

$$X_o(t) = \text{constant} \tag{5-75}$$

he obtains

$$\int_0^1 \frac{\partial \lambda_2 \phi}{\partial t} dz = - \frac{dX_1(t)}{dt} - \int_0^1 [\lambda_1 F \frac{\partial \psi K_o}{\partial t} - \lambda_1 F \left(\frac{1}{F} \frac{\partial^2 X}{\partial z \partial t} - \frac{F'}{F^2} \frac{\partial X}{\partial z} \quad \frac{\partial X}{\partial t}\right)] dz$$

Using continuity properties of X (see 3.6) interchange the order of differentiation and using the first state equation (3-54) to give:

$$\int_0^1 \frac{\partial \lambda_2 \phi}{\partial t} dz = - \frac{dX_1(t)}{dt} - \int_0^1 [\lambda_1 F \frac{\partial \psi K_o}{dt} - \lambda_1 \frac{\partial (\psi K_o F)}{\partial t} + \lambda_1 F' \ \psi K_o \frac{\partial X}{\partial t}] dz$$

combining the terms inside the square brackets, the integrand is easily seen to be zero; hence we have

$$\boxed{\frac{dX_1(t)}{dt} = \int_0^1 \frac{\partial}{\partial t} (\lambda_2 \ k_o \ gf) dz \qquad \text{for all } 0 \leq t \leq 1} \tag{5-76}$$

Crowe's condition (5-76), is a necessary condition for the optimum exit profile irrespective of whether or not, k_o is constrained.

Define $\bar{t}$ as that point in time t at which the optimum (stationary) profile reaches its upper constraint and remains there. It is easy to see, if one considers the fixed point formulation of the necessary conditions (4-33) for $p \neq 1$ that as $t \to 1$, $\lambda_2 \to 0$ and k_o (optimum) tends to infinity. So, as expected, the optimum profile will always end on its upper temperature constraint.

From (5-76) and (5-65) it is seen that the expression for $\frac{dX_1}{dt}$ is simply the derivative of the right half of the Hamiltonian equation (5-65). If we restrict ourselves to the optimum unconstrained profile region, that is for $0 \leq t \leq \bar{t}$ we may equate the remaining half of (5-65) to the expression for $\frac{dX_1}{dt}$; hence

$$\boxed{\frac{dX_1(t)}{dt} = p\int_0^1 \frac{\partial}{\partial t}(K_o\,\lambda_1\,F\,\psi)dz \quad \text{for } 0 \le t \le \bar{t}} \tag{5-77}$$

Thus (5-77) applies only over the unconstrained region, and is equal to (5-76) over this region.

We may obtain an expression for the optimum exit conversion itself by considering (5-76). Interchanging the order of differentiation and integration (continuity properties of variables see 3.6 above), since the derivatives of the two quantities X_1 (t) and $\int_0^1 \lambda_2 k_o gfdz$ are equal, their values differ by a constant c_1 that is

From (5-77) $$\frac{dX_1}{dt} = \frac{d}{dt}\int_0^1 \lambda_2 k_o gfdz \tag{5-78}$$

Therefore $$X_1(t) = \int_0^1 \lambda_2 k_o gfdz + c_1 \tag{5-79}$$

Now since (5-79) holds for <u>all</u> $0 \le t \le 1$ (see (5-76)) we may use the boundary condtion at t=1 on λ_2 (z,1)=0 to obtain

$$\boxed{X_1(t) - X_1(1) = \int_0^1 \lambda_2 k_o gfdz \qquad \text{all } 0 \le t \le 1} \tag{5-80}$$

Now since the integral in (5-80) is equal to the left hand side of (5-65) over the unconstrained region we may write

$$\boxed{X_1(t) - X_1(1) = p\int_0^1 \lambda_1 \psi\, K_o F\, dz \qquad 0 \le t \le \bar{t}} \tag{5-81}$$

A general expression for the derivative of the exit conversion can be obtained directly from the first state equation (3-54). From 5.2.2, with z=1, we have

$$\int_{X_0}^{X_1} \frac{\partial X}{F} = \int_0^1 \psi K_0 \, dz' \tag{5-82}$$

Differentiating both sides using Leibnitz's rule, we have, remembering that $X_0(t)$=constant

$$\boxed{\frac{dX_1(t)}{dt} = F[X_1(t)] \int_0^1 \frac{\partial \, \psi K_0}{\partial t} \, dz} \tag{5-83}$$

Derivative of the Hamiltonian with respect to Time

A very useful expression to obtain, is that of the time derivative of the Hamiltonian over the unconstrained region. This leads to another form for the necessary condition for the optimum and provides an invaluable relation between the adjoints and state variables, which in fact, leads to a proof for constant conversion at the optimum for the case where p=constant [see appendix B].

If we multiply the Hamiltonian through by $k_0(t)$ under the integral sign, which we are permitted to do since integration is along z only, and then differentiate with respect to t, we have over the unconstrained region

$$\frac{d}{dt}\int_0^1 k_0 \frac{\partial H}{\partial k_0} dz = \int_0^1 [\frac{\partial}{\partial t} (p\lambda_1 F\psi K_0 - \lambda_2 k_0 g f)]dz = 0$$

using (5-66) $= \int_0^1 [p\lambda_1 F\frac{\partial \psi K_0}{\partial t} + p \, \psi K_0 \frac{\partial \lambda_1 F}{\partial t} + \frac{\partial \lambda_2 \phi}{\partial t}]dz = 0$

Now substituting for $\frac{\partial \lambda_2 \phi}{\partial t} dz$ from (5-73) over the unconstrained region we obtain the necessary condtion

$$\boxed{\int_0^1 [(p-1)\ \lambda_1 F \frac{\partial\ \psi K_o}{\partial t} + p\psi K_o \frac{\partial\ \lambda_1 F}{\partial t} - \frac{1}{F}\ \frac{\partial\ \lambda_1 F}{\partial z} \cdot \frac{\partial\ X}{\partial t}]dz = 0} \tag{5-83a}$$

(5-83a) is used to prove the constant conversion optimal policy for f=1 [see appendix B].

5.4.2 Decay Rate Independent of Conversion

It has been shown [Crowe (1970)] that for the simplified decay rate, where f(X) is taken to be constant, that a necessary condition for the optimum of the objective function P is that the temperature is chosen so as to maintain constant exit conversion. This result drops out directly from the derivative of the Hamiltonian (5-83a), (see appendix B).

It is assumed in the above paper, that ψ is essentially constant over z. Note that this requires specifying a uniform initial activity. For this case, the activity is uniform in z for all t and we may integrate (5-82) to give

$$\int_{X_o}^{X_1} \frac{\partial\ X}{F} = \psi K_o(t) \tag{5-84}$$

Differentiating both sides using Leibnitz's rule we have

$$\boxed{\frac{1}{F[X_1(t)]}\ \frac{dX_1(t)}{dt} = \frac{\partial\ (\psi K_o)}{\partial\ t}} \tag{5-85}$$

Now from Appendix B we have, at the unconstrained optimum,

$$\frac{dX_1}{dt} = 0 \qquad 0 \leq t \leq \bar{t} \tag{5-86}$$

hence from (5-85) $\frac{\partial \psi K_o}{\partial t} = 0 \qquad 0 \leq t \leq \bar{t}$ (5-87)

Now integrating (5-82) up to a general z from (5.2.5)

$$\frac{\partial X}{\partial t} = F\int_0^z \frac{\partial (\psi K_o)}{\partial t} \; dz' \tag{5-88}$$

From (5-87) $\boxed{\frac{\partial X}{\partial t} = 0}$ At optimum $0 \leq t \leq \bar{t}$, for all z (5-89)

Hence constant exit conversion of the optimum (unconstrained) implies constant conversion at each point along the reactor length as well.

We may obtain a closed form expression for the optimum rate constant (hence temperature) profile by making use of (5-87) and remembering that f=1 in the second state equation (3-55), differentiating (5-87) we obtain

$$\psi \frac{dK_o}{dt} - K_o k_o g(\psi) = 0 \tag{5-90}$$

For the case g= ψ using (5-70a)

$$\psi K_o \left[\frac{p}{k_o} \frac{dk_o}{dt} - k_o\right] = 0 \qquad \text{at optimum} \quad 0 \leq t \leq \bar{t}$$

From section 3.6 above, K_o is non negative, and provided activity remains non zero up until the control reaches the upper constraint at $\bar{t}$ we have

$$\frac{dk_o}{dt} = \frac{k_o^2}{p} \qquad \text{At optimum for } g = \psi \tag{5-100}$$

Integrating between $0 \le t \le t$ we have the closed form expression for the optimum rate constant profile

$$k_o(t)_{opt} = \left[\frac{1}{k_o(o)} - \frac{t}{p} \right]^{-1} \quad 0 \le t \le \bar{t} \tag{5-101}$$

for $f=1$ $g=\psi$

5.4.3 Alternative Expression for the Optimum Exit Conversion

If we depart from the more general expression $g(\psi)$ and choose the specific case where $n=1$ we can obtain another expression for the optimum (stationary) exit conversion profile using (5-51).

$$\frac{\partial \lambda_2 \psi}{\partial t} = - \lambda_1 \psi K_o F \tag{5-51}$$

for $g = \psi$

If we multiply both sides of (5-51) by p and integrate over z between $0 \le z \le 1$ we have

$$p \int_0^1 \frac{\partial \lambda_2 \psi}{\partial t} \, dz = -p \int_0^1 \lambda_1 \psi K_o F dz \tag{5-102}$$

If we restrict ourselves to the unconstrained region $0 \le t \le \bar{t}$ and compare (5-102) to (5-81) we obtain

$$\boxed{X_1(t) - X_1(1) = -p \int_0^1 \frac{\partial \lambda_2 \psi}{\partial t} \quad \text{at the optimum for } g=\psi \text{ and } 0 \le t \le \bar{t}} \tag{5-103}$$

The derivative of the optimum exit converstion may be obtained simply as

$$\boxed{\frac{dX_1(t)}{dt} = - p \int_0^1 \frac{\partial^2 (\lambda_2\psi)}{\partial t^2}} \tag{5-104}$$

The integrand in (5-103) is non positive. The proof of this statement is given below in section 5.6.

Consider also, the integral of the following product

$$\int_0^1 \lambda_1 \frac{\partial X}{\partial z} \, dz = K_o \int_0^1 \lambda_1 F\psi dz \tag{5-105}$$

Integrating the left hand side by parts and using the boundary conditions on $\lambda_1(1,t)=1$, we have

$$X_1(t) - \lambda_1(0,t) \cdot X_o(t) = \int_0^1 (\frac{\partial \lambda_1}{\partial z}) X \, dz + K_o \int_0^1 \lambda_1 F\psi dz \tag{5-106}$$

If we consider the case of zero initial conversion the second term on the left is eliminated; comparing the second integral on the right with (5-81) an expression for the optimum exit conversion in the unconstrained region is obtained.

$$X_1(t) = \int_0^1 (\frac{\partial \lambda_1}{\partial z}) X \, dz + \frac{1}{p} [X_1(t) - X_1(1)] \tag{5-107}$$

rearranging we obtain

$$\boxed{\begin{array}{l} X_1(t) = \frac{p}{p-1} \left[\int_0^1 (\frac{\partial \lambda_1}{\partial z}) X \, dz - \frac{X_1(1)}{P}\right] \\ \qquad\qquad\qquad \text{At the optimum for} \\ \qquad\qquad\qquad 0 \le t \le \bar{t} \quad \text{and} \\ \qquad\qquad\qquad X_o(t) = 0 \end{array}} \tag{5-108}$$

5.5 Analytically Predictable Optimal Exit Conversions

Using the properties of the adjoints and state variables derived above in particular the expression for the optimal exit conversion, the derivative of $\lambda_1 F$ with respect to z and the boundary derivative of λ_1 with respect to t, all derived above in 5.3.3, several statements concerning the character of the optimal exit conversion may be made. Four propositions regarding the slope of the exit conversion, at the optimum, for certain forms of $F(X)$ and $f(X)$, are proved.

5.5.1 Zero Order Reactions

Proposition 1:

Given the two conditions below, a necessary condition for the system to be optimal is that the exit conversion be constant over the unconstrained region

Conditions: (i) $f(X)=cX$ c arbitrary positive constant

(ii) $X_0(t)=0$ for all $0 \leq t \leq 1$

Proof

From (5-43) $\dfrac{\partial \lambda_1 F}{\partial z} = \lambda_2 k_0 F g f'$

for zero order reaction, we may set F=1 without loss of generality, and applying condition (i) we have

$$\frac{\partial \lambda_1}{\partial z} = \lambda_2 k_0 g c \tag{5-109}$$

Multiply both sides of (5-109) by f and integrating between $0 \leq z \leq 1$

$$c \int_0^1 \lambda_2 k_0 g f dz = \int_0^1 f \frac{\partial \lambda_1}{\partial z} dz \tag{5-110}$$

A necessary condition for optimality for all $o \leq t \leq 1$ from (5-80) is

$$\int_0^1 \lambda_2 k_o g f dz = X_1(t) - X_1(1) \qquad (5\text{-}80)$$

Hence using (5-110) and (5-80) we have at the optimum

$$X_1(t) - X_1(1) = \frac{1}{c} \int_0^1 f \frac{\partial \lambda_1}{\partial z} dz$$

Integrating the right hand side by parts we have, using the boundary condition on $\lambda_1(1,t)=1$, (3-54) and condition (i):

$$X_1(t) - X_1(1) = \frac{1}{c}\left[f[X_1(t)] - f[X_o(t)].\lambda_1(0,t)\right] - \int_0 \psi K_o \lambda_1 \, dz \qquad (5\text{-}110a)$$

A further necessary condition for optimality but over the unconstrained region only, i.e., $0 \leq t \leq \bar{t}$, is given by (5-81); for zero order reaction

$$\int_0^1 \lambda_1 \psi \, K_o \, dz = \frac{(X_1(t) - X_1(1))}{P} \qquad (5\text{-}111)$$

From (5-110a) and (5-111), rearranging, we have

$$X_1(t) = p.\left[\frac{f[X_1(t)] - f[X_o(t)] \; \lambda_1(0,t)]}{c(p+1)} \right] + X_1(1) \qquad (5\text{-}111a)$$

using conditions (i) and (ii) on (5-111a) and rearranging

$$\boxed{X_1(t) = X_1(1) \; (1+p)} \qquad (5\text{-}112)$$

The right hand side of (5-112) is constant, so differentiating we have

$$\boxed{\frac{dX_1}{dt} = 0} \qquad (5\text{-}113)$$

If we do not specify zero initial conversion (condition (ii)), but instead initial conversion just constant, i.e.

$X_0(t)=c_1$, constant

then (5-112) may be written as

$$X_1(t)=X_1(1)\ (1+p) - pc_1\lambda_1(0,t)$$

and $$\boxed{\frac{dX_1}{dt} = -\ pc_1\ \frac{d\lambda_1(0,t)}{dt}} \qquad (5\text{-}114)$$

A discussion on the difficulties involved in determining the sign of $\frac{d\lambda_1(0,t)}{dt}$, (F = 1), is given in the paragraph following (5-54) above.

An alternative proof of (5-113) is given in appendix C. This proof is somewhat more involved, but perhaps more general in that an analytical form for the derivative in (5-114) is used and $\frac{dX_1}{dt}$ is calculated directly from (5-76) above.

5.5.2 Non Zero Order Reactions

The type of reaction forms referred to in this section, cannot be conveniently classified under a general n th order reaction scheme.

Certain reaction schemes (eg. autocatalytic) are generated by the requirement of the three specified conditions below and do not fit into a general n th order reaction scheme.

Propostion 2

Given the three conditions below, a necessary condition for the system to be optimal, is that the exit conversion be constant over the unconstrained region.

Conditions (i) $Ff'=cf$ c non zero constant

(ii) $F[X_0(t)]=0 \quad [X_0(t)=0] \qquad 0 \leq t \leq 1$

(iii) $F'[X_1(t)]\neq c \qquad 0 \leq t \leq 1$

Proof

It is instructive to consider the limitations imposed by the conditions, on the allowable forms of F and f.

Rewriting (i) as a differential equation in X and integrating to solve for a particular f (with zero constant of integration) we obtain

$$f = \exp\ [c\int\frac{1}{F}\ dX] \tag{5-115}$$

using the first state equation (3-54) we may write (5-115) as

$$f = \exp\ [c\int\psi K_0 dz] \quad \text{(zero constant of integration)} \tag{5-115a}$$

Example For an autocatalytic reaction we will have F of the form (in a uniform temperature reaction $\bar{F}$=F)

$$F = X\ (1-X) \tag{5-116}$$

(5-116) certainly satisfies the last two conditions and from (5-115) we have

$$f = [\frac{X}{1-X}]^c \tag{5-116a}$$

c may be any constant as long as the last condition is not violated.

There are obviously an unlimited numer of forms which satisfy the conditions above; however, only a limited number are realistic from the physical point of view, nevertheless if we remove the physical interpretation of the two state equations, the system defined mathematically should still exhibit the stationarity property, that the far end boundary derivative of the first state variable (X) must be zero, for unconstrained optimal control. This fact is made use of in chapter 6 in order to test the validity of the computer program used for the numerical studies. For this purpose, then, we may use the mathematically acceptable (see 3.6 above) but physically unrealistic form of F=X this produces via (5-115) $f=X^c$ $c\neq 1$, and indeed these forms produce a constant "conversion" profile at the optimum, which is validated by the numerical studies.

From (5-43) $\frac{\partial \lambda_1 F}{\partial z} = \lambda_2 k_o g F f'$

From condition (i) $= c\lambda_2 k_o g f$ (5-117)

Integrating with respect to z and using the necessary condition (5-80)

$$X_1(t) = X_1(1) + \frac{1}{c}\int_0^1 \frac{\partial \lambda_1 F}{\partial z}\, dz$$

Integrating out, using the boundary condition on $\lambda_1(1,t)=1$,

$$X_1(t) = X_1(1) + \frac{1}{c}\left[F[X_1(t)] - \lambda_1(0,t)\, F[X_o]\right]$$

Applying condition (ii) and differentiating both sides we have

$$\frac{dX_1}{dt}\left[c - F'\,[X_1(t)]\right] = 0 \tag{5-118}$$

Using condition (iii), (5-118) implies that

$$\boxed{\frac{dX_1(t)}{dt} = 0} \quad ■ \tag{5-119}$$

If condtion (ii) did not hold and $F[X_o]$ was a non zero constant we would have instead of (5-119)

$$\boxed{\frac{dX_1}{dt} = \frac{F[X_o]}{[F'(X_1)-c]}\;\frac{d\lambda_1(0,t)}{dt}} \tag{5-119a}$$

<u>Example</u>

It is instructive to consider the example of a <u>first order reaction,</u> here we have using (5-115)

$$F = (1-X) \tag{5-120}$$

$$f = (1-X) \tag{5-120a}$$

with c obviously equal to -1 in (5-115). Referina to condition (iii) notice that

$$F'(X) = c \tag{5-121}$$

deliberately.

From (5-115a) and (5-121) a particular value for f is given by

$$\frac{f(X)}{f(X_o)} = \exp\,[-\int_0^z \psi K_o dz']\tag{5-122}$$

Now from (5-33) making use of the fact that, from (5-120), F' = -1, and substituting the exponential in (5-122) for f we have (X_o constant)

$$\lambda_1(0,t) = \frac{f[X_1(t)]}{f(X_o)} - \int_0^1 \frac{f(X)}{f(X_o)} \cdot \lambda_2 k_o g f'\, dz$$

substituting for f' and $f(X_o)$ from(5-120a), and using the optimal condition (5-80) we obtain, at the optimum

$$\boxed{\lambda_1(0,t) = \frac{1-X_1(1)}{1-X_o}\ \text{, constant}}\tag{5-122a}$$

It would appear then, from (5-122a) and (5-119a), that the constant conversion policy holds for a first order reaction, but (5-122a) holds only subject to <u>all three</u> conditions listed below propostion 2. With the first order form for F in (5-120), equation (5-121) deliberately violates condtion (iii) thereby rendering (5-119a) invalid and hence the constant conversion conclusion.

For $c = +1 \neq F'$ we have for a first order reaction from (5-115)

$$f = \frac{1}{1-X}$$

Following the same steps, and using the fact that $f' = f^2$, for this form of f

$$\boxed{X_1(t) = \frac{1 + X_1(1) - \lambda_1(0,t)\,[1-X_o]}{2}}\tag{5-123}$$

If we now substitute in (5-119a) we obtain an identity which provides no information.

A point to notice, is that, in neither of the above propositions, is any restriction placed on the form of $g(\psi)$ as it occurs in the second state equation (3-55).

5.6 Optimal Control where Exit Conversion is Constant

It has been demonstrated in 5.5 above, that the policy of constant exit conversion of the optimum does hold true for specific forms of the conversion dependence term $f(X)$ in the first state equation (3-54). For these cases a formal (but not closed) expression for the optimal unconstrained control may be obtained as follows:

From the necessary condition (5-76) with constant exit conversion we have the necessary condition

$$\frac{d}{dt}\left[k_o \int_0^1 \lambda_2 g f dz\right] = 0 \tag{5-124}$$

this gives on differentiating,

$$\frac{dk_o}{dt} \int_0^1 \lambda_2 g f dz = - k_o \int_0^1 \left[\lambda_2 g f' \frac{\partial X}{\partial t} + f \frac{\partial \lambda_2 g}{\partial t}\right] dz \tag{5-125}$$

from (3-55) and (4-8)

$$\frac{\partial \lambda_2 g}{\partial t} = g\left[\lambda_2 k_o f g' - \lambda_1 K_o F\right] - \lambda_2 g' k_o g f$$

$$\boxed{\frac{\partial \lambda_2 g}{\partial t} = - g \lambda_1 K_o F \leq 0} \tag{5-126}$$

[see also (5-51) above in section 5.3.3.]

From (5-126) and (5-125)

$$\frac{dk_o}{dt} = \frac{-k_o^2 D\ (z,t)}{k_o \int_0^1 \lambda_2 fg dz} \tag{5-127}$$

$$\text{where } D = \int_0^1 [\lambda_2 g f' \frac{\partial X}{\partial t} - fg\lambda_1 K_o F] dz \tag{5-128}$$

Using the necessary condition (5-80) again, and the fact that $X_1(t) = X1$, (5-129) a constant here for $o \leq t \leq \bar{t}$,

$$\frac{dk_o}{dt} = -\ k_o^2 \ \frac{D}{[\ (X1 - X_1(1))]} \tag{5-130}$$

(5-130) is analogous to the, expression derived previously (5-100). The expression (5-130), reverts to (5-100) for the case where constant conversion is known to exist (see appendix B) that is for $f(X)$ = constant.

So, for f = constant, say 1, D becomes

$$D = -\int_0^1 g\lambda_1 K_o F dz \tag{5-131}$$

using the further necessary condition (5-81) and specifying $g = \psi$ we may write (5-131) as

$$D = \frac{-[X1 - X_1(1)]}{P} \tag{5-132}$$

substituting into (5-130) we revert to (5-100)

$$\frac{dk_o}{dt} = \frac{k_o^2}{p} \tag{5-100}$$

5.7 Falling Exit Conversion at the Optimum

Falling exit conversion is by far the most common form of profile found in all the numerical studies. Most reasonable forms for F (first and higher order reactions) and f(X) (linear and higher order in X, exponential, etc. produce a falling exit conversion at the optimal. See Chaper 6 below.

Using the expression for the derivative of the optimal exit conversion [(5-76) above], a sufficient condition on f(X) is provided so as to guarantee a falling exit conversion.

The results of proposition 3 may also be used as a numerical test: should there be any doubt as to the slope of the exit conversion profile [see Chapter 6], the proposition 3 provides both a weak and a stronger test as to whether the exit conversion is falling in time. It also provides and indication of the effect of f(X) and its derivative on the slope of the optimal profile [see 6.7.2 below].

Proposition 3

If the conversion dependent term, f(X), in the catalyst decay rate equation, is chosen so that the derivative in time, of the product $k_o f$ is non positive for all z and some t; then the optimal necessary condition, is a falling exit conversion for those t; unless 100 percent conversion is reached or catalyst activity is zero.

Proof

From (5-126)

$$\frac{\partial \lambda_2 g}{\partial t} = - g \lambda_1 K_o F \tag{5-133}$$

Now if we have not reached 100 percent conversion $F(X) > 0$ and if catalyst activity is not zero then $g(\psi) > 0$ [see (3-36) and (3-37)]. $K > 0$ and from (5-46) $\lambda_1 > 0$. Thus from (5-133)

$$\frac{\partial \lambda_2 g}{\partial t} < 0 \tag{5-134}$$

Proposition 3 contains the sufficient condition that f be chosen so that

$$\frac{\partial k_o f}{\partial t} \leq 0 \qquad (5\text{-}135)$$

Consider the necessary condition for the optimal exit conversion (5-76) and differentiate

$$\frac{d X_1(t)}{dt} = \int_0^1 [k_o f \frac{\partial \lambda_2 g}{\partial t} + \lambda_2 g \frac{\partial k_o f}{\partial t}]dz \qquad (5\text{-}136)$$

Now, from the properties of the variables in section 3.6 above and non negativety of λ_2 (5-47), from (5-134), the first integrand is negative and the second is non positive. This gives rise to a falling exit conversion at the optimum, for those t at which the sufficient condition (5-135) holds. ■

The necessary condition is less stringent and simply requires that the average value, in z, of the product $[\lambda_2 g \frac{\partial k_o f}{\partial t}]$ if it is positive, be less than the absolute value of the average of $[k_o f \frac{\partial \lambda_2 g}{\partial t}]$, at the times in question.

One cannot extend the conclusions of proposition 3, and should the inequality be opposite in (5-135), we would require knowledge about the relative magnitudes for all z, of the two integrands, before a statement on the slope of the exit conversion profile can be made. ,

Proposition 4

There exists an f(X) which produces a falling exit conversion profile at the optimum, for all forms of the catalyst decay term $g(\psi)$.

Proof

The proof is provided by producing a counter example to the statement of constant conversion at the optimum.

For a uniform temperature reactor with first order reaction we have

$$F = (1-X)$$

From (5-4) above we can solve directly for the form of conversion X, to give

$$X = 1 - c' \exp\left[-K_o(t)\int_0^z \psi dz'\right] \tag{5-4}$$

$c' = 1 - X_o$, constant

choose $f(X) = (1-X)^r > 0$ (5-137)

r = order of conversion dependence

Multiply (5-137) by k_o, to give

$$k_o f = ck_o \exp\left[-rK_o \int_0^z \psi dz'\right] \tag{5-138}$$

c = constant

From (5-126) above we have

$$\frac{\partial \lambda_2 g}{\partial t} = - g\lambda_1 K_o F < 0 \tag{5-126}$$

which is negative as long as we do not have 100% conversion or zero activity

The optimal condition (5-136) above gives after substitution of (5-126)

$$\frac{dX_1}{dt} = - \int_0^1 k_o fg \left[\lambda_1 K_o F - \lambda_2 \frac{\partial \ln k_o f}{\partial t}\right] dz \tag{5-134}$$

All variables are positive except for the trivial case (of 100% conversion zero activity) stated above. [See Chapter 3.6 and equations (3-46) and 5-47) above].

Hence, if we can show that the derivative $\frac{\partial \ln k_o f}{\partial t}$ is non positive for some value of r, we will have the required proof of existence, and $\frac{dX_1}{dt}$ will be negative at the optimum.

From (5-138) substituting for f from (5-137) and for $\frac{\partial \psi}{\partial t}$ from (3-55) and using (5-70a)

$$\boxed{\frac{\partial \ln k_o f}{\partial t} = \frac{\partial \ln k_o}{\partial t}\ [1 - r\, pK_o \int_0^z \psi dz'] + rK_o k_o \int_0^z (1-X)^r g dz'} \tag{5-140}$$

r sufficiently large and positive

Consider the expression (5-140) and note that z, k_o, K_o, $g(\psi)$ are bounded functions [see chapter 3.6 above].

Note also that the term $r\,(1-X)^r$ is convergent at all times for which we do not have 100% conversion or zero conversion and hence by choosing r sufficiently large and positive the term

$$rK_o k_o \int_0^z (1-X)^r g dz'$$

can be made arbitrarily small and positive.

But in choosing r large and positive the remaining term in (5-140) becomes large and negative (provided we have a rising temperature profile at the optimum) and will dominate and thus for r sufficiently large and positive.

$$\frac{\partial \ln k_o f}{\partial t} < 0 \tag{5-141}$$

From (5-141) and (5-139) we have

$$\boxed{\frac{dX_1}{dt} < 0} \tag{5-142}$$

for all t, as long as we do not have 100% or zero conversion, or zero activity, and we have a rising temperature profile at the optimum.

r equal to zero

This is the well analysed case where decay rate is independent of conversion and from Appendix B,

$$\frac{dX_1}{dt} = 0$$

Here we would have over the unconstrained region

$$k_o \int_o^1 \frac{\partial \lambda_2 g}{\partial t} dz = - \frac{dk_o}{dt} \int_o^1 \lambda_2 g dz \qquad (5\text{-}143)$$

r large and negative

This case is not clear cut and probably produces a negative derivative, as in (5-141), as well.

Necessary Condition

Notice that the condition (5-141) is a sufficient condition for falling optimum profile and that it is only necessary that the negative half of the integral in (5-139) be larger in absolute value than the remaining half, which includes $\frac{\partial \ln k_o f}{\partial t}$ and this will produce a falling exit conversion at the optimum, even if $\frac{\partial \ln k_o f}{\partial t}$ is positive.

In practice then a value of $r = 1$ or 2 is sufficient to cause a falling exit profile,as is borne out by the numerical studies in Chapter 6 below. (see table 6-12)

5.8 Summary of Important Equations and Results

A summary of the important equations, may be gleaned directly from the boxed ▭ results and equations of chapter 5; in point form by equation number:

1. (5-6) Conversion X. First order reaction
2. (5-7) Exit Conversion X_1. First order reaction
3. (5-12) Catalyst decay ψ. First order decay
4. (5-15) Conversion X,n th order reaction
5. (5-16) Exit Conversion X_1,n th order reaction
6. (5-19) Catalyst decay , m th order decay
7. (5-23) t derivative of conversion:
8. (5-25) z derivative of catalyst activity:
9. (5-33) Integral expression for $\lambda_1(z,t)$
10. (5-35) Integral expression for $\lambda_2(z,t)$
11. (5-43) z derivative of $\lambda_1 F$:
12. (5-45) Integral expression for $\lambda_1(z,t)$
13. (5-46) Sign of $\lambda_1(z,t)$
14. (5-47) Sign of $\lambda_2(z,t)$
15. (5-54) t derivative of $\lambda_1 F$
16. (5-59) Boundary condition for $\lambda_1(z,1)$
17. (5-60) Boundary condtion for $\lambda_1(z,1)$ (alternative)
18. (5-61) Boundary condition for $\lambda_2(1,t)$
19. (5-62) Boundary Derivative in z for λ_1: $\partial\lambda_1/\partial z$ at (z,1)

20 (5-64) Boundary Derivative in t for λ_2: $\partial\lambda_2/\partial t$ at (z,1)

21. (5-71) t derivative of the variables $\lambda_2\phi$: $\partial(\lambda_2\phi)/\partial t$
22. (5-76) Optimum exit conversion $o \le t \le 1$ (t derivative)
23. (5-77) Optimum exit conversion $o \le t \le \bar{t}$ (t derivative)
24. (5-83a) t derivative of Hamiltonian $\bar{H}$
25. (5-103) Optimum exit conversion as function of $\lambda_2\psi$
26. (5-104) t derivative of optimum exit conversion as function of $\lambda_2\psi$
27. (5-108) Optimum exit conversion as function of $\partial\lambda_1/\partial z$ and X
28. (5-126) t derivative of $\lambda_2 g$
29. Propositions 1 Zero order reactions: constant conversion
30. 2 Non zero order reactions: constant conversion
31. 3 Condition on f(X): falling conversion
32. 4 Counter example: falling conversion
33. C Zero order reaction: constant conversion (alternative) (see Appendix C)

CHAPTER 6

NUMERICAL ANALYSIS

6.1 Introduction

When no general analytical methods are available and one has, to some extent, to rely on numerical methods to investigate the properties of the system, more confidence is generated if one can, by some other independent method, verify the numerical methods ability to predict the system properties accurately. In the present system for example, the zero order reaction system, with a particular form for f(X), has been shown, analytically, to give constant conversion at the optimum [see 5.5.1 above]. The program when provided with the specific conditions, should without exception, provide a constant conversion policy in agreement.

For the known case of constant conversion at each point along the length of the reactor [section 5.4.3], i.e., for the case f=constant, the computer program should again be in agreement and predict constant conversion at each point in the reactor.

Very many analytical examples are provided by the non zero reaction order scheme in 5.5.2 above. Only some will be physically realistic, but as explained in 5.5.2, the mathematical system equations still provides for a zero time derivative at the exit for the 'conversion' (first state variable X) at the optimum, as long as F(X), f(X) have the properties indicated in 3.6 above.

If, for all the above analytically predictable optimal 'conversions', we are able to verify the program's ability to predict the correct optimal profiles, we will have more confidence in the program's ability to predict profiles in those areas for which no general analytical results are available. Also, proposition 4 above, assures us that there exists an f that will produce a falling optimum conversion if we choose the order of conversion dependence r sufficiently large. In table 6-12 r=1 is sufficient to produce a falling exit conversion profile.

A valid query exists as to whether or not the optimal profile is reached; especially in view of the known difficulties with gradient methods in the vicinity of the optimum. This query may be answered partially by testing the optimum reached, from new initial guesses, but more strongly so by using a completely independent algorithm, not based on the gradient methods, and comparing the profiles and objective functions obtained.

6.2 Verification of Program

6.2.1 f(X) Constant

The constant conversion policy is known to be valid for this case (Appendix B), f was set equal to unity. The optimum exit conversion is seen in figure 6-1 to be constant as long the temperature policy remains unconstrained. As soon as the temperature reaches an upper constraint at $t=\bar{t}$ the exit conversion begins to fall, and continues to do so until final time t=1. Also, parametric studies performed, agree with those of Ogunye and Ray's (1971) [see section 2.5 above].

Table 6-1 gives the data produced for this case.

6.2.2 Zero and Non Zero Reaction Orders for f=f(X)

As a rule, the form of $\bar{f}$ in (3-20) was taken to be

$$\bar{f}(X) = X^{n1} (c + dX)^{n2} \tag{6-1}$$

c,d constants

so, for a uniform temperature reactor ($\bar{f}=f$), with n1=0 and n2=1, we have a

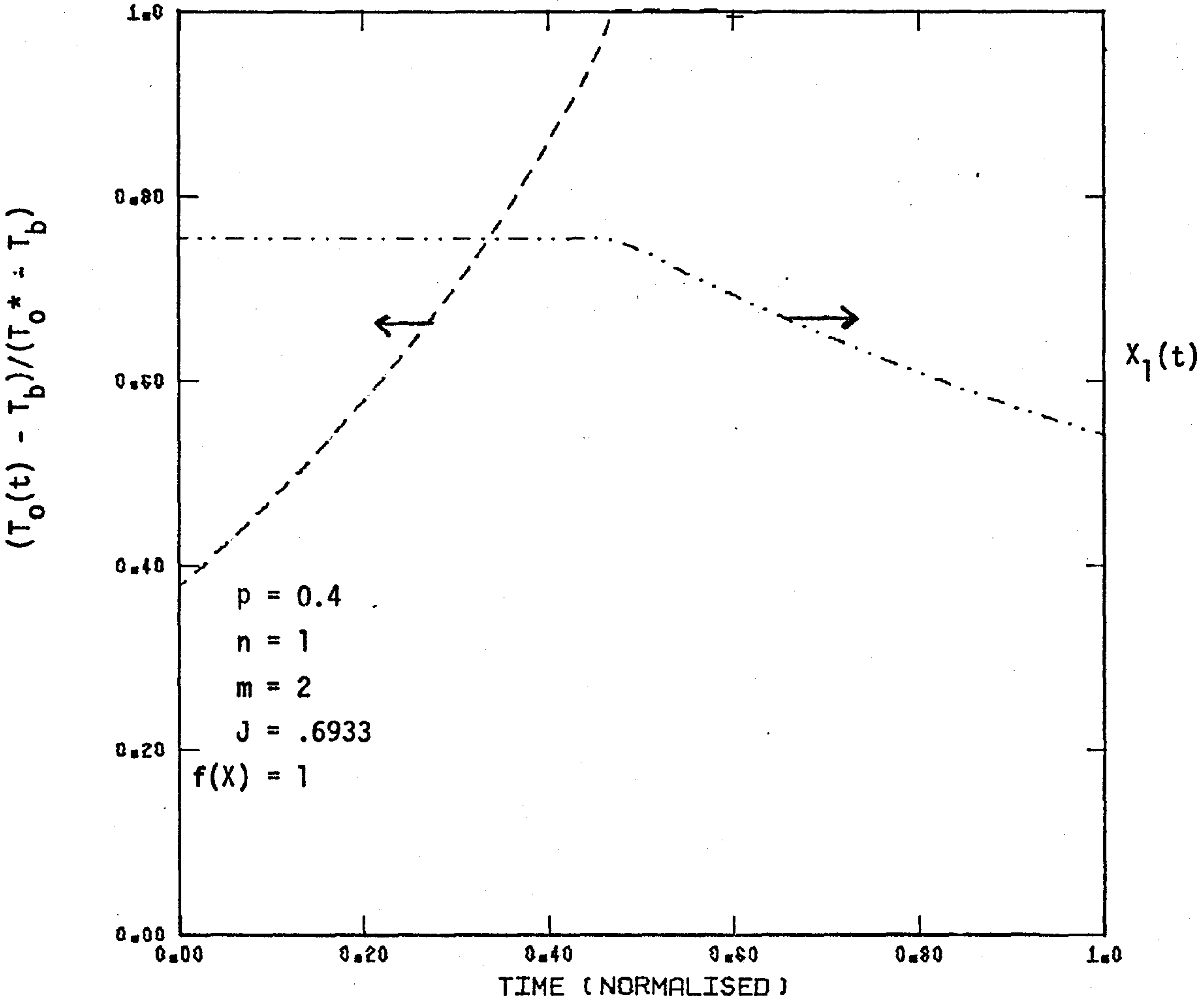

Figure 6-1 The constant conversion policy for decay independent of conversion (f=1) $T_o(t)$ and $X_1(t)$ vs. t $T_o^* = 900°K$, $T_{o*} = 700°K$, $T_b = 800°K$

t	$T_0(t)$ °K	$X_1(t)$
0	837.9	.75 47
1	841.6	.75 49
2	845.5	.75 49
3	849.6	.75 49
4	854.1	.75 49
5	858.8	.75 49
6	863.8	.75 49
7	869.3	.75 49
8	875.2	.75 49
9	881.7	.75 49
10	888.8	.75 49
11	896.7	.75 50
12	900.0	.74 21
13	900.0	.72 02
14	900.0	.70 05
15	900.0	.68 10
16	900.0	.66 23
17	900.0	.64 45
18	900.0	.62 75
19	900.0	.61 12
20	900.0	.59 57
21	900.0	.58 07
22	900.0	.56 67
23	900.0	.55 31
24	900.0	.54 01

Table 6-1 Exit conversion $X_1(t)$ and initial temperature $T_0(t)$ vs. t at the optimum for figure 6-1

linear dependence of decay rate on conversion; n1=1 and n2=-1 would fit the form for f encountered in 5.5.2, etc.

Zero order reaction in a uniform temperature reactor with f=X is shown in figure 6-2 to give a constant optimal conversion for all unconstrained temperatures and a falling conversion for $t>\bar{t}$, in agreement with the analytically predicted optimal conversion in 5.5.1. The data for the plots are again provided (to four significant figures) so that the high degree of numerical constancy can be ascertained. As soon as the temperature reaches the upper constraint, the conversion profiles drops sharply and continues to do so, until final time, t=1.

For the case f=1 the two state equations are uncoupled and this serves to make the numerical integration far more stable giving rise to 3 figure numerical constancy as opposed to 2 figure constancy for the case where f=f(X).

To demonstrate that only the particular form of f(X) specified in 5.5.1 gives rise to constant conversion, the author chose f(X) from (6-1) with n1 = 0 n2 = 3 for zero order reaction, and this produced a rising exit conversion at the optimum [see figure 6-3 and the figures in Table 6-3]. Again, a sharp drop in the conversion profile occurs as soon as the temperature reaches its upper limit (see also section 6.7 below). For other choices of f, falling profiles occur; see table 6-10.

For non zero order reactions several forms for F and f, as indicated in 5.5.3, were used and all produced constant exit conversion in agreement with analytically predictable 'conversions', over the unconstrained region. The case for an autocatalytic reaction is shown in table 6-4.

For falling conversion from proposition 4 we must choose r sufficiently large and positive with f(X) such that

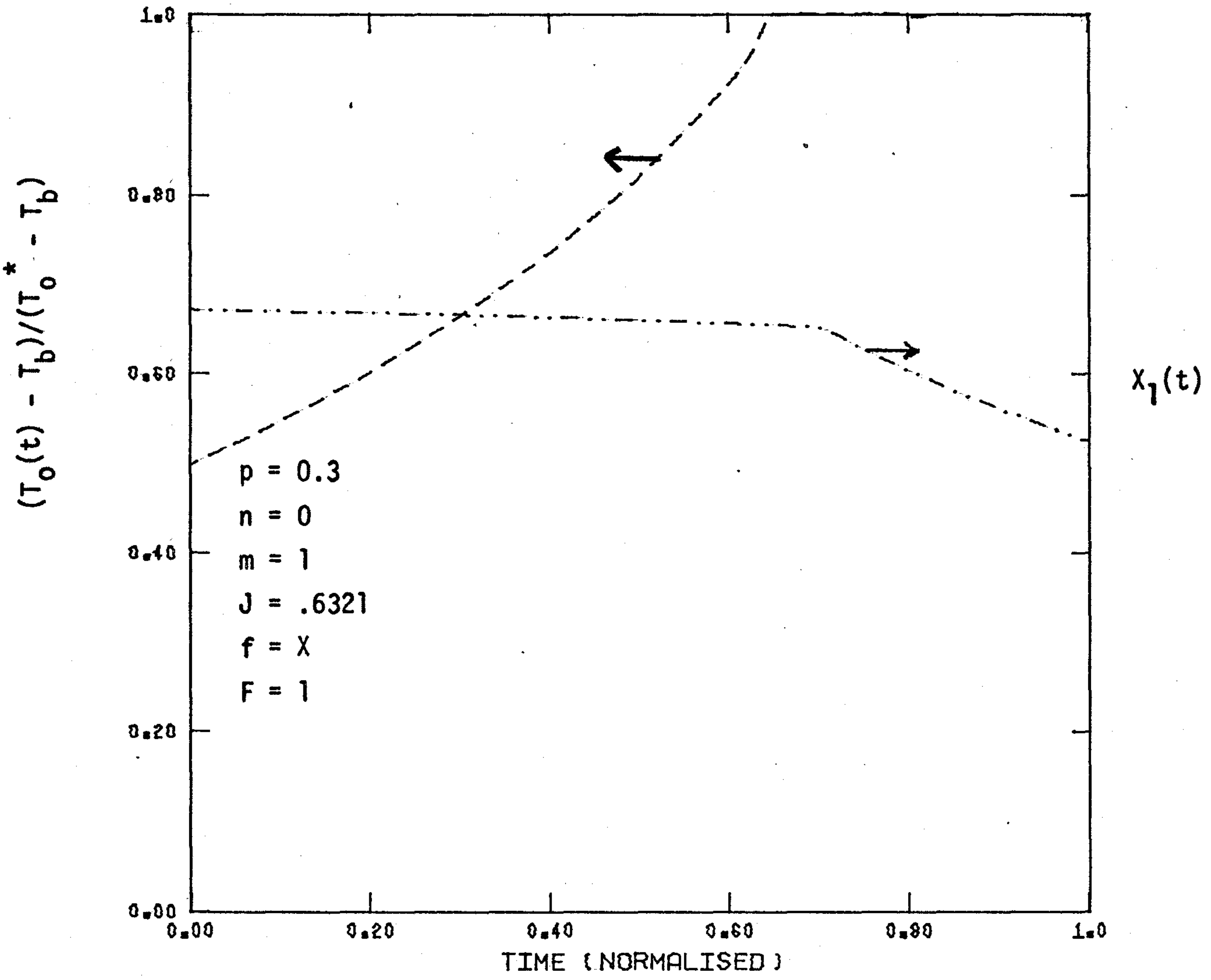

Figure 6-2 The constant conversion policy for decay dependent on conversion with zero order reaction. $T_o(t)$ and $X_1(t)$ vs t $T_o^* = 900°K$, $T_{o*} = 700°K$, $T_b = 800°K$

t	$T_0(t)$°K	$X_1(t)$
0	849.9	.67 04
1	851.9	.66 96
2	853.9	.66 88
3	856.1	.66 78
4	858.3	.66 78
5	860.7	.66 69
6	863.2	.66 59
7	865.9	.66 49
8	868.7	.66 38
9	871.7	.66 26
10	874.9	.66 13
11	878.4	.66 00
12	882.1	.65 87
13	886.2	.65 87
14	890.6	.65 57
15	895.6	.65 42
16	900.0	.65 28
17	900.0	.64 72
18	900.0	.62 60
19	900.0	.60 60
20	900.0	.58 73
21	900.0	.56 97
22	900.0	.55 32
23	900.0	.53 76
24	900.0	.52 28

Table 6-2 Exit conversion $X_1(t)$ and initial temperature $T_0(t)$ vs t for figure 6-2

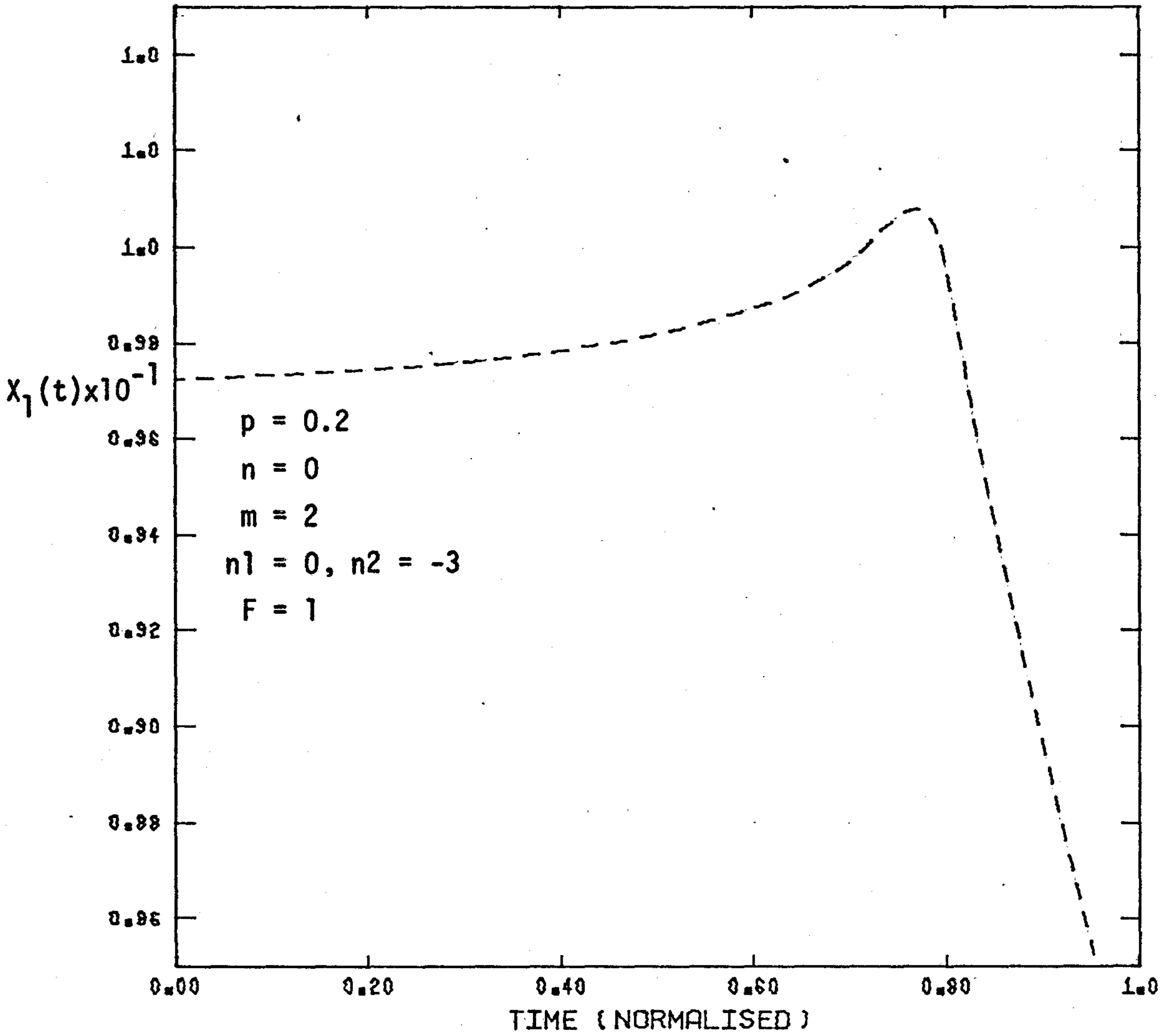

Figure 6-3 Rising exit conversion at optimum for zero order reaction, $f=(2+X)^{-3}$ $X_1(t)x10^{-1}$ vs t, $T_o^* = 1000°K$, $T_{o*} = 800°K$

t	$T_o(t)$ °K	$X_1(t)\times10^{-1}$
0	886.3	.97 24
1	888.9	.97 28
2	891.7	.97 32
3	894.6	.97 36
4	897.7	.97 41
5	901.0	.97 46
6	904.4	.97 52
7	908.1	.97 60
8	912.1	.97 68
9	916.4	.97 77
10	921.0	.97 89
11	926.1	.98 02
12	931.7	.98 18
13	937.9	.98 38
14	944.8	.98 63
15	952.8	.98 89
16	962.1	.99 28
17	973.2	.99 82
18	987.1	1.00 60
19	1000.0	1.00 30
20	1000.0	.95 92
21	1000.0	.91 90
22	1000.0	.88 20
23	1000.0	.84 78
24	1000.0	.81 60

Table 6-3 Rising exit conversion $X_1(t)$ and initial temperature $T_0(t)$ t at the optimum for figure 6-3 [zero order reaction, $f=(2+\chi)^{-3}$, $T_0^*=1000$°K, $T_{0*}=800$°K, $m=2$, $J^{\cdot}_1=\infty$ $p=0.2$]

t	$T_o(t)$ °K	$X_1(t)x10^{-2}$
0	969.4	.19 63
1	972.6	.19 78
2	975.9	.19 77
3	979.5	.19 77
4	983.2	.19 77
5	987.1	.19 76
6	991.3	.19 76
7	995.8	.19 75
8	1000.6	.19 75
9	1005.8	.19 74
10	1011.3	.19 74
11	1017.3	.19 73
12	1023.9	.19 72
13	1031.1	.19 71
14	1039.1	.19 70
15	1048.0	.19 69
16	1058.2	.19 68
17	1069.8	.19 66
18	1083.5	.19 65
19	1099.6	.19 61
20	1100.0	.19 17
21	1100.0	.18 77
22	1100.0	.18 40
2	1100.0	.18 06
24	1100.0	.17 75

Table 6-4 Constant conversion policy for autocatalytic reaction [$F=X(1-X)$, $f=X/(1-X)$, $p=0.15$, $m=2$, $T_o^* = 1100$°K, $T_{o*} = 900$°K]

$f(X)=(1 - X)^r$

We also require $F=(1 - X)$ for a 1st order uniform temperature reactor. Table 6-11 shows a falling conversion for $r=1$.

6.2a Numerical Integration

6.2a.1. Integration Procedure

The method of characteristics has been widely used as the method of integration for the present system [Acrivos (1956)] and is well described in any competent book on digital computation [Lapidus (1962) Carnahan et al, 1962].

The present system consists of two sets of simultaneous, semi-linear hyperbolic, partial differential equations, which remain hyperbolic throughout the entire region of integration.

We write the two general state equations in differential form as

$$dX = \left[\frac{\partial X}{\partial z} + \frac{\partial X}{\partial t}\frac{dt}{dz}\right] dz \tag{6-2}$$

$$d\psi = \left[\frac{\partial \psi}{\partial z}\frac{dz}{dt} + \frac{\partial \psi}{\partial t}\right] dt \tag{6-3}$$

It is seen that if we choose the two characteristic directions:

$$\text{I} \quad \frac{dt}{dz} = 0 \text{ or } t \text{ constant} \tag{6-4}$$

$$\text{II} \quad \frac{dz}{dt} = 0 \text{ or } z \text{ constant} \tag{6-5}$$

The resulting characteristic equations are then

$$\frac{dX}{dz}\Big/_{\text{I}} = \psi K_o F \tag{6-6}$$

$$\frac{d\psi}{dt}\Big/_{\text{II}} = -k_o g f \tag{6-7}$$

The characteristics I are parallel to the z axis and the characteristics II are parallel to the t axis (see figure 6-4).

Since the equation (6-6) and (6-7) are coupled, and the directions of integration do not coincide, several of the common numerical integration schemes will lead to trial and error (or iterative) procedures [Acrivos (1965)].

Figure 6-4 shows a simplified grid pattern. From the given boundary conditions

$$X(0,t_i) = \text{constant } i=0..N_t \tag{6-8}$$

$$\psi(z_i,0) = \text{constant } i=0..N_z \tag{6-9}$$

Hence one initial boundary, for each of the two equations, is known.

For the modified Euler scheme [Lapidus (1962), Chapter 3] we require the value of X and ψ at the present point and the subsequent point in order to proceed; eg., to calculate X_{10} we require knowledge of ψ_{10}, $\psi_{0,0}$ and $X_{0,0}$. This presents no difficulty along the boundaries in (6-8) and (6-9), but off the boundary we require simultaneous iteration of (6-6) and (6-7). For example to calculate X_{11} the following simultaneous iteration scheme would be required:

(i) Guess ψ_{11} and X_{11} (using predictor of the modified Euler scheme)

(ii) Recalculate ψ_{11} from X_{11}, ψ_{10}, X_{10} using (6-7) (in corrector form)

(iii) Using New ψ_{11}, recalculate X_{11} from ψ_{11}, ψ_{01}, X_{01} from (6-6)

(iv) Using New X_{11}, return to step (ii)

(v) Iterate simultaneously until the relative error between two successive values of both variables meet a given error bound.

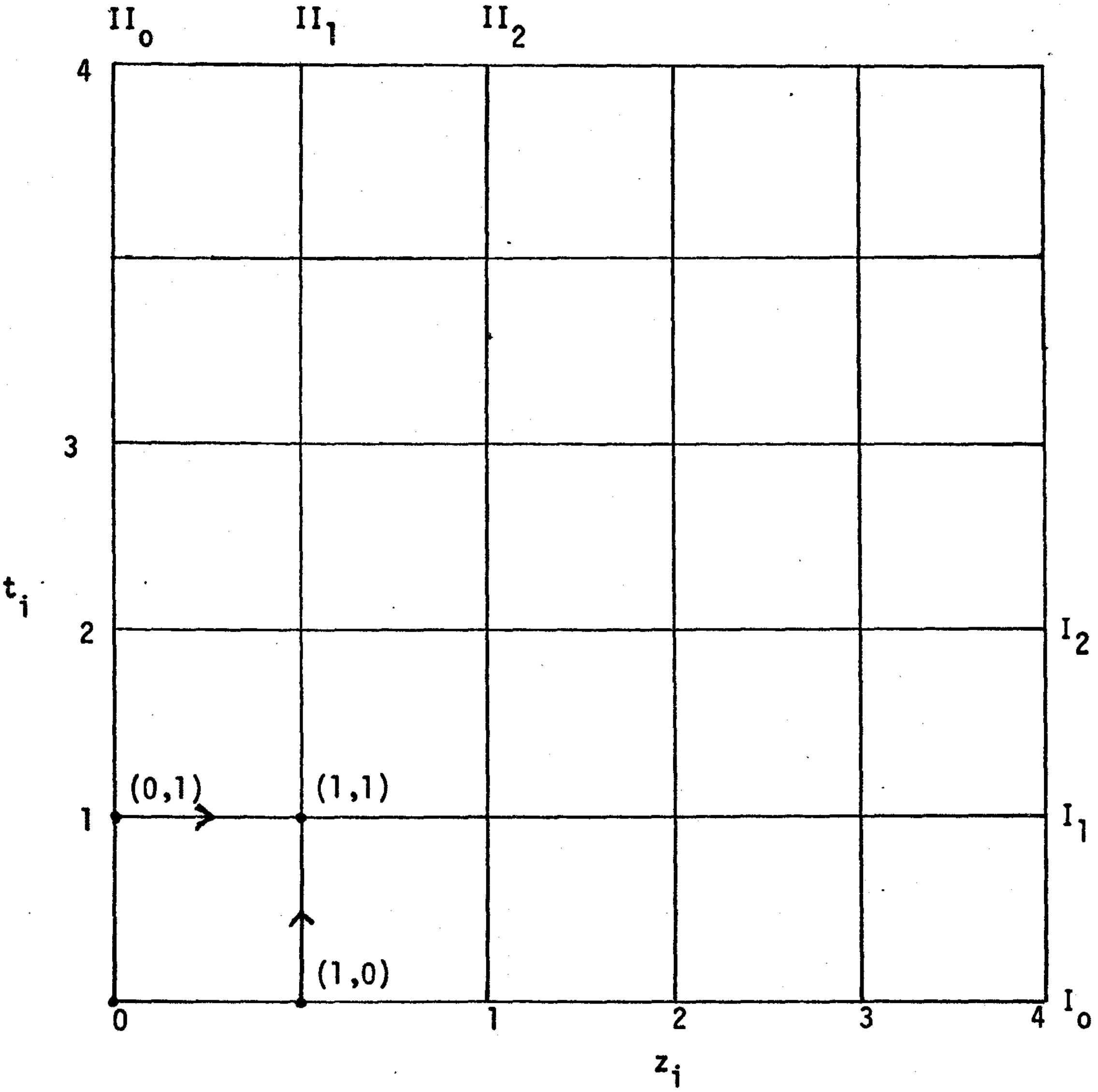

Figure 6-4 Grid scheme for numerical integration of system equations along characteristics I and II, showing directions for simultaneous iteration

It is possible to eliminate the iterative nature of the integration scheme by using one of the Newton-Cotes open ended integration formulas [Lapidus (1962), Chapter 2]; these require only the values of the integrand at the present point and one or more past points in order to calculate the next point, unlike the Euler or Runge-Kutta schemes which require information about the integrands at the future point as well.

The modified Euler was found to be far superior to either the Runge-Kutta 3rd or 4th order and Milne Predictor corrector schemes which suffered from stability problems in the simultaneous iteration scheme, or to the Newton-Cotes open ended systems which had no iteration, but were plagued by error propagation.

The modified Euler on the other hand, was iteratively stable and could produce the desired accuracy by simply iterating the predictor corrector parts to within the desired error limits

Needless to say, the modified Euler scheme had great advantages in terms of computation time in view of the large number of sets of simultaneous equations that had to be solved. A grid size of 15 x 25 ($N_z \times N_t$) was found to be quite adequate and doubling both dimensions to give a 30 x 50 system produced no appreciable change in the numerical values of any of the dependent variables (4th or 5th decimal place) or in the objective functions (4th decimal place).

In a similar manner the adjoint equations were solved along the same characteristics as in figure 6-4, but in view of the given boundary conditions

$$\lambda_2(z_i,0) = 0 \qquad i = 0..N_z \qquad (6\text{-}10)$$

$$\lambda_1(N_z,t_i) = 1 \qquad i = 0..N_t \qquad (6\text{-}11)$$

integration is backwards.

The adjoint characteristic equations for (4-4) and (4-8) are:

$$\frac{d\lambda_1}{dz}\Big/_{I} = \lambda_2\, k_o g f' - \lambda_1 \psi K_o F' \tag{6-12}$$

$$\frac{d\lambda_2}{dt}\Big/_{II} = \lambda_2 k_o f g' - \lambda_1 K_o F \tag{6-13}$$

6.2 a.2 System Constants

The numerical values of the parameters and constants were as follows:

Inlet conversion

$X_o(t) = 0$ all $t \varepsilon [0,1]$

Initial activity

$\psi_i(z) = 1$ all $z \varepsilon [0,1]$

Reactors average space time (3-18)

$t_\theta = 1.0$ second

Total operational time (3-14)

$\tau = 2.16 \times 10^6$ seconds (25 days)

Bounds on temperature °K

$T_o{}^* = 900$, (1000, 1100)

$T_{o*} = 700$, (800, 900)

Catalyst deactivation energy divided by gas constant

$E_c = 15000$ °K

Arrhenius pre-exponential constant (3-24a)

$$k_+^{\cdot} = k_+ = 20.24$$

The reaction activation factor E_R is easily calculated from (3-27) i.e., $E_R = pE_c$.

The Arrhenius constant K_+° is calculated using (5-16) or (5-7) and corresponds to a maximum attainable exit conversion of $X_1^*(t) = 0.9$ with fresh catalyst $\psi(z,t) = 1.0$ and maximum inlet temperature $T_0^* = 900$ °K from which a maximum exit temperature $\textcircled{T}$ for the adiabatic reactor is calculated.

eg. for $n \neq 1$

$$K_+^{\cdot} = \frac{[E_C \cdot p/\textcircled{T}]\ (1 - (0.1^n))}{t_\theta\ (1-n)} \tag{6-14}$$

where $\textcircled{T} = T_0^* + 0.9/J_1^{\cdot}$ maximum exit temperature (6-15)

and $J_1^{\cdot} = -C_p/\Delta H^{\circ}$ (3-42)

eg. for $n = 1$

$$K_+^{\cdot} = \frac{-\exp\ [E_c . p/T]\ \ln(0.1)}{t_\theta} \tag{6-16}$$

6.3 Optimum Seeking Methods

6.3.1 Gradient Method in Function Space

The well known gradient or steep descent methods [Denn (1967)] are easily extended to the distributed system via the Hamiltonian expression (4-13) and from (4-1) it can be seen that, if, at any iteration $\delta k_0(t)$ is chosen, so that

$$\delta k_0(t) = \gamma\ (t) \int_0^1 \frac{\partial H}{\partial k_0}\, dz \tag{6-17}$$

where $\gamma(t)$ is a sufficiently small positive function of t (usually taken as constant), then $\delta P>0$ and the objective function will increase at each iteration towards the maximum value of the objective function.

Gradient Algorithm

1. Guess $T_o^q(t_j)$, hence $k_o(t_j)$ for all t_j $j = 0..N_t$, $q=0$ for 1st iteration.
2. Integrate the two state equations forward and store the values of $X^q(z_i,t_j)$ and $\psi^q(z_i,t_j)$.
3. Using the variables in steps 1. and 2. integrate the adjoint equations backwards and store the values of $\lambda_1{}^q(z_i,t_j)$ and $\lambda_2{}^q(z_i,t_j)$.
4. From the values of the variables in steps 1. 2. and 3. form H from (4-2) and integrate over all z at each time interval t_j $j=0..N_t$, to form $\bar{H}$.
5. Calculate $\delta k_o(t_j)$ at each time interval according to (6-17) given some γ .
6. Set $k_o^{(q+1)}(t_j) = k_o^{(q)}(t_j) + \delta k_o(t_j)$ (6-18)
   If $k_o \geq k_o{}^*$ set $k_o = k_o{}^*$
7. Test the objective function P (3-58) for an increase (decrease).
8. If there is an increase (decrease), double (halve) the value of γ and repeat step 2, and return to 6; save the values of γ_i and P_i and continue in this manner until the objective function decreases; double (halve) once more and save γ_i, P_i.
9. Pass a quadratic curve through the values of γ_i, P_i, find maximum of the curve to estimate that γ which gives the largest value of P_i call this γ, γ_{opt}.

One alternative, occasionally used is simply to double (or halve) the value of γ until a decrease occurs in the objective function, at say γ_N, and set $\gamma_{opt} = \alpha \gamma_N$ where α is some fraction eg 0.7. This saved total computation time even though the total number of iterations may have increased.

7. Set $k_o^{(q+1)}(t_j) = k_o^{(q)}(t_j) + \gamma_{opt} \int_0^1 \frac{\partial H}{\partial k_o} \, dz \quad j = 0..N_t$ (6-19)

   If $k_o \geq k_o^*$ set $k_o = k_o^*$

8. Return to step 1. and continue until successive values of the objective function differ by less than a given error criterion.

On a grid of 30 x 20 ($N_t x N_z$) approximately 3 1/2 minutes of computing time on a CDC 6400 computer was required. This corresponded to about 6 iterations from a constant starting function as a first guess. In many cases though, it was obvious that, due to a slowing down of the method in the vicinity of the optimum, the optimum had not been reached. This was indicated by the fact that the profile has not yet reached the upper constraint at the final time [see paragraphs following (4-34)]. See figure 6-5.

Another point that was observed, was the occassional sensitivity of the derivative of the conversion profile to change in the temperature profile. For example, in the case where f=1 (figure 6-1) to obtain a reasonably good constant exit conversion profile, each optimum temperature profile point had to converge to within a relative error of less than 0.1 of one percent. See 6.3.2 below.

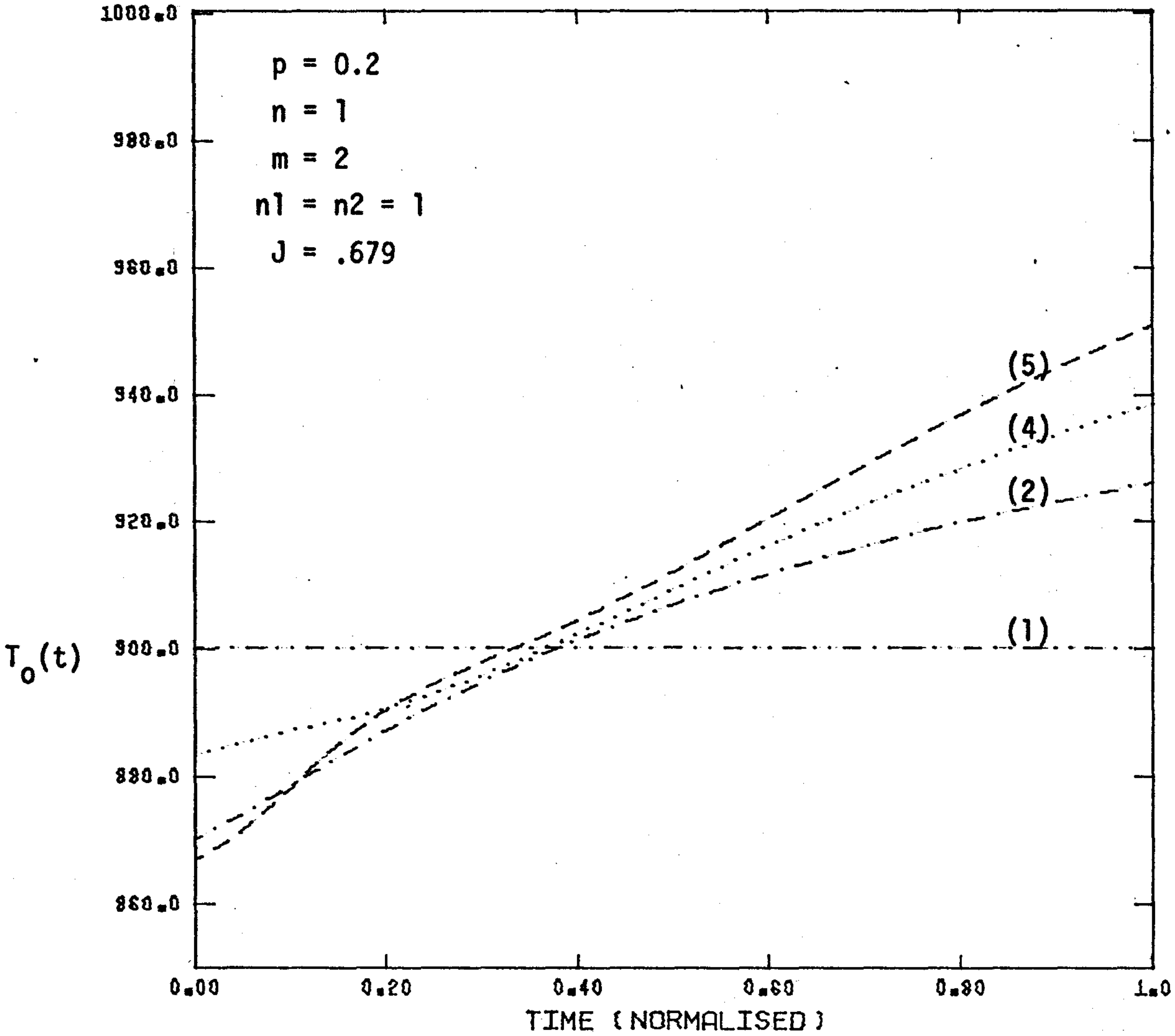

Figure 6-5 Gradient method iterations in the numerical search for the optimum $T_o^* = 1000°K$, $T_{o*} = 800°K$

6.3.2 Fixed Point Method In Function Space

In some cases the exit conversion profile character was sensitive to the temperature profile; this condition was aggravated by the fact that the gradient method failed, in many cases, to approach the optimum profile sufficiently closely. So that in these cases, the slope of the exit conversion could not, without doubt, be separated into a rising, constant or falling profile.

The fixed point formulation of the necessary condition for the optimum profile has been given (4-34) and the successive iteration method based on this form has been discussed (4.4.1).

In general, one has no guarantee that the operator $G[k_o]$ in (4-34) will be a contraction mapping and that the process

$$k_o^{(q+1)}(t_j) = G[k_o^{(q)}(t_j)], \; j=0..N_t \tag{6-20}$$

will converge for whatever starting function $k_o^{(o)}$ we use.

Solving for the optimal profile is now no longer viewed as a stepwise climbing process, where, at each step, a higher value of the objective function is guaranteed. Now we have a fixed point equation of the form.

$$k_o(t) = G[k_o(t)] \tag{6-21}$$

and we wish to find that function, $k_o(t)$, by whatever method, which satisfies (6-21)

We may now use many of the well known fixed point iterative techniques in function space, which are analogous to the more usual forms in a one dimensional vector space. Examples are the Newton Raphson Reguli-Falsi and Richmond iterative schemes applied to a function or n dimensional vector space [Lapidus (1962) Chapter 6].

Due to the complex nature of the operator G (4-34) any scheme which requires even the simplest numerical derivative is out of the question (eg. Newton Raphson).

An alternative formulation of (6-20) is

$$k_o^{(q+1)} = \alpha[G(k_o^{(q)}) - k_o^q] + k_o^q \tag{6-22}$$

$$0 \leq \alpha \leq \alpha_{max} \tag{6-23}$$

α may be varied between 0 and α_{max} at each iteration according to some rule or may be kept constant at some value indicated by numerical experience of the specific problem. For the present problem fastest convergence was obtained for $0.6 \leq \alpha \leq .92$.

The paramater, α, in a sense, regulates the fraction of the full correction to be used at each iteration. For $\alpha = 1$ in (6-22), we have full correction and (6-22) reverts to (6-20), and for $\alpha = 0$, there is no correction and $k_o^{q+1} = k_o{}^q$. Note that α_{max} may in principle be greater than unity. If we set $\alpha_{max} = 1$, the α acts as a damping factor on the correction to k_o as explained above; however, if the problem indicates it, $\alpha_{max}>1$ may speed up convergence of the process. Convergence promotion of this iterative scheme is discussed below in section 6.4.

With a scheme such as (6-22), there is, of course, no guarantee that the value of the objective function P will increase at each step as it does in the gradient method. In using the gradient method, where, essentially, the numerical process proceeds as if all the discretised control points $k_o(t_j)$ $j = 0..N_t$, were unconstrained, predicts each point, and if the point is outside the bound, the predicted $k_o(t_j)$ is replaced with k^* (or k_*)

So also, for the scheme (6-22) the iterations converge and when a predicted value converges outside a bound, this predicted value is replaced by its bound [See (4-34a) and (4-34b)].

There are, in addition, several methods [Wegstein,(Lapidus (1962) Chapter 6), Orbach and Crowe (1971) and Crowe (1972)] for accelerating the iterations obtained from (6-22) and these will be discussed in 6.4 below.

The fixed point algorithm was often used in conjunction with the gradient method. An efficient scheme was found to be:

(1) First iteration with Gradient Method

(11) Followed by several convergence iterations with the fixed point method until the optimum is reached.

However, in spite of the excellent performance of the gradient method in the first iteration, an initial iteration with the fixed point method almost always bettered the prediction of the gradient method and reduced the total numer of iterations by about 20 percent. One notable exception was the case where the optimal profile was such that most of the profile lay at an upper limit the remaining unconstrained section lay close to the constraint so that any oscillating iteration on either side of the true unconstrained value was hindered by the close proximity of the upper constraint. The first few iterations of the fixed point method were almost always oscillatory in nature.

Fixed Point Algorithm

1. Guess $T_o^{(o)}(t_j)$ hence $k_o^{(o)}(t_j)$ for all t_j and proceed to obtain the gradient estimate of $T_o^{(1)}$ using the gradient algorithm.
2. Integrate all the equations with the value of $T_o^{(1)}$ as in steps

2. and 3. of the gradient algorithm.

3. With all the stored variables calculate the value of $G(t_j)$ at each point in time, using

$$G(t_j) = \left[\frac{ap_o \int_0^1 \lambda_1 \psi F(z,t_j)dz}{\int_0^1 \lambda_2 g f(z,t_j)dz} \right]^{\frac{1}{1-p}} \qquad j=0..N_t \tag{6-24}$$

4. With a given α, set $k_o^{q+1}(t_j)$ by

$$k_o^{(q+1)}(t_j) = k_o^{(q)}(t_j) + \alpha\, [G(t_j) - k_o^{(q)}(t_j)] \qquad \text{(6-25}$$

5. Option: accelerate the value of $k_o^{(q+1)}$ by one of the procedures in 6.4 below, to obtain an accelerated k_o, say $\bar{k}_o^{(q+1)}$, and if $\bar{k}_o^{(q+1)} \geq k_o^*$ set $\bar{k}_o^{(q+1)} = k_o^*$

6. Test for convergence in the norm

$$\text{eg.} \quad ||\, k_o \,|| = \int_0^1 |k_o^{(q+1)} - k_o^{(q)}|\, dt \tag{6-26}$$

$$\text{or} \quad ||\, k_o \,|| = \sum_j (k_{o(j)}^{q+1} - k_{o(j)}^{q})^2 \tag{6-27}$$

$$\text{or} \quad ||\, k_o \,|| = \underset{j}{\text{Max}} \; k_o(j) \tag{6-28}$$

Comparison

Not only does the fixed point reduce the total computation time by between 30 and 50 %, but a much closer approach to the optimal profile is obtained. This last point is shown by:

(i) Significantly larger value of the objective function.

(ii) For those cases where constant exit conversion is optimal a much finer level of constancy (10 or more-fold decrease in numerical derivative) is observed, thus allowing the author to distinguish far more carefully, those cases where the sign of the slope of the exit conversion is in doubt.

The large saving on computer time is due, partly to the saving of

(i) Calculation and test of objective function at each iteration.

(ii) Integration of the state equations several times in the calculation of γ_i (step 8, gradient algorithm).

(iii) Curve fit and the calculation of γ_{opt}.

In some cases, due to the relative insensitivity of the objective function in the vicinity of the optimum, appreciably different profiles may be obtained with a finer approach to the optimum, via the fixed point method but with only a mild increase in the objective function. Figure 6-6 compares the two optimum profiles obtained as well as the corresponding objective functions and computation times.

6.3.3 Predictor-Corrector Method

Rather than use the gradient method or the fixed point method independently, the question arises as to whether some combination of the two methods may cause faster convergence. A predictor-corrector scheme was implemented whereby the gradient step provided the predictor estimate, and this estimate was refined using the fixed point formulation as a corrector:

$$\begin{aligned} P: &\quad k_o^{(P)} = k_o^{(o)} + \delta k_o \quad (\delta k_o \text{ from 6-17}) \\ C: &\quad k_o^{(c)} = k_o^{(P)} + \alpha[G(k_o^{(P)}) - k_o^{(P)}] \end{aligned} \tag{6-29}$$

This scheme may be varied to suit the problem insofar as how many correctors follow one predictor. In the present problem two correctors after one predictor, seemed to produce the least number of total iterations and total computation time.

Predictor-Corrector Algorithm

1. Proceed as in steps 1. → 6. gradient method to obtain $k_o^{(P)}=k_o^{(q+1)}$ from (6-18).
2. Use $k_o^{(P)}$ to calculate $k_o^{(c)}$ as in steps 3. and 4. of fixed point algorithm using (6-29).
3. Set $k_o^{(c)} = k_o^{(P)}$ and repeat iteration 2. n times (n= # corrector steps following a single predictor).
4. Set $k_o^{(c)} = k_o^{(P)}$ and use to integrate both the state variables and the adjoint variables as in gradient algorithm steps 1. → 6. and use the H obtained, to calculate the new predictor, via (6-18).
5. Option: accelerate as in fixed point algorithm step 5.
6. Test for convergence in the norm, as in fixed point algorithm step 6.

Comparison

The comparison between the predictor-corrector and the gradient method are analogous to those made between the fixed point and gradient methods.

It is more instructive to compare the last two algorithms and it turns out that the predictor-corrector may reduce the computation time in some cases, but the reverse is true for the remainder of cases and neither method stands out exclusively.

However, the predictor corrector does have one distinct advantage over the fixed point method in that its rate of convergence is not as sensitive to the choice of the paramater α in (6-23). Since a 'good' value of this paramater is not known initially, a substantial improvement on the fixed point method may be obtained see table 6-5.

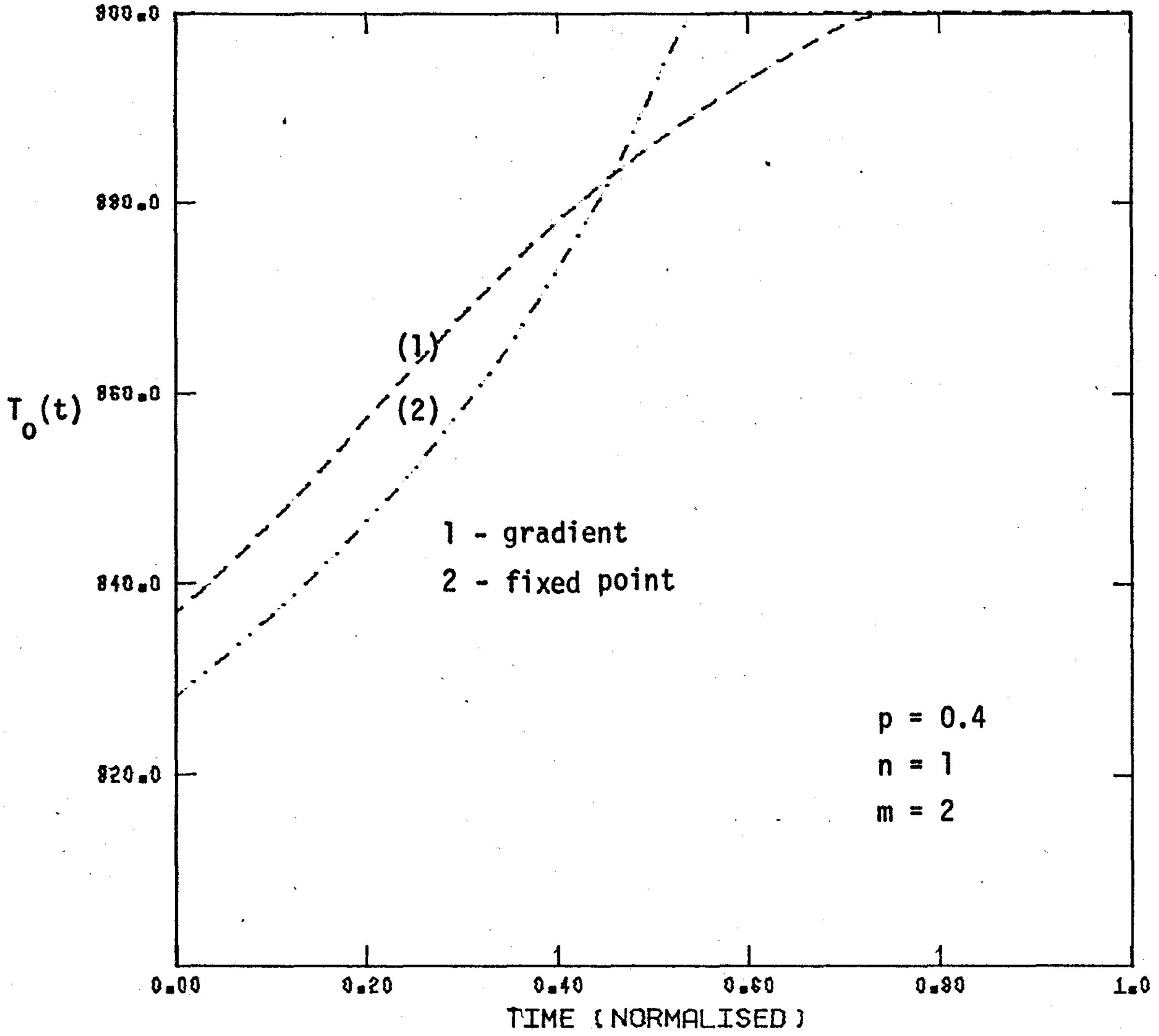

Figure 6-6 Comparison of Gradient and Fixed point methods

Curve	Computation time †	Objective Function
1	232.0 secs	.69532
2	161.8 secs	.69671

†CDC 6400

Table 6-5 Legend to figure 6-6

	Computation Time †	α	Objective Function T	Remarks
Fixed Point	144 secs	0.9	.69455	Time limit
Predictor-Corrector	93 secs	-	.69443	

† CDC 6400

Table 6-6 Comparison of Fixed point and predictor corrector method for the parameters: $T_0^* = 900°K$, $T_{0*} = 700°K$, $m = 2$, $n = 1$ $p = 0.4$, uniform temperature reactor

6.4 Convergence Acceleration in Optimum Seeking Methods

6.4.1 Earlier Methods

Wegstein (1958) developed a method for promoting (accelerating) the convergence of an iterative process which may be represented as [see 4.4.1].

$$x_{n+1} = T_f(x_n) \tag{6-30}$$

or

$$x_{n+1} = \alpha\, [T_f(x_n) - x_n] + x_n \tag{6-30a}$$

where the solution to the fixed point problem of the form

$$x = T_f(x) \tag{6-31}$$

is required. [cf equation 6-21)].

Newton's method, which has a higher order of convergence than Wegstein's method, is out of the question in the present system, because it requires an estimate of the first derivation of T_f if x is simply a one dimensional vector, or the derivative of T_f at each point, as a discretised function space, as is required by the numerical method here. To estimate the derivatives we would be required to integrate both sets of equations twice at each iteration (unless the modified Newton method is used) causing a substantial increase in the computation time.

Wegstein's method does not require calculation of a derivative and is much more feasible in the present system. The convergence order is 1.618 [Wegstein (1958)], compared to second order convergence for the regular Newton Raphson method; nevertheless, if one includes the time necessary to calculate the derivatives, Wegstein's method would converge faster, even though more iterations would be required.

Since, for the numerical calculations, the t and z scales are discretised, we may consider the iteration scheme (6-30) or (6-30a) to be in a vector space instead of a function space as it truly is, and instead the vector $\underset{\sim}{k}_o$ with components $k_o(t_i)$ $i=0..N_t$ is iterated instead of the continuous or piecewise continuous function $k_o(t)$.

$$\underset{\sim}{k}_o = [k_o(t_o) \quad k_o(t_1) \text{ ----- } k_o(tN_t)] \tag{6-31a}$$

Now in the Wegstein method each one of the $k_o(t_i)$ would be accelerated separately based on its particular past three values. No account is taken for the possible interaction between the components of the 'vector'. A method, which takes interaction into account is discussed in 6.4.2 below.

Crowe (1972a) has indicated that promotion using Wegstein's method at every iteration (after the first three), may not be advisable: Wegstein's method perturbs the normal iteration pattern, based on a direction indicated by the past three iteration points. However, the system normally requires several iteration steps to reestablish its normal iterative pattern (geometric in nature) and indicate a direction upon which the rest of the promotion can be based. If Wegstein acceleration is immediately applied before the system is allowed to settle, convergence may be hindered and result in an increase in the total number of iterations.

In the following section (6.4.2) a more recent method due to Orbach and Crowe (1971) develops a measure of the extent to which the system has 'settled down', before a convergence promotion is applied.

Unfortunately all these methods require a fair number of iterations before an appreciable saving in the total numbers of iterations is obtained. In most of the present applications the total number of iterations does not exceed ten (for the fixed point methods) and hence no dramatic saving in computation time is obtained. In some cases the time involved in calculating the promoted values may outweigh the decrease in the total number of iterations; however the Wegstein predictions involve relatively simple calculations and if any extra time was involved it ususally led to a finer approach to the optimum profile see Table 6-7.

	Computation † Time	Objective Function
Fixed Point Without Acceleration	74 secs	.7549
Fixed Point With Acceleration Every 3rd Step	83 secs	.7582

Table (6-7) Comparison of Acceleration vs No acceleration in fixed point iterations, for parameters: $T_o^* = 900$, $T_{o^*} = 700°K$, $m = 2$, $n = 1$, $p = 0.2$, $J_1 = .01$

† CDC 6400

6.4.2 Recent Methods

The Dominant Eigenvalue Method (DEM) for convergence promotion was developed by Orbach and Crowe (1971) and can be applied to fixed point problems of the form

$$\underline{Y} = \underline{F}(\underline{Y}) \tag{6-32}$$

where $\underline{Y}$ and $\underline{F}$ are vectors and vector functions respectively. Because the method is aimed at handling convergence of vector systems it is directly applicable to the present vector system defined by equation (6-31a) and the discretised version of (6-21), i.e.,

$$[\underline{k}_o] = G[\underline{k}_o] \tag{6-33}$$

where $$\underline{k}_o = [k_o(t_o)\ k_o(t_1) \ldots\ldots k_o(t_{N_t})] \tag{6-31a}$$

The method is based on the observations that most iterations eventually approach a geometric progression. It is assumed that G can be linearised by means of some method (Taylor), so that the iterations may be represented, sufficiently accurately, by a linear matrix difference equation of the form

$$\underline{Y}_{n+1} = \underline{\underline{A}}\,\underline{Y}_n + \underline{b} \tag{6-34}$$

where $\underline{\underline{A}}$ represents a linearisation of G about some reference point and $\underline{b}$ is a constant vector. If μ is the largest (in absolute value) eigenvalue of the matrix $\underline{\underline{A}}$, a necessary and sufficient condition that the process in (6-34) converge is that [Orbach and Crowe (1971)],

$$|\mu_1| < 1 \tag{6-35}$$

They express (6-34) as a sum containing the eigenvalues of $\underline{\underline{A}}$ and use the fact that, as the number of iterations become large, only the largest eigenvalue μ_1 will contribute significantly to the sum. They obtain an expression which estimates the limit of the sequence of vectors $\underline{Y}_n$, called $\underline{Y}_s$, in terms of the latest two observations, μ_1, and an acceleration factor, α as in (6-23).

$$Y_s = Y_{n-1} + \frac{\alpha}{(1-\mu_1)}(Y_n - Y_{n-1}) \tag{6-36}$$

$$0 \leq \alpha \leq \alpha_{max} \tag{6-37}$$

μ_1 is estimated as $$|\mu_1| = \frac{||Y_n - Y_{n-1}||}{||Y_{n-1} - Y_{n-2}||} \tag{6-38}$$

where $||\ \ ||$, as usual, represents the norm [see (6-26), (6-27), (6-28)].

We see from (6-36) that iterations proceed in such a manner that the entire vector is iterated and not each component separately and independently, as in the Wegstein method. The dominant eigenvalue μ_1 is estimated using (6-38) to which all components of the vector contribute, thus accounting for interactions among the vector components.

The DEM provides a criterion as to when to accelerate in (6-39); for if successive values of μ_1 are sufficiently close in value the system can be said to have 'settled down' to a natural iterative pattern (which will be geometric in nature) and this is the stage at which the acceleration step (6-36) is applied. Several more iterations are required before the process recovers and another acceleration is applied.

The point is made, that each acceleration is not necessarily guaranteed to approach the fixed point solution more closely, but that these random divergences are to be taken lightly, insofar as the objective of the DEM is to reduce the total number of iterations required to solve (6-33).

A major disadvantage of the DEM for the solution of (6-33) is the requirement of waiting several iterations until (6-38) produces sufficiently constant values of μ_1 before an acceleration may be applied. Initially, up to ten iterations of (6-33) may be required before the system approaches a geometric convergence pattern, but by then all the optimum seeking methods described in 6.3 above are "home and dry".

Hence the DEM method was used to best advantage only for those cases where convergence was particularly stubborn or alternatively those cases which approached geometric convergence rapidly thus enabling an early acceleration to be applied.

Crowe (1972b) recently generalised the DEM to include all N eigenvalues to estimates $\underline{Y}_s$ and this method may allow the user to accelerate earlier and far more precisely.

This generalised DEM reduces to the previous estimating equation with the modification that a ratio of two inner products is used to estimate μ_1 instead of a ratio of norms as in (6-37).

It was mentioned, that for those cases where the convergence pattern quickly settled to a geometric pattern, and this was fairly common, the convergence promotion routine, particularly the method due to Orbach and Crowe (1971), showed improvement over the unpromoted cases even where a single promotion was used.
See table 6-8.

	With Orbach/Crowe Convergence Promotion	Without Convergence Promotion
Paramaters m	2	2
n	1	1
p	0.4	0.4
J_1'	0.01	0.01
T_o	700-900°K	700-900°K
Objective Function J	.4706	.4660
No. of iterations	4	7
Promotion on iteration no.	4	-
Computation Time (CDC6400)	87.4 secs	117.0 secs (Time limit)

Table 6-8 Comparison of Convergence Promotion using Orbach/Crowe method vs no promotion for a given set of paramaters.

6.5 Influence of Integration Step Size on Optimum Seeking

A question of practical importance arises when one is iteratively searching for the optimum profile and one wishes to know whether a particular iteration has brought the search 'closer' to the optimum (unconstrained).

There are two indicators that one can use to provide an answer:

(i) Is the numerical value of P (objective function) increasing?

(ii) Are the absolute values of the derivatives of the Hamiltonian at each discrete point in time decreasing?

Neither of the two indicators actually guarantee that the true optimum is being approached but they are good pointers and besides, we have no other method.

The gradient methods rely on the first indicator and use this as a test to determine whether the optimum has been reached.

The fixed point method ignores (i) and may use (ii) to determine when the necessary condition (4-12) has been obeyed on each discrete point in time. However a better method is to test for convergence in the norm for the profile $k_o(t)$ at each iteration, and use indicator (ii) above, only to verify than the optimum has been reached.

The use of (ii) as a criterion of closeness to the optimum at each iteration step, may be dangerous, since we know only that the derivative of the Hamiltonian is zero once we have already reached the unconstrained optimum. We do not know that the approach to the optimum is accompanied by a uniform decrease in the norm of $\frac{\partial \bar{H}}{\partial k_o}$, that is $\left|\left|\frac{\partial \bar{H}}{\partial k_o}\right|\right|$ does not necessarily converge uniformly to zero as $d^* \rightarrow 0$

where $d^* = || k_o(t) - k_o(t)_{opt} ||$ (6-39)
[Horn (1972)].
Also the measure of 'closeness' to the optimum will depend on what norm we choose [see (6-26) et seq.]. In many cases though, an increase of P will be accompanied by a decrease in d*.

It is possible numerically, even when $||\frac{\partial \bar{H}}{\partial k_o}||$ converges uniformly with d*, to obtain a decrease in the objective function at an iteration which gives a profile which is 'closer' to the optimum. This may be caused by a coarse selection of the integration step size and occurs in the close vicinity of the optimum:

Referring to figure 6-7, $T_0(t)$ represents a profile in the close vicinity of the optimum such that the next iteration will move the unconstrained profile up and closer to the optimum that is $t_1' \to t_1$ etc.

The profiles shown in figures 6-7 close to the optimum may be divided into 3 distinct sections, two of which have a fixed number of discrete points.

(i) Those discrete points which are unconstrained and move up towards the optimum eg. t_1 and t_2 (fixed in number).

(ii) Those discrete points which are constrained and remain so (fixed in number).

(iii) The middle section between t_3 and t_2 which would, if the time steps were finer, experience a change in the number of discrete points, in this case registering an increase in the number of points on the constrained section as the profile 2 moves up toward the optimum but due to a coarse grid this section contains no points.

Since in reality, a point is either constrained or unconstrained, we divide the objective function into two parts: that part due to the unconstrained section of the profile P_1, and that due to the constrained section P_2 such that the total objective function P is

$$P = P_1 + P_2 \tag{6-40}$$

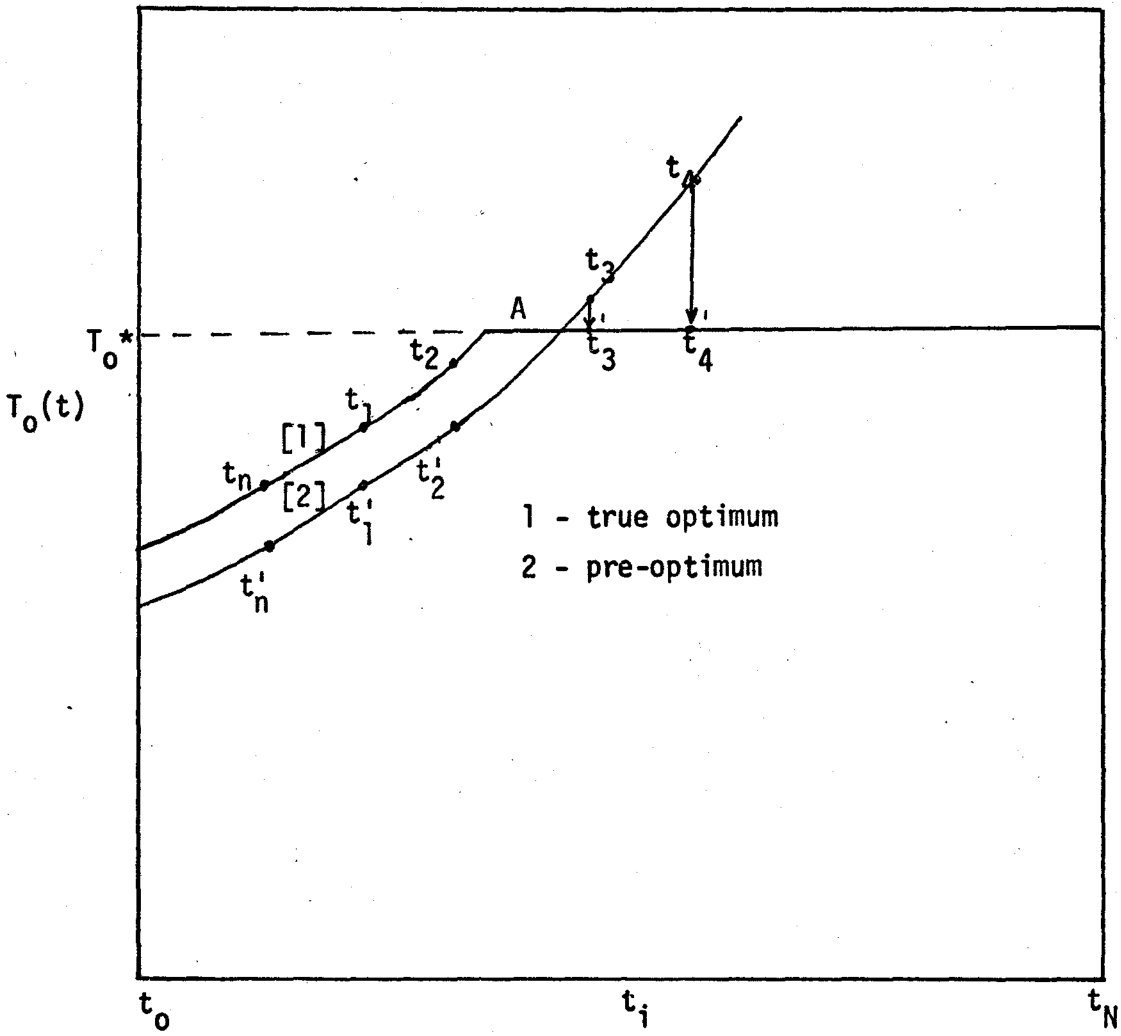

Figure 6-7 Effect of integration step size on the optimum seeking methods. Number of discrete points for unconstrained and constrained section is fixed

Curve 1 represents the true optimum. We suppose that curve 2 which is approaching the optimum, will move upwards towards the optimal curve 1 and register an increase in P_1. The length of the constrained profile will increase by A (see Figure 6-7). Length A is less than one time step unit. Since the length of a discrete profile can only be measured in terms of whole units A will be lost and the constrained profile will not have increased in length. P_2 which depends on the length of unconstrained profile may accordingly decrease in value.

The increase in P_1 may be outweighed by the decrease in P_2 such that the total objective function P, from (6-40), registers a net decrease, even though profile 1 is given as closer to the optimum than 2.

This problem will be most noticeable in the vicinity of the optimum when the objective function is increasing more slowly, but will always be present due to the discretised approximation of the optimal profile. It may, however, be minimised by choosing the grid sufficiently small.

6.6 Parametric Analysis of the Optimal Profile

6.6.1 Paramater p

The parameter $p = E_R/E_c$ features prominently in the character of the optimal profile (see Chapter 4 above) and if the strong form of the Hamiltonian were assured, $p > 1$ would eliminate the possibility of an unconstrained temperature profile for any finite time. For all the numerical examples $p > 1$ was accompanied by a totally constrained temperature profile with $T_o = T_o^*$ and $\frac{\partial \bar{H}}{\partial k_o} > 0$, for all t [see figure 6-8].

An increase of p in the range $0 < p < 1$ was accompanied by an increase in the average temperature in the reactor, as well as the length of time spent at the upper temperature limit. Also a decrease

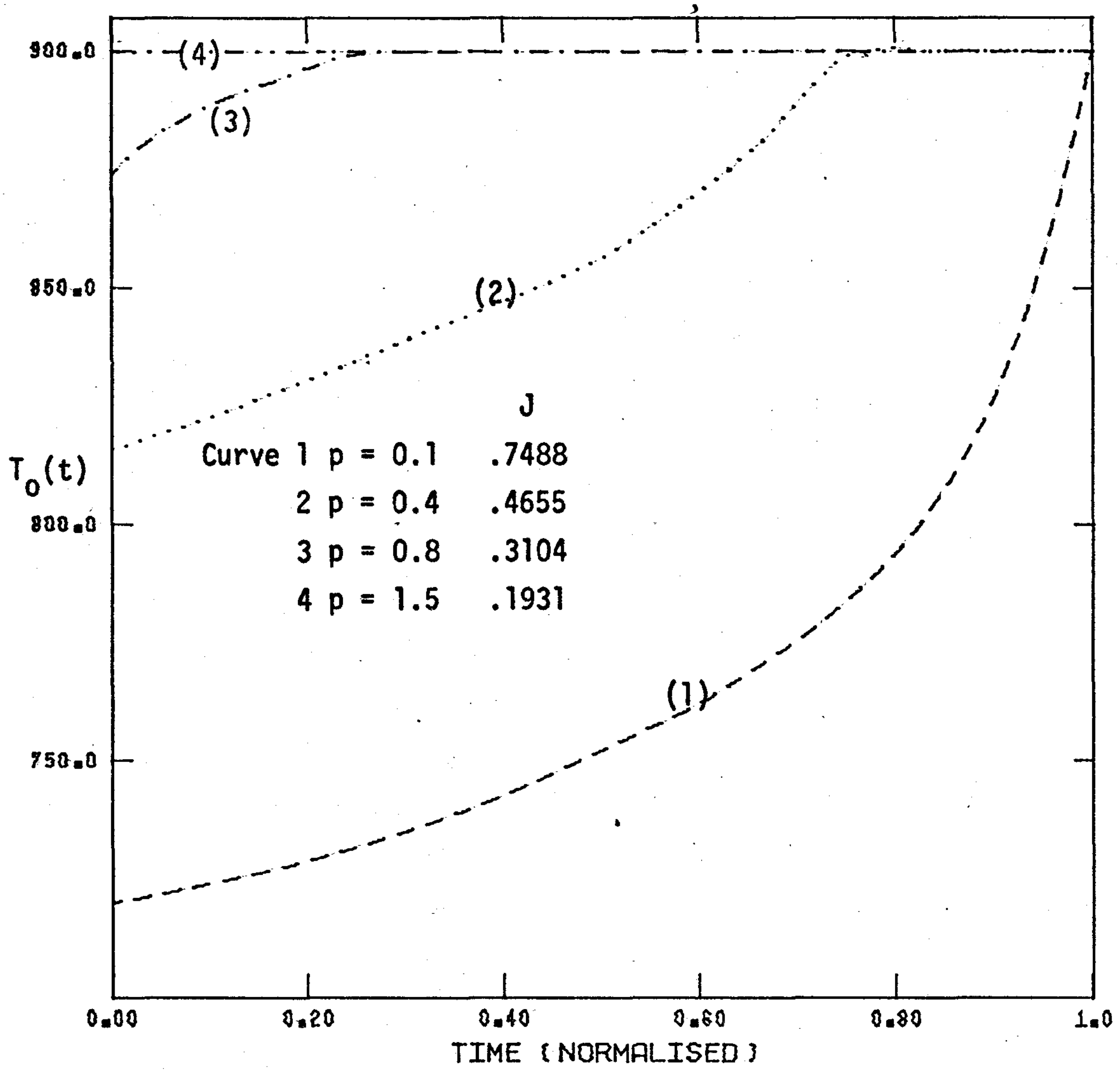

Figure 6-8 Influence of $p = E_R/E_c$ on the character of optimal profile with paramaters.
$n = 1$, $m = 2$, $J_i = .01$, $\tau = 25$ days, $f = (1+0.6X)$

in the objective function with an increase in p was observed.

These trends agree with those found by Ogunye and Ray (1971) and Therien (1971) and are to be expected, since as p increases the catalyst decay becomes relatively less sensitive to temperature and the reactor can operate more profitably at higher temperatures.
See figure 6-8.

6.6.2 Parameter τ

In agreement with Ogunye and Ray (1971) and Therien (1971), increasing the operation time τ (usually 25 days) decreases the average temperature in the reactor and causes the temperature to reach an upper constraint closer towards the end of operation time. In general one would expect that if more operational time were available a gentler initial treatment (via lower temperature) of the catalyst would seem desirable.
See Table (6-9)

Operation time τ days	% time on T_o^*	Objective Function J
10	60%	.6710
25	24%	.4655
50	6%	.3418

Table 6-9 Influence of Operational time τ on the length of the constrained temperature profile parameter n=1, m=2, $J_1^{\cdot}$ = .01, p=0.4, f=(1+0.6X)

6.6.3 Parameter m

A decrease in the parameter m in $g=\psi^m$ cause the decay rate of the catalyst via equation (3-55) to increase, thus making it less

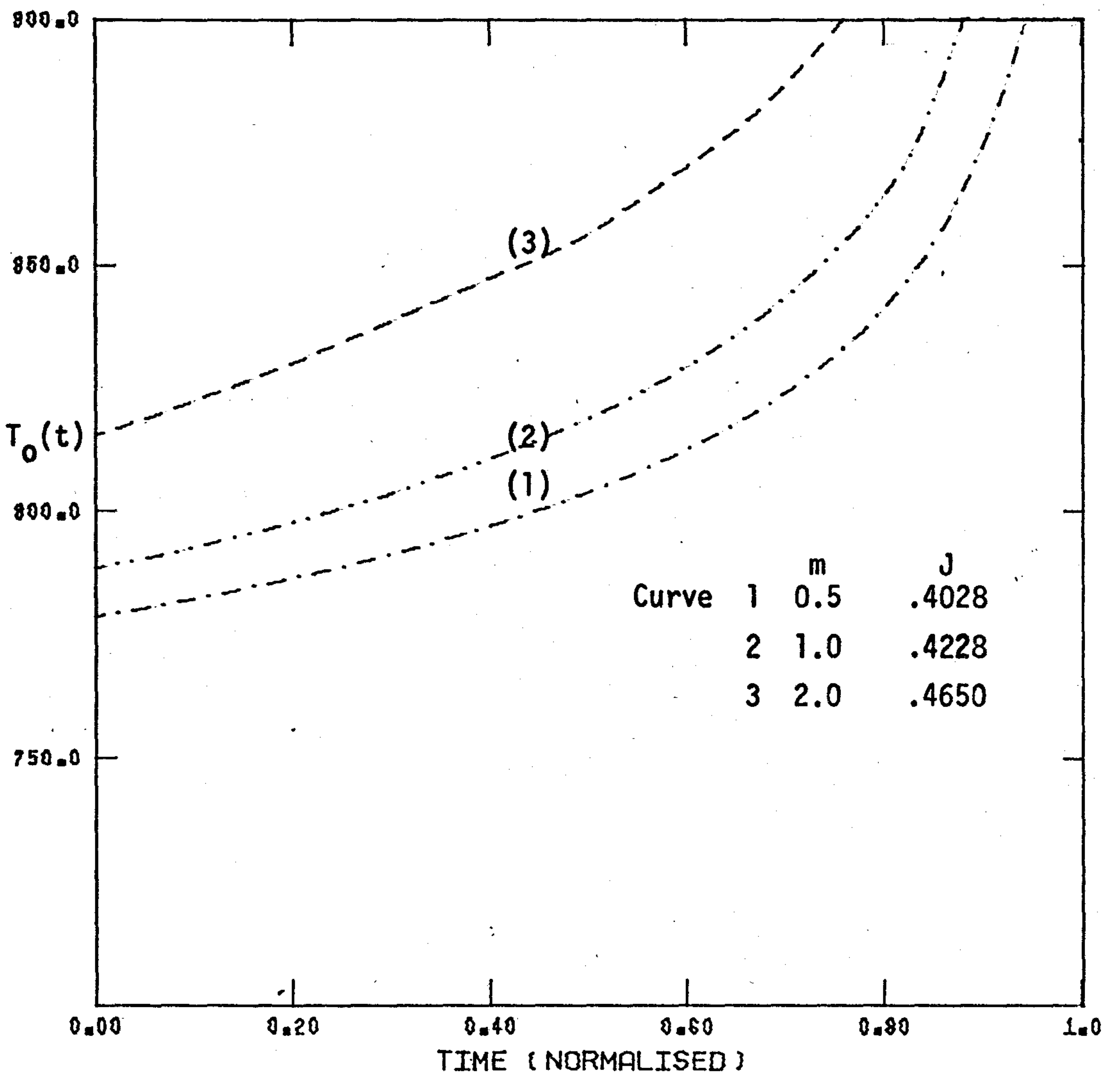

Figure 6-9 Influence of decay order n or character of optimal profile, n = 1, $J_1^{\cdot} = .01$, τ = 24 days, f = (1+0.6X), p = 0.4

desirable to maintain a higher temperature and decreasing the time spent at the upper temperature constraint. These results agree with those of Thérien (1971) and Ogunye and Ray (1971).
See figure 6-9.

6.6.4 Paramater n

In agreement with Thérien (1971) an increase in the order of the reaction causes a decrease in the average temperature in the reactor. From the first state equation (3-54) it can be reasoned that for large n the term $\bar{F} = (1-X)^n$ will tend to dominate the right hand side of (3-54). The effect of an increase in temperature with the resultant increase in reaction rate, would be diminished by the $\bar{F}$ term. It would thus not be profitable to raise the temperature as much for large n.

See Figure 6-10.

6.7 Rising and Falling Optimal Exit Conversions

6.7.1 Euler Formulation of Exit Conversion Derivative

From (5-76) we have an expression for the derivative of the exit conversion at the optimum

$$\frac{dX_1(t)}{dt} = \int_0^1 \frac{\partial}{\partial t}(\lambda_2 \, k_o g f) \, dz \tag{6-41}$$

substituting for $\frac{\partial \lambda_2}{\partial t}$ from (4-8) we have

$$\frac{dX_1(t)}{dt} = \int_0^1 [(k_o{}^2 g g' \lambda_2) f^2 - (\lambda_1 K_o k_o g) F f + (\lambda_2 \frac{\partial k_o g}{\partial t}) f + (k_o g \lambda_2 \frac{\partial X}{\partial t}) f'] dz \tag{6-42}$$

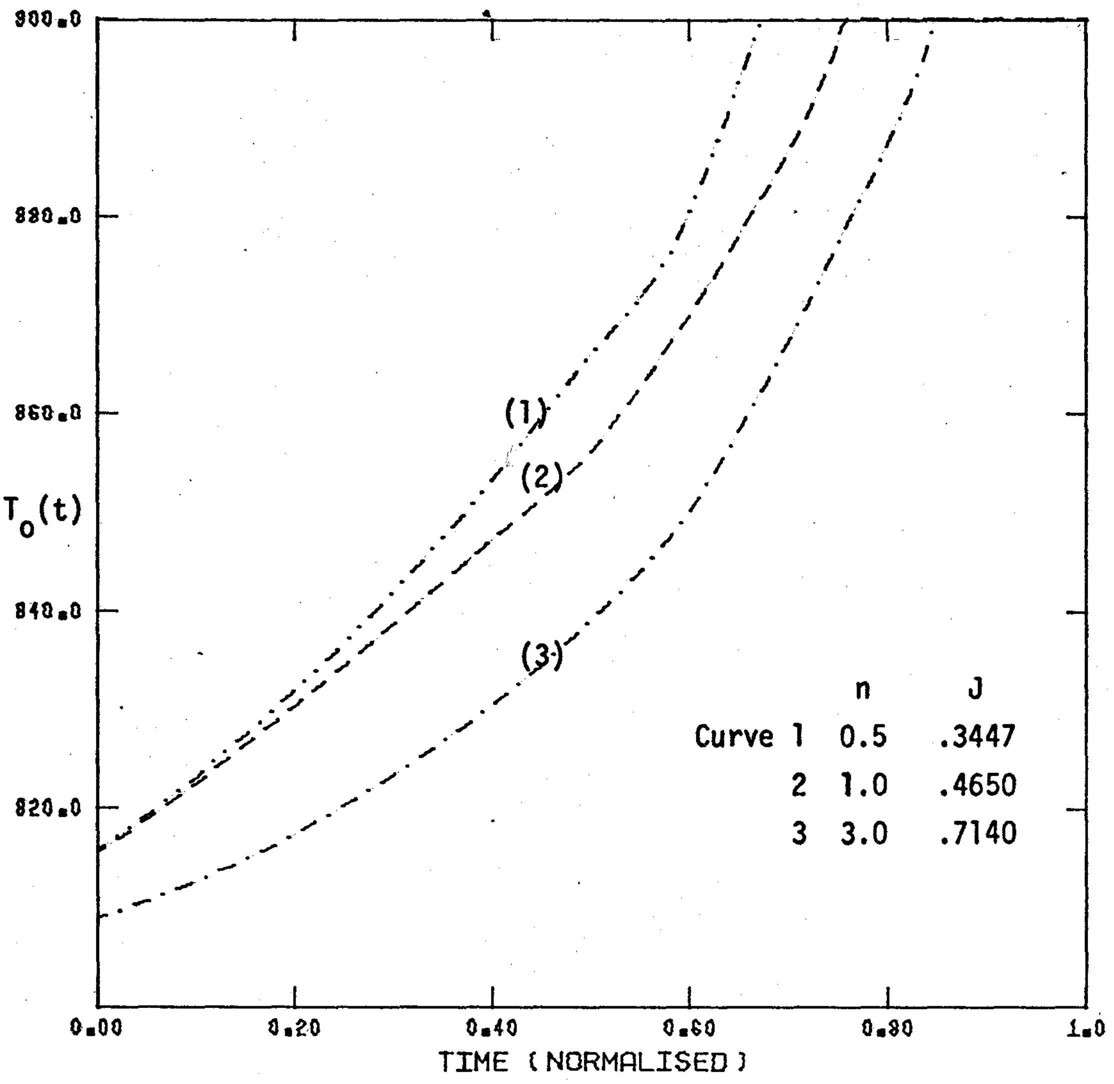

Figure 6-10 Influence of the reaction order n in the character of the optimal profile m = 2, $J_1' = .01$, τ = 25 days, $f = (1+0.6X)$, $p = 0.4$

Equation (6-42) is an expression for the derivative of the exit conversion at the optimum expressed as an explicit function of F and f.

We can view equation (6-42) as an objective function and choose f and F at every point in z at some time, say t_o, in order to maximize the derivative at time t_o.

$$\underset{F,f(z,t_o)}{\text{Max}} \left[\frac{dX_1(t_o)}{dt}\right] = \int_o^1 \left[B_1 f^2 - b_2 Ff + B_3 f + B_4 f^1\right]\Big|_{t_o} dz \tag{6-42}$$

where
$$B_1 = k_o{}^2 gg' \lambda_2'(z,t_o) \tag{6-43}$$
$$B_2 = \lambda_1 K_o k_o g\ (z,t_o) \tag{6-44}$$
$$B_3 = \lambda_2 \frac{\partial\, k_o g}{\partial\, t}\ (z,t_o)$$
$$B_4 = k_o g \lambda_2 \frac{\partial\, X}{\partial\, t}\ (z,t_o) \tag{6-46}$$

It is seen that all the Bi's i=1,4 are functions, either directly or indirectly, of many variables including f(X), F(X). However, it turns out for certain paramaters, the changes in the numerical values of the Bi are small in comparison with the changes caused in the values of F and f by changing their forms within a given restricted form [see (6-48) and (6-49) below].

The Bi are thus not constants with respect to F and f and the correct procedure would be to obtain the Bi's as explicit functions of f, F and obtain true constants in the integrand of (6-42). However, closed form analytical expressions for most of the variables as functions of F and f are unavailable.

A semiquantitative approach is to numerically examine the Bi to see whether (for a particular set of system paramaters) they are approximately constant with respect to any variations in F and f (caused by a change

Table 6-10 Typical falling exit conversion profiles

t	m=0.5, m=2, $J_1^{\cdot}=.01$ $f=(1+0.6X)$ p=0.4 $T_0^* = 900°K$	n=1, m=1, $J_1^{\cdot} = .01$ $f=(1+0.6X)$ p=0.4, $T_0^*=900°K$	n=1, m=1, $J_1^{\cdot}=\infty$ $f=(1+X)$, p=0.5, $T_0^*= 1000°K$
0	.4232	.4615	.6435
1	.4178	.4565	.6261
2	.4121	.4542	.6110
3	.4063	.4523	.5977
4	.4005	.4506	.5859
5	.3947	.4488	.5753
6	.3886	.4470	.5655
7	.3823	.4451	.5565
8	.3756	.4431	.5482
9	.3687	.4410	.5403
10	.3614	.4388	.5330
11	.3542	.4366	.5259
12	.3478	.4342	.5192
13	.3440	.4317	.5127
14	.3449	.4291	.5064
15	.3440	.4262	.5002
16	.3440	.4231	.4941
17	.3111←($T_0=T_0^*$)	.4197	.4881
18	.2960	.4157	.4822
19	.2956	.4112	.4763
20	.2779	.4055	.4707
21	.2625	.3989←($T_0=T_0^*$)	.4659←($T_0=T_0^*$)
22	.2490	.3654	.4581
23	.2371	.3081	.4466
24	.2264	.2629	.4365
J	0.3433	0.4228	0.5158

in the form of F or f). If this is found to be true over a particular range of paramaters in the system, the Bi's are said to be "weak functions" of f and F at some point in time t_0. This numerical property is made use of at a later point [see (6-52) below].

Nevertheless, even if the Bi are not "weak functions" of F and f we can simply proceed as if they were and if we find that we are able to change the objective function in (6-42) to produce say, a rising conversion, then this is indeed justification in itself.

By far the most common exit profile at the optimum is one of a <u>falling exit conversion</u> and all the figures referred to in Chapter 6 except 6.2 exhibited a falling exit conversion profile at the optimum. Some typical optimal exit conversion profiles for various reaction systems are given in table 6-10. [See also Chapter 5 proposition 3].

The <u>constant conversion profiles</u> were used to verify the program and were given in 6.2.

The question naturally arises as to whether it is possible to choose some form for F and f which will cause a <u>rising exit conversion</u> at the optimum. To this end we refer back to equation (6-42) and attempt to use this equation to indicate the form that F and f should take, in order to produce a rising optimum exit conversion at a particular point in time (t_0)

For convenience we choose t_0=0 and we choose a form for F and f so as to produce a positive value for the slope:

$$\left[\frac{dX_1(o)}{dt}\Big|_{opt}\right] > 0 \qquad (6\text{-}47)$$

t	$X_1(t)$	$T_o(t)$ °K
0	.8820	889.4
1	.8764	891.0
2	.8698	892.3
3	.8626	893.5
4	.8550	894.5
5	.8470	895.4
6	.8387	896.2
7	.8300	897.0
8	.8210	897.7
9	.8118	898.3
10	.8023	898.9
11	.7926	899.4
12	.7827	899.9
13	.7718	900.0
14	.7605	900.0
15	.7493	900.0
16	.7381	900.0
17	.7269	900.0
18	.7157	900.0
19	.7047	900.0
20	.6936	900.0
21	.6827	900.0
22	.6719	900.0
23	.6612	900.0
24	.6506	900.0

Table 6-12 Falling optimal exit conversion profiel for r=1 in $f=(1-\chi)^r$, $T_o^* = 900°$, p=0.4, m=2, n=1

There is no guarantee that the optimal profile will continue to rise for $t_o > 0$, but at least we have a direction in which to search among possible forms for F and f (or $\bar{F}$ and $\bar{f}$; $F=\bar{F}$ for uniform temperature).

If we insist on a particular form for $\bar{F}$ and $\bar{f}$ such that [using (6-1) (3-36)],

$$f(\text{or } \bar{f}) = (c+d\chi)^{n2} > 0 \qquad c,\ d \text{ constants} \tag{6-48}$$

$$F(\text{or } \bar{F}) = (1-\chi)^{n} > 0 \tag{6-49}$$

then F and f are no longer our controls but instead n2 and n are manipulated to produce different forms of F and f amongst the class of functions restricted to forms (6-48) and (6-49). Strictly speaking n and n2, since they are controls at t_o, become functions of z, but since the whole analysis is semi quantitative and we require only to differentiate between possible forms of $\bar{f}$ and $\bar{F}$ in a direction of increasing $\frac{d\chi_1(o)}{dt}$, n and n2 are perceived as average values.

A bound is placed on n so that $\bar{F}$ conforms to a general n th order reaction scheme, i.e.,

$$n \geq 0 \tag{6-50}$$

whereas n2 is allowed negative and positive values, but not zero. Bounds are placed on F such that $F_{min} \leq F \leq 1$. (6-51)

From (6-48) and (6-42) we have

$$\max_{F,\, f} \left[\frac{d\chi_1(o)}{dt}\right] = \int_0^1 \left[B_1 f^2 - B_2 F f + B_3 f + dn2\ B_4 f^{\frac{n_2-1}{n2}}\right] dz \Big|_{t_o=0} \tag{6-52}$$

A further assumption is necessary regarding (6-52) which requires that the function B_1 to B_4 are not 'strong' functions of F or f: that is, any change in F or f within limits imposed by (6-48), (6-49) and (6-50) will cause significantly smaller changes in the B_i $i=1,4$ so that we may treat them as approximately constant with respect to changes in f and F. This assumption can be tested numerically for a specific problem over a range of given paramaters.

We may now cast (6-52) in the form of an Euler type optimisation problem and since the integrand does not depend on $\frac{df(z)}{dz}$ explicity, we may maximize the integral by maximizing the integrand [Denn (1967)].

$$R = B_1 f^2 - B_2 Ff + B_3 f + dn2\ B_4\ f^{\frac{n2-1}{n2}} \qquad (6\text{-}53)$$

For a particular set of system paramaters with

$c = 1$, $d = 2$ in(6-1), $p = 0.2$, $m = 2$

it was determined numerically an average set of values for Bi were

$$\begin{aligned} B_1 &= 0.0011 \\ B_2 &= 0.1610 \\ B_3 &= 0.0200 \\ dB_4 &\approx 10^{-6} \end{aligned} \qquad (6\text{-}53a)$$

Referring to Table 6-3 the following paramater signs are easily verified numerically where analytical properties are unavailable. We can show (as long as we have less than 100% conversion or zero catalyst activity).

$B_1 > 0$	analytically	from (6-48), 3.6, and (5-46), (5-47)
$B_2 > 0$	analytically	
$B_3 > 0$	numerically	from (6-53a) (6-54)
$B_4 > 0$	numerically	

From (6-53) we can see that R is linear in F and since B_2 $f > 0$ [(6-54), (6-48)] to maximize R we must choose from (6-51).

$$F = F_{min} \qquad (6\text{-}55)$$

F_{min} is a constant which can be normalised by adjusting the rate constant term K_+(3-23) in the first state equation so (6-55) says, choose a <u>zero order reaction</u> i.e.

$$F = \text{constant} \qquad (6\text{-}56)$$

Maximizing R with respect to f and solving simultaneously with (6-55).

$$\frac{\partial R}{\partial f} = 2Bf_1 - B_2F_{min} + B_3 + B_4d(n2-1)f^{\frac{-1}{n2}} \Bigg|_{t_o=0} = 0 \qquad (6\text{-}57)$$

If we choose c, d > 0 (6-54)

Substituting for f from (6-48) and solving for n2 (6-57) (with F_{min}=0.1) using the average values in (6-53a) we obtain a large negative value for n2.

$$n2 \simeq -6 \times 10^3 \qquad (6\text{-}58)$$

6.7.2 Numerical Results

If we now use (6-55) and a negative n2 but of a more realistic magnitude,the form of F and f, for example; become

$$F = 0.1 \quad \text{constant} \qquad (6\text{-}59)$$

$$f = (2 + X)^{-3} \quad (n2 = -3) \qquad (6\text{-}60)$$

We expect a positive value for $\frac{dX_o(o)}{dt}$ and in fact with the above examples a rising exit conversion is obtained at the optimum [see Table 6-3 above] at time t_o which continues to rise until an upper constraint is reached, at which point the exit conversion decreases sharply.

Using the result of proposition 3 in 5.7, we have

$$\left.\frac{dX_1}{dt}\right|_{opt} = \int_0^1 [-(k_o K_o g \lambda_1)Ff + (\frac{dk_o}{dt})f + (k_o)f'] \, dz \qquad (6\text{-}61)$$

the terms in brackets ( ) are all positive and one may, using similar semi-quantitative analysis (as in 6.7.1, but now with analytically obtainable signs of the bracket '( )' factors) to determine the relative properties of f and F so as to maximize $\frac{dX_1}{dt}$ in (6-61) at some time t_o. For example, one obvious starting point for positive $\frac{dX_1}{dt}$ would be to choose

$F = F_{min}$ = constant

$f(X)$ = fairly small in absolute value

$f'(X)$ = large positive value

For many numerical cases examined, a rising exit conversion profile at the optimum was obtained only for zero reaction order systems.

6.8 Optimum Uniform Temperature Profile vs Best Constant Temperature

A valid method for evaluating the optimum uniform temperature profile for a reactor, is to compare the objective function so obtained, with the objective function for the best constant temperature (i.e. constant in time and uniform over all z).

The second objective function is obtained simply by a one dimensional search for that single temperature which produces the highest value of the objective function.

It is unrealistic to compare this case with the adiabatic reactor where the temperature constraint is on the inlet temperature. For an exothermic reaction the temperature constraint is most likely to be violated towards the exit end of the reactor; it makes more sense to place a temperature constraint on the outlet temperature.

The improvement of the optimal temperature profile over the best constant temperature was of the order of 10%, but usually it was closer to 13%; a typical example is given in Table 6-11.

Any numerical scheme which places a constraint on the exit temperature of an adiabatic reactor will involve considerably more computation. This is so because one cannot determine, a priori, whether a particular inlet temperature will cause violation of the exit end constraint and thus trail and error integration of the state equations along z is necessary at each point in time.

	Profile 1	Profile 2
f	2/(2-X)	2./(2-X)
n	1	1
m	2	2
p	0.4	0.4
T_o^*	900°K	-
T_{o*}	700°K	-
$\dot{J}_1$	∞(uniform temp)	-
$T_o(t)$	$T_o(t)$ optimal	875°K
J	.2624	.2329
$\Delta\% = \frac{J_1-J_2}{J_1} \times 100 = 13.05\%$		

Table 6-11 Optimal uniform temperature (1) vs best constant temperature (2)

CHAPTER 7

SUMMARY AND CONCLUSIONS

A quasi-steady state catalytic reaction deactivation system in a plug flow, fixed bed, adiabatic, tubular reactor is considered. The chemical reaction scheme is an n th order (or autocatalytic), single and irreversible reaction. Both the reaction rate and the deactivation rate are expressed as a product of separable functions of conversion, (catalyst) activity and inlet temperature.

A first order perturbation analysis of the system equations has been performed, and the problem of choosing the inlet temperature profile, so as to maximize the total amount of reaction has been considered.

A common industrial practice of choosing this temperature profile, so as to maintain the exit conversion constant, while the choice of temperature is unconstrained, has been examined. This practice is designated the "constant exit conversion policy".

Analytical expressions for the optimal exit conversion were derived and used to prove that for certain forms of F(X) and f(X), choosing the inlet (or uniform) temperature in time so as to maximize the total amount of reaction, produces a constant exit conversion, when the choice of the inlet temperature is unconstrained.

The analytical forms, together with the case where f(X) is constant, were used to verify a program which uses an efficient fixed point search algorithm. The program was further used to investigate the reactor system with the more general forms of F and f. The necessary condition for the optimum was recast into a fixed point form. The more usual gradient method in function space was replaced by an iterative fixed point method in function space. The fixed point method was found to be superior to the gradient method; it reduced the computation time and also produced a more precise optimal profile. Various convergence promotion techniques were used to even further cut computation time and were partially successful.

A general analytical property of $f(X)$, as a sufficient condition to produce a falling optimum conversion was derived. This led to the proof of the existence of an $f(X)$, such that a falling optimal exit conversion would result, and further, that this was valid for any form of catalyst decay term $g(\psi)$.

The analytical expression for the time derivative of the optimal exit conversion was cast into the form of a suboptimal problem, in which the forms of F and f were chosen so as maximize this derivative, in order to produce a rising optimal exit conversion. This sub problem was analysed semi-qualitatively by casting it into a classical Euler form.

It was demonstrated that all three types of exit conversion profiles can exist at the optimum, viz., rising, constant and falling profiles. Falling profiles are by far the most common type and rising profiles were observed only for zero order reaction schemes, but the possibility of rising profiles, for higher reaction order schemes accompanied with special decay kinetics cannot be ruled out. So a general policy of constant exit conversion cannot be extended to the case of boundary control of this reactor system, where decay depends on conversion.

The existence of a totally constrained temperature profile at the upper limit, was demonstrated for all cases in which the paramaters $p = E_R/E_C$ is greater than unity. The lack of a well established proof of a maximum principle for boundary control of non linear distributed systems was noted and thus any analytical analyses of this constrained profile, although tempting, were dispensed with.

A parametric investigation of the optimal profile showed agreement with related studies in this area, as well as satisfying a more intuitive analysis. The optimal uniform temperature policies are assessed by showing considerable improvement, in the total amount of reaction produced, over the best isothermal temperature.

7.1 Future Work

The forms of equations derived in Chapter 3 are general and allow the extension to include more complex reaction systems eg. reversible reactions.

In 2.3.2 the co-problems of choosing the initial catalyst distribution to maximize the total amount of production is mentioned. A natural direction would be to combine the catalyst choice problem with the present problem and seek to choose both the initial catalyst distribution and the inlet temperature profile, so as to produce the maximum amount of reaction.

An extension of the pseudo-homogeneous system considered here, to the simplest heterogeneous system, along the lines mentioned in 3.2.3, may be fruitful; this extension would allow the analysis of highly exothermic or endothermic reactions systems or for those systems where catalyst particles are fairly large.

LIST OF SYMBOLS

a	constant defined (3-26)
A	general reactant species for irreversible n th order reaction (3-40).
$A(t)$	switching function (4-27).
$\underline{\underline{A}}$	matrix defined (6-34).
$\underline{b}$	constant vector (6-34).
B	general product species for irreversible n th order reaction (3-40)
B_1, B_2, B_3, B_4	variables defined in (6-34) et seq.
C_j	molar concentration of j th species (3-1).
C_p	specific heat capacity
$C(z,t,z',t')$	function defined by (5-38).
$\tilde{C}(z,t,z',t')$	function defined by (5-41).
c,c_1	arbitrary positive constants used in 5.5.1.
c	paramater used in (6-1).
$D_j(r,\theta,z)$	diffusivity of j th species in cylindrical coordinates, (3-1).
d^*	a normed measure of 'closeness' to the optimum (6-39).
d	parameter used in (6-1).
E_c	activation energy for catalyst decay, divided by the gas constant (3-7).
E_R	activation energy for reaction divided by the gas constant (3-3).
$F_j(C)$	concentration dependent term for j th species (3-2).
$\underline{F}$	vector function of variables (6-32).
$F,F(X)$	conversion dependent term in reaction rate used in (3-52) and (3-54).
$F'(X)$	first derivative of F with respect to X.

$\bar{F}(X)$	function related to F and used in (3-12), (3-36), and (3-52).
$f, f(X)$	conversion dependent term in ϕ used in (3-53), and (3-55).
$f'(X)$	first derivative of f with respect to x.
$G[k_o]$	functional expression used in fixed point formulation of necessary condition (4-34).
$g(\psi)$	activity dependent term in ϕ, (3-5).
$g'(\psi)$	first derivative of g with respect to ψ.
g_k	reaction rate for species k (2-10).
$\bar{H}$	Hamiltonian function for the system (3-54) and (3-55) defined in (4-3) as integral of H.
H	Hamiltonian integrand (4-2), (A-29).
$I_1(z,t)$	non negative function (5-37).
$I_2(z,t)$	non positive function (5-40).
I	objective function for which extreme required (2-1), (2-11).
$J^{\cdot}$	variable considered approximately constant (3-45).
$J_1^{\cdot}$	ratio of heat capacity to heat of reaction (3-42).
J	maximum value of P (3-58).
$K_j[T]$	reaction rate constant for j th species (3-3).
$K, K[T]$	Arrhenius reaction rate constant (single species) (3-3), (3-38).
$\bar{K}$	reaction rate constant defined (3-16).
$K_+^{\cdot}$	preexpoenential constant (3-3).
K_+	preexponential constant (3-24a).
$K_o, K_o[T_o]$	inlet Arrhenius reaction rate constant, bounded through its relation to K_o (3-51a) and defined in (3-49).
$k_o, k_o[T_o]$	inlet Arrhenius deactivation rate constant and boundary control of the system in 3.8; bounded between two finite limits as in (3-47) and defined in (3-48) and (3-50).

$\underline{k}_o$	vector of discrete values; made up of $k_o(t_i)$, (6-31a).
$k, k[T]$	Arrhenius decay rate constant used as distributed control; defined (3-7), (3-39).
$k^{\bullet}_{+}$	preexponential constant (3-7).
k_+	preexponential constant (3-24a).
$\bar{k}$	decay rate constant defined (3-17).
k_*, k^*	lower and upper bounds resp., on k_o (or k), (3-35).
L	total length or distance dimension of system $0 \le z' \le L$, (3-15).
L*	Lagrangian of P for system in 3.8 (see also App. A).
$\ell_1, \ell_2, \ell_3, \ell_4$	functions defined in (5-28) to (5-30).
m	order of decay (3-37).
n	order of reaction (3-36).
n1,n2	parameters used in (6-1).
N_z	number of grid points along z'.
N_t	number of grid points along t'.
P	objective function of system defined in 3.8.
P_1	unconstrained portion of objective function see 6.5.
P_2	constrained portion of objective function see 6.5.
p	equals E_R/E_c (3-27).
Q	reaction rate expression (2-9).
q	iteration count, chapter 6.
R	function defined by (6-53).
R_j	reaction rate for species; (3-2).
r	order of conversion dependence (5-137).
S(z,t)	function defined in (6-13).
S*	closed subset of Hilbet space X*.
T,T(z,t)	distributed temperature (3-34).
T_{o*}, T_o^*	lower and upper bounds on T_o (3-34).

$T_o(t)$	equals $T(o,t)$, inlet temperature to the reactor (3-43).
T_f	transformation in Hilbert space (4-35).
$\bar{t}$	point in time t, at which the optimum temperature profile reaches the upper constraint and remains there; defined in paragraph following (5-76).
t	independent normalized time variable for system 3.8.
t'	independent time variable for system $0 \le t' \le \tau$
t_i	discrete version of $t', i = 0, N_t$.
t_θ	average space time of reactor (3-18).
U	set of allowable control functions.
$\underline{u}$	vector of allowable control function $\underline{u} \in U$ (2-2).
$V(z,t)$	function defined in (C-10).
v_r, v_z, v_θ	bulk flow velocities in cylindrical coordinates (3-1).
v	bulk flow in z direction (equals v_z), assumed constant (3-4).
W	defined in (2-3).
$\underline{w}$	boundary control vector in z (2-1).
$X, X(z,t)$	distributed conversion, first state variable of system 3.8, governed by (3-54).
$X_o(t)$	equals $X(0,t)$ inlet conversion (3-21).
$X_1(t)$	$X(1,t)$ exit conversion (3-58), (A-6).
X1	equals $X_1(t)$ for the case where $X_1(t)$ = constant at the optimum (5-130).
X^*	a Hilbert space containing vectors x_n.
x_n	sequence of vectors in X^* (4-36).
$\underline{Y}$	vector of variables defined (6-32).
$\underline{Y}_s$	limiting vector in sequence $\underline{Y}_n$ (6-34), (6-36).
z'	independent variable of system in 3.8; distance along reactor $0 \le z' \le L$.

z	independent normalized variable of system in 3.8, distance along reactor.
z_i	discrete version of z', i=0, N_z.

Mathematical Symbols

$\| \quad \|$	norm on a Hilbert space (2-4), (4-38) etc.
$<\cdot,\cdot>$	inner produce of the above Hilbert space.
$\Rightarrow$	mathematical symbol, read as: "implies without exception".
■	mathematical symbol, signifying end of a proof.
ε	symbol read as: "element contained in the set..".
$\notin$	symbol read as: "element not contained in the set..".

Greek Symbols

Φ	average activity over length of reactor (5-7).
ϕ	rate of deactivation (3-5), (5-66).
$\psi, \psi(z,t)$	relative catalyst activity defined (3-8), goverened by (3-55).
$\psi_i(z)$	equals $\psi(z,0)$, initial catalyst activity, (3-22).
τ	final time for process (2-1), (3-14).
$\gamma(t)$	positive multiplying function (6-17)
μ_1	dominant eigenvalue of $\underset{=}{A}$ (6-15).
α	accelerating factor (4-37) (6-23).
$\lambda_1, \lambda_1(z,t)$	first adjoint variable defined by (4-4).
$\lambda_2, \lambda_2(z,t)$	second adjoint variable defined by (4-8).
$\Delta H°$	standard heat of reaction for irreversible reaction $A \rightarrow B$ (3-40).
δP	first order perturbation of P (4-1).
δk_o	first order perturbation of k_o(4-1).

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APPENDIX A

A Weak Maximum Principle for Boundary Control

Proceeding directly from the state equations (3-54) and (3-55) with their associated boundary conditions (3-21) and (3-22) we have

$$\frac{\partial X}{\partial z} = K_o F \psi \tag{A-1}$$

$$\frac{\partial \psi}{\partial t} = - k_o fg \tag{A-2}$$

Boundary Conditions:

$$X(0,t) = X_o(t) \ . \tag{A-3}$$

$$\psi(z,0) = \psi_i(z) \tag{A-4}$$

Objective Function $P = \int_0^1 [X_1(t) - X_o(t)]dt$ (A-5)

where $X_1(t) = X(1,t)$ (A-6)

Perturbing this equation by small admissible amounts and subtracting from the original equations one obtains the variational equations:

$$\frac{\partial(\delta X)}{\partial z} = \delta(K_o F\psi) \tag{A-7}$$

$$\frac{\partial(\delta\psi)}{\partial t} = - \delta(k_o fg) \tag{A-8}$$

$$\delta P = \int_0^1 (\delta X_1 - \delta X_o)dz \tag{A-9}$$

The δ notation simply represents a small admissible variation. It may be viewed more strictly as the Gateaux differential, eg.,

$$\delta P \overset{\text{def}}{=} \frac{d}{d\beta}\int_0^1 [X_1 + \beta h_1(t) - X_o - \beta h_o]dz\Big|_{\beta=0} \tag{A-10}$$

$$\delta P = \int_0^1 [h_1(t) - h_o(t)]dz \tag{A-11}$$

where h_1 and h_o are small admissible variations in the same vector space as X, and, in our notation, would be equivalent to $\delta X_1(t)$ and $\delta X_o(t)$, respectively.

If we now specify that $X_o(t)$ and $\psi_i(z)$ are given functions in time (t) and distance (z) respectively then,

$$\delta X_o = 0 \qquad \text{(A-12)}$$

$$\delta \psi_i = 0 \qquad \text{(A-13)}$$

Accordingly δP may be written

$$\delta P = \int_0^1 \delta X_1(t)dt \qquad \text{(A-14)}$$

Introduce two Lagrange-type multipliers $\lambda_1(z,t)$ & $\lambda_2(z,t)$ called adjoint variables, (associated with a Lagrangian L*) and consider the two equations

$$\frac{\partial}{\partial z}(\lambda_1 \delta X) = \lambda_1 \frac{\partial}{\partial z}(\delta X) + \delta X \frac{\partial \lambda_1}{\partial z} \qquad \text{(A-14)}$$

$$\frac{\partial(\lambda_2 \delta \psi)}{\partial t} = \lambda_2 \frac{\partial(\delta \psi)}{\partial t} + \delta \psi \frac{\partial \lambda_2}{\partial t} \qquad \text{(A-15)}$$

We define a Lagrangian of the system (A1 → A6) to be L*, and we require P to be stationary subject to equations (A-1),(A-2). Integrating both sides with respect to z and t and applying the boundary conditions (A-12) and (A-13).

$$-\int_0^1 \lambda_i(1,t)\, \delta X_1(t)\, dt + \int_0^1\!\!\int_0^1 [\lambda_1 \frac{\partial(\delta X)}{\partial z} + \delta X \frac{\partial \lambda_1}{\partial z}]dzdt = 0 \qquad \text{(A-16)}$$

$$-\int_0^1 \lambda_2(z,1)\, \delta\psi(z,1)dz + \int_0^1\!\!\int_0^1 [\lambda_2 \frac{\partial}{\partial t}(\delta\psi) + \delta\psi \frac{\partial \lambda_2}{\partial t}]dzdt = 0 \qquad \text{(A-17)}$$

From (A-9), (A-16) and (A-17) form the Lagrangian perturbation δL^* from the Lagrangian L*

$$\begin{aligned} \delta L^* = {} & \int_0^1 \delta X_1 dt - \int_0^1 \lambda_1(1,t)\, \delta X_1 dt - \int_0^1 \lambda_2(z,1)\delta\psi(z,1)dz \\ & + \int_0^1\!\!\int_0^1 [\lambda_1 \frac{\partial}{\partial z}(\delta X) + \delta X \frac{\partial \lambda_1}{\partial z}]dzdt \\ & + \int_0^1\!\!\int_0^1 [\lambda_2 \frac{\partial}{\partial t}(\delta\psi) + \delta\psi \frac{\partial \lambda_2}{\partial t}]dzdt \end{aligned} \qquad \text{(A-18)}$$

Now from (A-7) and (A-8) using (3-51a)

$$\delta(\psi K_o F) = K_o F\, \delta\psi + \frac{\psi F p K_o}{k_o}\, \delta k_o + \psi\, K_o\, F'\, \delta X \qquad \text{(A-19)}$$

$$\delta(k_o fg) = k_o fg'\, \delta\psi + gf\, \delta k_o + k_o gf'\, \delta X \qquad \text{(A-20)}$$

where $F' = \frac{dF}{dX}$ $f' = \frac{df}{dX}$ and $g' = \frac{dg}{d\psi}$ (A-21)

Substituting in (A-18) from (A-19), (A-20) and (A-7) and (A-8) we obtain

$$\begin{aligned}\delta L^* = & \int_0^1 [1 - \lambda_1(1,t)]\, \delta X_1(t)dt - \int_0^1 \lambda_2(z,1)\, \delta\psi(z,1)dz \\ & + \int_0^1\int_0^1 [\frac{\partial \lambda_1}{\partial z} + \lambda_1 K_o F'\psi - \lambda_2 k_o g f']\, \delta X \, dzdt \\ & + \int_0^1\int_0^1 [\frac{\partial \lambda_2}{\partial t} + \lambda_1 K_o F - \lambda_2 k_o f g']\, \delta\psi \, dzdt \\ & + \int_0^1 (\int_0^1 [\frac{p\lambda_1 \psi F K_o}{k_o} - \lambda_2 g f]dz)\, \delta k_o(t)dt\end{aligned} \qquad (A-22)$$

If one now specifies the following conditions for the adjoint variables

$$\frac{\partial \lambda_1}{\partial z} + \lambda_1 K_o F'\psi - \lambda_2 k_o g f' = 0 \qquad (A-23$$

$$\frac{\partial \lambda_2}{\partial t} + \lambda_1 K_o F - \lambda_2 k_o f g' = 0 \qquad (A-24)$$

with boundary conditions

$$\lambda_1(1,t) = 1 \qquad (A-25)$$

$$\lambda_2(z,1) = 0 \qquad (A-26)$$

We then have the adjoint system defined by equations (4-4) to (4-10).

We may now write the Lagrangian δL^* as:

$$\delta L^* = \int_0^1 (\int_0^1 [\frac{p\lambda_1 \psi F K_o}{k_o} - \lambda_2 g f]dz)\, \delta k_o(t)dt \qquad (A-27)$$

The necessary conditions for an maximum Lagragian is

$$\delta L^* \leq 0 \qquad (A-27)$$

Note only the stationarity of L^* may be identified as a necessary condition for the optimum of the constrained objective function P.

Seeing that for unconstrained k_0, δk_0 may be of either sign, it is thus necessary, to satisfy (4-27), that

$$\int_0^1 [\frac{p\lambda_1 \psi F K_0}{k_0} - \lambda_2 g f] dz = 0 \tag{A-28}$$

If we now define the Hamiltonian function

$$\bar{H} = \int_0^1 H dz \tag{A-29}$$

where

$$H = \lambda_1 \psi F K_0 - \lambda_2 g f k_0 \qquad \text{(A-29)}$$

we have the necessary condition (A-28) equivalent to

$$\frac{\partial \bar{H}}{\partial k_0} = \int_0^1 \frac{\partial H}{\partial k_0} dz = 0 \tag{A-30}$$

Hence equation (4-12) for the weak maximum principle.

We may write δP in place of δL^* if it is understood that the perturbation of the objective function P, is subject to the constraints placed upon the system through equation A1 and A2 and their associated boundary conditions.

APPENDIX B

The Constant Conversion Policy for Decay Independent of Conversion

From the equations derived in Chapter 5 we have, from (5-83a), the necessary condition for the unconstrained optimum

$$\int_0^1 [(p-1)\ \lambda_1 F \frac{\partial\ \psi K_o}{\partial\ t} + p\psi K_o \frac{\partial\ \lambda_1 F}{\partial\ t} - \frac{1}{F}\ \frac{\partial\ \lambda_1 F}{\partial z}\ \frac{\partial\ X}{\partial\ t}\ ]dz = 0 \qquad \text{(B-1)}$$

Now when decay rate does not depend on conversion we set f(X) to a constant (unity for convenience).

$$f(X) = 1 \qquad \text{for all } z,\ t \qquad \text{(B-2)}$$

From (B-2) we have $f' = 0$ and using (5-43)

$$\frac{\partial\ \lambda_1 F}{\partial\ z} = \lambda_2 k_o g F f' \qquad \text{(5-43)}$$

$$= 0 \quad \text{all } z \text{ and } t \qquad \text{(B-3)}$$

thus $\lambda_1 F$ is a function of t only and using the boundary condition of λ_1 (A-25) we have

$$\lambda_1 F = F[X_1(t)] \qquad \text{(B-4)}$$

and

$$\frac{d\lambda_1 F}{dt} = F'[X_1(t)]\ \ \frac{dX_1(t)}{dt} \qquad \text{(B-5)}$$

substituting (B-4) and (B-5) into (B-1) we obtain

$$pK_o F'[X_1(t)]\ \frac{dX_1(t)}{dt} \int_0^1 \psi\ dz = (1-p)\ F(X_1(t)] \int_0^1 \frac{\partial\ \psi K_o}{\partial\ t}\ dz \qquad \text{(B-6)}$$

at the unconstrained optimum

From (5-83) we have

$$\frac{dX_1(t)}{dt} = F[X_1(t)] \int_0^1 \frac{\partial\ \psi K_o}{\partial\ t}\ dz \qquad \text{(B-7)}$$

From (B-7) and (B-6) we have

$$\boxed{\frac{dX_1(t)}{dt}\left[pK_oF'(X_1(t)]\int_0^1 \psi dz \quad + (p-1)\right] =0} \qquad \text{(B-8)}$$

At the unconstrained optimum

Now if $p < 1$ and from 3.6 $F' \leq 0$ then the term in the square brackets is negative, and thus we require

$$\boxed{\frac{dX_1(t)}{dt} = 0} \qquad \text{at the unconstrained optimum} \quad ■ \qquad \text{(B-9)}$$

This is the constant exit conversion policy and represents a necessary condition for the optimum of the unconstrained region.

See also section 5.4.2.

APPENDIX C

An Alternative Proof of the Constant Conversion Policy for Zero Order Reactions

Proposition C

Given the two conditions below, a necessary condition for the system to be optimal, is that the exit conversion be constant over the unconstrained region.

(i) $f(X) = cX$ c arbitrary positive constant

(ii) $X_0(t) = 0$ for all $0 \leq t \leq 1$

Proof

From (5-77) with F=1 (without loss of generality) for an unconstrained optimum, we require

$$\frac{1}{p}\ \frac{dX_1(t)}{dt} = \int_0^1 \frac{\partial\,(\lambda_1 \psi K_0)}{\partial\, t}\, dz \tag{C-1}$$

$$\frac{1}{p}\ \frac{dX_1}{dt} = \int_0^1 \psi K_0\, \frac{\partial\, \lambda_1}{\partial\, t}\ dz + \int_0^1 \lambda_1 \frac{\partial\, \psi K_0}{\partial\, t}\, dz \tag{C-2}$$

From condition (i) and (5-43) remembering that F=1

$$\frac{\partial\, \lambda_1}{\partial\, z} = \lambda_2 k_0 gc \tag{C-3}$$

From (4-8)

$$\frac{\partial\, \lambda_2}{\partial\, t} = \lambda_2 k_0 fg' - \lambda_1 K_0 \tag{C-4}$$

Integrating (C-3) gives

$$\lambda_1(z,t) = 1 + c\int_1^z \lambda_2 k_0 g dz' \tag{C-5}$$

Differentiating (C-5) with respect to t, we have, using (C-4) and second state equations (3-55)

$$\frac{\partial \lambda_1}{\partial t} = c \int_1^z [\lambda_2 g \frac{dk_o}{dt} - K_o k_o \lambda_1 g] dz' \qquad \text{(C-6)}$$

From the first state equation (3-54), for zero order reaction, we have (using the properties of variables in 3.6)

$$\frac{\partial \psi K_o}{\partial t} = \frac{\partial}{\partial z} (\frac{\partial X}{\partial t}) \qquad \text{(C-7)}$$

and also the particular integral

$$X = \int \psi K_o dz \qquad \text{(C-8)}$$

Substitute (C-6) and (C-7) into (C-2)

$$\frac{1}{p} \frac{dX_1}{dt} = c \int_0^1 \psi K_o \; [\int_1^z (\lambda_2 g \frac{dk_o}{dt} - K_o k_o \lambda_1 g) dz'] dz + \int_0^1 \lambda_1 \frac{\partial}{\partial z} (\frac{\partial X}{\partial t}) dz \qquad \text{(C-9)}$$

Define
$$V = \int_1^z (\lambda_2 g \frac{dk_o}{dt} - K_o k_o \lambda_1 g) dz' \qquad \text{(C-10)}$$

Substituting (C-10) and (C-5) into (C-9)

$$\frac{1}{p} \frac{dX_1}{dt} = c \int_0^1 (\psi K_o) V \, dz + \int_0^1 [\frac{\partial}{\partial z} (\frac{\partial X}{\partial t}) \; (1 + c \int_1^z \lambda_2 k_o g dz')] dz \qquad \text{(C-11)}$$

Integrating the first integral on the rhs by parts, we have, using (C-8)

$$\frac{1}{p} \frac{dX_1}{dt} = cXV \Big|_{z=o}^{z=1} - c \int_0^1 XV' \, dz + \frac{dX_1}{dt} - \frac{dX_o}{dt} + c \int_0^1 \frac{\partial}{\partial z} (\frac{\partial X}{\partial t}) S \, dz \qquad \text{(C-12)}$$

where
$$S = \int_1^z \lambda_2 k_o g dz' \qquad \text{(C-13)}$$

Now using condition (ii), we may eliminate the second derivative on the rhs of (C-12), also the conditions on V are such that

$$V(z=1,t) = 0 \qquad \text{(C-14)}$$

From condition (ii) $X(z=0,t) = 0$, thus the first term on the rhs of (6-12) is eliminated, leaving

$$\frac{1}{p}\frac{dX_1(t)}{dt} = -c\int_0^1 XV'\,dz + \frac{dX_1}{dt} + c\int_0^1 \frac{\partial}{\partial z}\left(\frac{\partial X}{\partial t}\right) S\,dz \qquad \text{(C-15)}$$

Integrating the last term on the rhs by parts and using the fact that

$$S(z=1,t) = 0 \qquad \text{(C-15)}$$

and condition (ii) we obtain

$$\frac{1}{P}\frac{dX_1}{dt} = -c\int_0^1 XV'\,dz \qquad - c\int_0^1 \frac{\partial X}{\partial t} S'\,dz + \frac{dX_1}{dt}$$

$$\frac{1}{P}\frac{dX_1}{dt} = -c\left[\int_0^1 X\left(\lambda_2 g\frac{dk_o}{dt} - K_o k_o\,\lambda_1 g\right)dz + \int_0^1 \frac{\partial X}{\partial t}\,\lambda_2\,k_o g\,dz\right] + \frac{dX_1}{dt}$$

$$= \frac{dX_1}{dt} + c\int_0^1 XK_o k_o g\lambda_1\,dz - c\left[\int_0^1 \left(X\lambda_2 g\frac{dk_o}{dt} + k_o\lambda_2 g\frac{\partial X}{\partial t}\right)dz\right] \qquad \text{(C-16)}$$

From (5-76) at the optimum, we require

$$\frac{dX_1}{dt} = \int_0^1 \left[k_o f\frac{\partial\,\lambda_2 g}{dt} + \lambda_2 k_o g f'\frac{\partial X}{\partial t} + \lambda_2 g f\,\frac{dk_o}{dt}\right]dz \qquad \text{(C-17)}$$

substituting the correct form for $f = cX$ from condition (i) and substituting for the last integral in (C-16): $\int_0^1 k_o\lambda_2 g\frac{\partial X}{\partial t}\,dz$ from (C-17) we have:

$$\frac{1}{P}\frac{dX_1}{dt} = \frac{dX_1}{dt} + c\int_0^1 XK_o k_o g\lambda_1\,dz - \left[\frac{dX_1}{dt} - c\int_0^1 k_o X\frac{\partial\,\lambda_2 g}{\partial t}\,dz\right] \qquad \text{(C-18)}$$

substituting for $\frac{\partial\,\lambda_2 g}{\partial t}$ in (C-18) using (C-4) and the second state equation (3-55).

Also,

$$\frac{\partial\, \lambda_2 g}{\partial\, t} = - \lambda_2 g' g k_o X + g(\lambda_2 k_o X g' - \lambda_1 K_o)$$

$$= - g\lambda_1 K_o \qquad \text{[cf 5-26 in 5.6]} \qquad \text{(C-19)}$$

substitute (C-19) into (C-18) giving

$$\boxed{\frac{1}{P} \quad \frac{dX_1}{dt} = 0} \qquad \text{(C-20)}$$

For non zero p this implies that the necessary condition for unconstrained optimum is

$$\boxed{\frac{dX_1(t)}{dt} = 0} \qquad 0 \leq t \leq \bar{t} \qquad \text{(C-21)}$$

See also 5.5.1

APPENDIX D

COMPUTER PROGRAMS

The computer program is divided into 10 sections. The first section is the main program; it sets all the paramaters and constants in the system and controls the iterations according to one of the three numerical algorithms outlined in Chapter 6. The remaining 9 sections are all subroutines which handle the integration and output of the system variables. The program division is summarized below.

1. Main Program

Sets paramaters, constants, boundary conditions, controls iterations according to either

(i) Gradient Algorithm (6.3.1)

(ii) Fixed point Algorithm (6.3.2)

(iii) Predictor-Corrector Algorithm (6.3.3)

2. Subroutine STATE

Controls the grid point structure in the integration of the state variables and uses subroutine EUL to perform the integrations.

3. Subroutine ADJNT

Controls the grid point structure in the backward integration of the adjoint variables and use subroutines EUL to perform the integrations.

4. Subroutines F1, F2, F3, F4

These equations supply the right hand sides of the system equations in the following order

SUB F1 = Right hand side of (6-6)
F2 = Right hand side of (6-7)
F3 = Right hand side of (6-12)
F4 = Right hand side of (6-13) (and calculates the Hamiltonian)

5. Subroutine EUL

This is a modified Euler integration subroutine. It performs the iterative, pointwise integration according to the scheme outlined in 6.2a.1. Used by subroutines STATE and ADJNT.

6. Subroutine ONC

Same as EUL, but used along boundaries where no trial and error, simultaneous iterations is required.

7. Subroutine OUTPUT

This is simply a data transfer routine and outputs all the variables of interest.

A correspondence is drawn between program variables and the symbols used here.

See Table 6-13.

PROGRAM VARIABLE	PRESENT VARIABLE
X	$X(z,t)$ (3-54)
SI	$\psi(z,t)$ (3-58)
B1	$\lambda_1(z,t)$ (4-4)
B2	$\lambda_2(z,t)$ (4-8)
GAMM	$\gamma(t)$ (6-17)
ALPHA	α (6-23)
NT	N_t (6-8)
NZ	N_z (6-9)
LC1	line counter for OUTPUT
LC2	line counter for OUTPUT
T0	$T_o(t)$ (3-43)
P	p (3-27)
XJ	J_1 (3-42)
TMAX	$T_o{}^*$ (3-47)
TMIN	T_{o*} (3-47)
TI	$T_o^{(o)}$ initial guess (6.3.1)
XM	m (3-37)
XN	n (3-36)
XK0	$k_o(t)$ (3-47)
A	c (6-1)
B	d (6-1)
XKK0	$K_o(t)$ (3-51a)
SIMIN	ψ_{min} (10-6)
XMAX	X_{max} (6 14)
TF	τ (3-14)

PROGRAM VARIABLE	PRESENT VARIABLE	
TZ	t_θ	(3-18)
XKP	$k_+^{\cdot}$	(3-24a)
PERROR	Test for increase in Objective P	
ECR	E_c	(3-7)
AAA	a	(3-26)
SII1	$\psi_i(z)$	(3-22)
B1I1	$\lambda_1(1,t)$	(4-4)
B2I1	$\lambda_2(0,z)$	(4-8)
XI1	$X_o(t)$	(3-21)
PX	P	(3-58)
F	$f(X)$	(3-53)
FF	$F(X)$	(3-52)

Table 6-13 Program variables correspondence

```
C            THE  GRADIENT  METHOD  IN  FUNCTION SPACE
C            =====================================

      PROGRAM TST (INPUT,OUTPUT,TAPE5=INPUT,TAPE6=OUTPUT)
      COMMON T0(26 ),X(17,26 ),SI(17,26 ),B1(17,26 ),B2(17,26 ),
     1 DHAM(17,26)
      DIMENSION Y(26),Z(26),XK0(26)
       DIMENSION XK01(26 ),PX(50),EA(26)
       COMMON /A1/P,TF,XN,XM,TZ,XJ,     XKP,XKKP,ECR,A,B ,TAV,SIMIN,
     1XMAX
      COMMON /A2/ JL2,IX2,JI1,IX1,LS2,LS1,J1,I1
       COMMON/A3/N1
      COMMON /A4/ NT,NZ,K11,LA11,LS3,LX3,LX4,LS4,L1,L2
       DIMENSION Z1(26),Y1(26),Y2(26),Z2(26),Y3(26),Z3(26)
       COMMON /A5/STOR1(17,26),LFIX        ,STOR2(17,26)
        INTEGER SWTCH

C    MAIN PROGRAM
C     SWTCH3=1  CAUSES  HAMILTONIAN EVALUATION AT EACH STEP
C   INTPOL=1   CAUSES BEST ESTIMATE OF GAMM USING CURVE FIT
C   INTPOL=0       GAMM= 70PERCENT OF LATEST GAMM/2.
C     NACEL  IS NUMBER OF ITERATIONS TO WAIT BEFORE ACCELERATION

C     COUNTERS AND INITIAL CONDITIONS
      ALPHA=0.7
      GAMM=0.02
      NT=25
      NZ=16
      LC2=1
      LC1=3
       XJ=.01
      P=0.4
       TMAX=900.
       TMIN=700.
       TI=800.
       XM=2.
      XN=4.0
        B=0.6
      A=1.0
      SIMIN=1.0E-06
      XMAX=0.99999
      TD=25.
      TF=8.64E+4 *TD
C     TF=(2.16E+06/25.)*25.
      TZ=1.
       XKP=.8096*TD
```

```
C       XKP=20.24/(2.16E+06)*TF
        PERROR=.00001
         ECR=15000.
        XKMAX=XKP*EXP(-ECR/TMAX)
        XKMIN=XKP*EXP(-ECR/TMIN)
         DMY=EXP(ECR*P/(TMAX +0.9/XJ))
        IF(XN.EQ.1.)XKKP=-DMY*ALOG(0.1)/TZ
         IF(XN.NE.1.)XKKP=DMY*(1.-(0.1)**(1.-XN))/(TZ*(1.-XN))
         AAA=XKKP/(XKP*TF)**P
         WRITE(6,2)XKKP
2       FORMAT(E16.5)
         TAV=(TMAX+TMIN)*0.5
        HZ=1./(NZ-1)
        HT=1./(NT-1)
         SII1=1.
        B1I1=1.
        B2I1=0.
        XI1=0.
         DO 15 I=1,NT
        X(1,I)=XI1
        T0(I)=TI
15      B1(NZ,I)=B1I1
         DO 16 I=1,NZ
         SI(I,1)=SII1
16      B2(I,NT)=B2I1
        WRITE(6,100)
100     FORMAT(1H1)
        SWTCH=0
        JJ=0
         DO 510 I=1,NT
510      XK01(I)=XKP*EXP(-ECR/T0(I))
        DO  2000 LITER=1,4
         JJ=JJ+1
        CALL STATE
        IF(JJ.EQ.1)GO TO 801
        GO TO 802
801     CALL ADJNT
        DO 141 JX1=1,NT
        DO 140 JX2=1,NZ
140     Y(JX2)=DHAM(JX2,JX1)
         CALL QSF(HZ,Y,Z,NZ)
        EA(JX1)=Z(NZ)
        WRITE(6,1004)Z(NZ)
1004     FORMAT(10X,E16.6)
141      CONTINUE
802      CONTINUE
        DO 42 I=1,NT
```

```
 42   Y(I)=X(NZ,I)-X(1,I)
      CALL QSF(HT,Y,Z,NT)
       PX(JJ)=Z(NT)
       WRITE(6,304)GAMM
 304   FORMAT( *   GAMM=*,E16.4)
       WRITE(6,107)PX(JJ)
 107   FORMAT(  *    PX=   *,F15.5,/)
      IF(JJ.EQ.1)WRITE(6,120)
 120   FORMAT(  *  ITER=0   *)
 121   FORMAT(  *  ITER=1   *)
      IF(JJ.EQ.1)CALL OUTPUT(LC1,LC2)
      IF(JJ.EQ.1)GO TO 806
      IF(PX(JJ).GT.PX(JJ-1))GO TO 803
      GO TO 804
 803   IF(LITER.EQ.4)GO TO 805
      GAMM=GAMM*2.
      GO TO 806
 804  SWTCH=1
      GAMM=GAMM/3.
 806   CONTINUE
      DO 700 I=1,NT
      GSTP=GAMM*FA(  I)/TF
      XK0(I)=XK01(I)  + GSTP
       IF(XK0(I).GE.XKMAX)XK0(I)=XKMAX
       IF(XK0(I).LE.XKMIN)XK0(I)=XKMIN
       T0(I)=-ECR/ALOG(XK0(I)/XKP)
 700  CONTINUE
      IF(SWTCH.EQ.1)GO TO 805
 2000  CONTINUE
 805   CONTINUE
      COMP1=PX(JJ)
       IF(SWTCH.EQ.1)COMP1=PX(JJ-1)
      WRITE(6,304)GAMM
       WRITE(6,107)COMP1
      WRITE(6,121)
      CALL OUTPUT(LC1,LC2)
      DO  2001 MITER=2,8
       CALL ADJNT
 57   DO  41 II1=1,NT
      DO 40 II2=1,N7
      Y(II2)=DHAM(II2,IT1)
       Y2(II2)=STOR2(II2,II1)
      Y1(II2)=STOR1(II2,II1)
 40    CONTINUE
      CALL QSF(HZ,Y,Z,N7)
        CALL QSF(HZ,Y2,72,N7)
      CALL QSF(HZ,Y1,Z1,NZ)
```

```
        IF(II1.EQ.NT)GO TO 81
       GO TO 82
81     XK0(II1)=XKMAX
        XK01(II1)=XKMAX
       GO TO 83
82      CONTINUE
       XK0(II1)= ALPHA*(((AAA*Z2(NZ)*P)/Z1(NZ))**(1./(1.-P)) /TF-XK0(II1
      1)) +XK0(II1)
         XK01(II1)=XK0(II1)
83      CONTINUE
       IF(XK0(II1).LE.XKMIN)XK0(II1)=XKMIN
       IF(XK0(II1).GE.XKMAX)XK0(II1)=XKMAX
       T0(II1)=-ECR/ALOG(XK0(II1)/XKP)
1000    FORMAT(E16.5)
       WRITE(6,1000)Z(NZ)
41     CONTINUE
       CALL STATE
       DO 72 I=1,NT
72     Y3(I)=X(NZ,I)-X(1,I)
       CALL QSF(HT,Y3,Z3,NT)
        PX(MITER)=Z3(NT)
        COMP2=PX(MITER)
       XXC=(COMP1-COMP2)/COMP2
       IF((ABS(XXC)).LT.PERROR)GO TO 505
        COMP1=COMP2
       WRITE(6,103) MITER,PX(MITER)
       CALL ADJNT
        CALL OUTPUT  (LC1,LC2)
       DO 341 JX1=1,NT
       DO 340 JX2=1,NZ
340    Y(JX2)=DHAM(JX2,JX1)
        CALL QSF(HZ,Y,Z,NZ)
       EA(JX1)=Z(NZ)
       WRITE(6,1003)Z(NZ)
1003    FORMAT(5X,E16.6)
341     CONTINUE
       DO 701 I=1,NT
       GSTP=GAMM*EA(  I)/TF
       XK0(I)=XK01(I) + GSTP
        IF(XK0(I).GE.XKMAX)XK0(I)=XKMAX
        IF(XK0(I).LE.XKMIN)XK0(I)=XKMIN
        T0(I)=-ECR/ALOG(XK0(I)/XKP)
701    CONTINUE
        CALL STATE
       DO 85 I=1,NT
85     Y3(I)=X(NZ,I)-X(1,I)
       CALL QSF(HT,Y3,Z3,NT)
```

```
           PX(MITER)=Z3(NT)
           WRITE(6,103) MITER,PX(MITER)
 103         FORMAT(*   ITER=  *.I3,5X,*  P=*,E16.6)
 2001        CONTINUE
 505        CONTINUE
           WRITE(6,100)
 507        WRITE(6,108)MITER .COMP2
 108       FORMAT(/,20X,*  ITER =*,I3,5X.* OBJECTIVE FUNCTION=*,E16.6)
            CALL OUTPUT (LC1.LC2)
           STOP
           END
```

```
C          THE   FIXED POINT  METHOD IN FUNCTION SPACE
C          USING ORBACH/CROWE  CONVERGENCE PROMOTION
C          =========================================

      PROGRAM TST (INPUT,OUTPUT,TAPE5=INPUT,TAPE6=OUTPUT)
      COMMON T0(26 ),X(17,26 ),SI(17,26 ),B1(17,26 ),B2(17,26 ),
     1 DHAM(17,26)
      DIMENSION PX1(9), Y(26 ),Z(26 ),AAX(30),XB(3),PQ(9),      XK0(26 )
       DIMENSION XK01(26 ),PX(50)
       COMMON /A1/P,TF,XN,XM,TZ,XJ,    XKP,XKKP,ECR,A,B ,TAV,SIMIN,
     1XMAX
      COMMON /A2/ JL2,IX2,JL1,IX1,LS2,LS1,J1,I1
       COMMON/A3/N1
      COMMON /A4/ NT,NZ,K11,LA11,LS3,LX3,LX4,LS4,L1,L2
       DIMENSION ACEL(3,26)    ,W1(26),W2(26)
       DIMENSION Z1(26),Y1(26)
       COMMON /A5/STOR1(17,26),LFIX
      INTEGER SWTCH1,SWTCH2 ,SWTCH3

C    MAIN PROGRAM
C     SWTCH1   USED TO BOUND MAX CORRECTION IN CONTROL
C     SWTCH2    USED TO  INITIATE 2ND GUESS USING BACKWARD STEP
C     SWTCH3=1  CAUSES  HAMILTONIAN EVALUATION AT EACH STEP
C   INTPOL=1   CAUSES BEST ESTIMATE OF GAMM USING CURVE FIT
C   INTPOL=0      GAMM= 70PERCENT OF LATEST GAMM/2.
C     NACEL  IS NUMBER OF ITERATIONS TO WAIT BEFORE ACCELERATION

C     COUNTERS AND INITIAL CONDITIONS
      SWTCH3=0
       INTPOL=0
       NACEL=3
       ALPHA=0.6
      GAM=.05
      NT=25
      NZ=16
      LC2=1
      LC1=3
      P=0.4
       XJ=.01
       TMAX=900.
       TMIN=700.
       TI=750.
        XN=1.0
        XM=2.0
       B=0.6
      A=1.0
```

```
        SIMIN=1.0E-06
       XMAX=0.99999
       TD=25.
       TF=8.64E+4 *TD
C      TF=(2.16E+06/25.)*25.
       TZ=1.
        XKP=.8096*TD
C      XKP=20.24/(2.16E+06)*TF
        PERROR=.00001
        ECR=15000.
       XKMAX=XKP*EXP(-ECR/TMAX)
       XKMIN=XKP*EXP(-ECR/TMIN)
       XKS=(XKMAX-XKMIN)
        DMY=EXP(ECR*P/(TMAX  +0.9/XJ))
       IF(XN.EQ.1.)XKKP=-DMY*ALOG(0.1)/TZ
        IF(XN.NE.1.)XKKP=DMY*(1.-(0.1)**(1.-XN))/(TZ*(1.-XN))
        AAA=XKKP/(XKP*TF)**P
        WRITE(6,2)XKKP
2      FORMAT(E16.5)
        TAV=(TMAX+TMIN)*0.5
       NZ1=NZ-1
       NT1=NT-1
        NT11=NT-2
       NZ11=NZ-2
       HZ=1./(NZ-1)
       HT=1./(NT-1)
        SII1=1.
       B1I1=1.
       B2I1=0.
       XI1=0.
999     CONTINUE
        DO 15 I=1,NT
       X(1,I)=XI1
       T0(I)=TI
15     B1(NZ,I)=B1I1
        DO 16 I=1,NZ
        SI(I,1)=SII1
16     B2(I,NT)=B2I1
       WRITE(6,100)
100    FORMAT(1H1)
       KOUNT=1
       JJ=0
        IJK=1
        IJK1=1
          LXS=0
       SWTCH1=0
        LFIX=0
```

```
      KOUNTY=-1
      IAC=0
      ICOUNT=-1
C   INTEGRATION OF STATE VARIABLES
500   CONTINUE
      SWTCH2=0
       CALL STATE
      IF(IJK.EQ.0)GO   TO 501
       DO 510 I=1,NT
510    XK01(I)=XKP*EXP(-ECR/T0(I))
C  INTEGRATION OF ADJOINT VARIABLES
       CALL ADJNT
501   CONTINUE
      JJ=JJ+1
      DO 42 I=1,NT
42    Y(I)=X(NZ,I)-X(1,I)
      CALL  QSF(HT,Y,Z,NT)
       PX(JJ)=Z(NT)
       WRITE(6,304)GAMM
304    FORMAT( *   GAMM=*,E16.4)
       WRITE(6,107)PX(JJ)
      IF(ICOUNT.EQ.0)WRITE  (6,10)
10    FORMAT(/,*   ACCELERATED*,/)
107    FORMAT(/,*   PX=   *,E15.5)
      IF(KOUNT.EQ.1.AND.JJ.EQ.1)GO  TO 48
       GO TO 49
48     COMP1=PX(JJ)
      WRITE(6,103)KOUNT,COMP1
       CALL  OUTPUT(LC1,LC2)
       KOUNT=2
       GO TO 51
49    IF(KOUNT.GT.1.AND.JJ.EQ.1)GO  TO 50
      GO TO 51
50    COMP2=PX(JJ)
      KOUNT=KOUNT+1
      KKOUNT=KOUNT-1
      XXC=(COMP1-COMP2)/COMP2
      IF((ABS(XXC)).LT.PERROR)GO TO 505
      IF(KKOUNT.LE.5.AND.LFIX.EQ.1)GO TO 220
       GO TO 221
220    LFIX=0
      SWTCH3=0
       KOUNTY=-1
       GO TO 421
221    CONTINUE
      IF(KOUNTY.EQ.1)GO TO 421
       IF((ABS(XXC)).LT.0.1) GO TO 420
```

```
      GO TO 421
420    LFIX=1
       KOUNTY=1
      CALL ADJNT
421   CONTINUE
       COMP1=COMP2
      IF(LFIX.EQ.1)SWTCH3=1
      WRITE(6,103)KKOUNT,COMP2
       CALL OUTPUT(LC1,LC2)
103    FORMAT(*   ITER=  *,I3,5X,*  P =  *,E16.6)
51     CONTINUE
       IF(LFIX.EQ.1)GO TO 4521
      IF(JJ.EQ.1)GO TO 47
      IF(IJK1.EQ.0)GO TO 512
       IF(PX(JJ).EQ.PX(JJ-1).AND.XK0(1).EQ.XKMAX.AND.XK0(NT).EQ.XKMAX)
     1 GO TO 4521
       IF(PX(JJ).EQ.PX(JJ-1).AND.SWTCH1.EQ.1)  GO TO 4521
       IF(PX(JJ).GT.PX(JJ-1))GO TO 44
      GO TO 45
44    GAMM=GAMM*2.
      GO TO 56
45     IF(JJ.EQ.2)GO TO 451
      GO TO 452
451    GAM=GAM/15.
       IF(GAM.LT.1.0E-10)GO TO 507
       JJ=1
       GO TO 47
600   GAMM=-  .005
       GAM=-GAMM/5.
      SWTCH2=1
      JJ=0
      GO TO 56
452    IF(INTPOL.EQ.0)GO TO 4521
      GO TO 4522
4521   GAMM=0.6*GAMM/2.
      GAM=GAMM*0.75
      IJK1=0
      IXI=8
      GO TO 56
4522   CONTINUE
       PX1(9)=PX(JJ)
       PX1(5)=PX(JJ-1)
       PX1(1)=PX(JJ-2)
      PQ(9)=GAMM
       PQ9=PQ(9)
       ZS=GAMM/2.
       FLESQ=GAMM-ZS
```

```
       YS=FLESQ*0.25
       PQ(1)=ZS*0.5
       PQ(2)=-YS*6.+ZS
       PQ(3)=-YS*4.+ZS
       PQ(4)=-YS*2.+ZS
       PQ(5)=ZS
       PQ(6)=ZS    +YS
       PQ(7)=ZS   +YS*2.
       PQ(8)=ZS   +YS*3.
      IJK1=0
       IJK=0
       IXI=1
       GO TO 513
512    PX1(IXI   )=PX(JJ)
       IF(IXI.EQ.4)IXI=5
       IF(IXI.EQ.8) GO TO 514
513    GAMM=PQ(IXI+1)
       GO TO 56
47    GAMM=GAM
56     CONTINUE
      IF(SWTCH3.EQ.1)GO TO 57
      IF(JJ.EQ.1)GO TO 57
      DO 700 I=1,NT
      GSTP=GAMM*B1(1,I)/TF
      IF((ABS(GSTP)).GT.XKS)GO TO 5
      GO TO 6
5     GSTP=XKS
      IF(GSTP.LT.0)GSTP=-XKS
       SWTCH1=1
6     CONTINUE
      XK0(I)=XK01(I) + GSTP
       IF(XK0(I).GE.XKMAX) XK0(I)=XKMAX
       IF(XK0(I).LE.XKMIN) XK0(I)=XKMIN
       T0(I)=-ECR/ALOG(XK0(I)/XKP)
700   CONTINUE
       GO TO 58
57    DO  41 II1=1,NT
      DO 40 II2=1,NZ
      Y(II2)=DHAM(II2,II1)
      IF(LFIX.EQ.0)GO TO 40
      Y1(II2)=STOR1(II2,II1)
40     CONTINUE
      CALL  QSF(HZ,Y,Z,NZ)
      IF(LFIX.EQ.0)GO TO 80
      CALL  QSF(HZ,Y1,Z1,NZ)
       IF(II1.EQ.NT)GO TO 81
      GO TO 82
```

```
81    XK0(II1)=XKMAX
      GO TO 83
82     CONTINUE
      XK0(II1)= ALPHA*(((AAA*Z(NZ)*P)/Z1(NZ))**(1./(1.-P))  /TF   -XK0(II1
     1)) +XK0(II1)
       ALPHA=ALPHA-.05
      IF(ALPHA.LT.0.7)ALPHA=0.7
83     CONTINUE
      IF(XK0(II1).LE.XKMIN)XK0(II1)=XKMIN
      IF(XK0(II1).GE.XKMAX)XK0(II1)=XKMAX
      ACEL(IAC+1,II1)=XK0(II1)
      IF(IAC.EQ.2)GO TO 91
      GO TO 90
91     CONTINUE
      W1(II1)=ACEL(3,II1)-ACEL(2,II1)
      W2(II1)=ACEL(2,II1)-ACEL(1,II1)
90     CONTINUE
      T0(II1)=-ECR/ALOG(XK0(II1)/XKP)
       GO TO 41
80     CONTINUE
      GSTP=GAMM*Z(NZ)/TF
      IF((ABS(GSTP)).GT.XKS)GO TO 7
      GO TO 8
7     GSTP=XKS
      IF(GSTP.LT.0)GSTP=-XKS
      SWTCH1=1
   8   CONTINUE
      XK0(II1)=XK01(II1)+GSTP
      IF(XK0(II1).GE.XKMAX)XK0(II1)=XKMAX
      IF(XK0(II1).LE.XKMIN)XK0(II1)=XKMIN
      T0(II1)=-ECR/ALOG(XK0(II1)/XKP)
      B1(1,II1)=Z(NZ)
      WRITE(6,1000)Z(NZ)
1000   FORMAT(E16.5)
41    CONTINUE
       IF(LFIX.EQ.0)GO TO 88
      IF(IAC.EQ.2)GO TO 85
      GO TO 86
85     IAC=2
      ICOUNT=ICOUNT +1
       IF(ICOUNT.EQ.NACEL)GO TO 92
      GO TO 98
92    ICOUNT=0
94    CONTINUE
      SUM1=0.
      SUM2=0.
      DO 96 I=1,NT
```

```
      SUM2=SUM2+W2(I)**2
 96   SUM1=SUM1+W1(I)**2
       WM=SQRT(SUM1/SUM2)
      SGN1=W1(1)*W2(1)
      SGN2=W1(10)*W2(10)
      IF(SGN1.LT.0.OR.SGN2.LT.0) WM=-WM
      DO 97 I=1,NT
      XK0(I)=ACEL(2,I)  +0.9   *(XK0(I)-ACEL(2,I))/(1.0-WM)
      IF(XK0(I).GT.XKMAX)XK0(I)=XKMAX
      IF(XK0(I).LT.XKMIN)XK0(I)=XKMIN
      T0(I)=-ECR/ALOG(XK0(I)/XKP)
 97   CONTINUE
 98   CONTINUE
      DO 87 I=1,NT
      ACEL(1,I)=ACEL(2,I)
 87   ACEL(2,I)=XK0(I)
      GO TO 88
 86    IAC=IAC+1
 88   CONTINUE
 58   IJK=0
      IF(SWTCH2.EQ.1)IJK=1
       IF(IJK1.EQ.1)GO TO 500
      IXI=IXI+1
      IF(IXI.EQ.9)GO TO 515
       GO TO 500
 514   IF(GAMM.LT.1.0.OR.GAMM.GT.100.)GO TO 516
      GO TO 518
 516   DO 517 I=1,9
 517  PQ(I)=PQ(I)/PQ(9)
      LXS=1
 518   CALL LESQ(AAX,XB,PQ,PX1,2,9)
       GAMM=-XB(2)/(2.*XB(3))  *0.70
       GAMPQ=GAMM*PQ9
      IF(LXS.EQ.1)GO TO 519
      GO TO 520
 519   GAMM=GAMPQ
      LXS=0
 520   CONTINUE
       GO TO 56
 515   JJ=0
        IJK=1
       IJK1=1
      SWTCH1=0
       GO TO 500
 505   CONTINUE
      LFIX=0
      CALL ADJNT
```

```
      WRITE(6,100)
507    WRITE(6,108)KKOUNT,COMP2
108   FORMAT(/,20X,*  ITER =*,I3,5X,* OBJECTIVE FUNCTION=*,E16.6)
       CALL OUTPUT (LC1,LC2)
      STOP
      END
```

```
C          THE  PREDICTOR-CORRECTOR METHOD  IN  FUNCTION SPACE
C          ===================================================

      PROGRAM TST (INPUT,OUTPUT,TAPE5=INPUT,TAPE6=OUTPUT)
      COMMON T0(51 ),X(31,51 ),SI(31,51 ),B1(31,51 ),B2(31,51 ),
     1 DHAM(31,51)
      DIMENSION PX1(9), Y(51 ),Z(51 ),AAX(30),XB(3),PQ(9),       XK0(51 )
       DIMENSION XK01(51 ),PX(50)
       COMMON /A1/P,TF,XN,XM,TZ,XJ,     XKP,XKKP,ECR,A,B ,TAV,SIMIN,
     1XMAX
      COMMON /A2/ JL2,IX2,JL1,IX1,LS2,LS1,J1,I1
       COMMON/A3/N1
      COMMON /A4/ NT,NZ,K11,LA11,LS3,LX3,LX4,LS4,L1,L2
      INTEGER SWTCH1,SWTCH2 ,SWTCH3

C    MAIN PROGRAM
C     SWTCH1   USED TO BOUND MAX CORRECTION IN CONTROL
C     SWTCH2    USED TO  INITIATE 2ND GUESS USING BACKWARD STEP
C     SWTCH3=1  CAUSES  HAMILTONIAN EVALUATION AT EACH STEP
C  INTPOL=1   CAUSES BEST ESTIMATE OF GAMM USING CURVE FIT
C  INTPOL=0      GAMM= 70PERCENT OF LATEST GAMM/2.

C     COUNTERS AND INITIAL CONDITIONS
       GAM=.03
      SWTCH3=0
        NT=25
       NZ=15
       LC2=1
        LC1=2
       XJ=.01
      TMAX=900.
      TI=800.
      TMIN=700.
       P=0.4
       XM=2.
       XN=1.
       B=0.0
      A=1.0
      SIMIN=.3
      XMAX=0.99999
      TF=(2.16E+06/25.)*25.
      TZ=1.
      ECR=15000.
      XKP=20.24/(2.16E+06)*TF
       PERROR=.00001
      XKMAX=XKP*EXP(-ECR/TMAX)
```

```
      XKMIN=XKP*EXP(-ECR/TMIN)
      XKS=(XKMAX-XKMIN)   /2.
       DMY=EXP(ECR*P/(TMAX +0.9/XJ))
      IF(XN.EQ.1.)XKKP=-DMY*ALOG(0.1)/TZ
       IF(XN.NE.1.)XKKP=DMY*(1.-(0.1)**(1.-XN))/(TZ*(1.-XN))
       WRITE(6,2)XKKP
2     FORMAT(E16.5)
       TAV=(TMAX+TMIN)*0.5
      NZ1=NZ-1
      NT1=NT-1
       NT11=NT-2
      NZ11=NZ-2
      HZ=1./(NZ-1)
      HT=1./(NT-1)
       SII1=1.
      B1I1=1.
      B2I1=0.
      XI1=0.
       DO 15 I=1,NT
      X(1,I)=XI1
      T0(I)=TI
15    B1(NZ,I)=B1I1
       DO 16 I=1,NZ
       SI(I,1)=SII1
16    B2(I,NT)=B2I1
      WRITE(6,100)
100   FORMAT(1H1)
      KOUNT=1
      JJ=0
       IJK=1
       IJK1=1
         LXS=0
      SWTCH1=0
      INTPOL= 0
C   INTEGRATION OF STATE VARIABLES
500   CONTINUE
      SWTCH2=0
       CALL STATE
      IF(IJK.EQ.0)GO   TO 501
       DO 510 I=1,NT
510    XK01(I)=XKP*EXP(-ECR/T0(I))
C  INTEGRATION OF ADJOINT VARIABLES
       CALL ADJNT
501   CONTINUE
      IF(SWTCH3.EQ.1)CALL ADJNT
      JJ=JJ+1
      DO 42 I=1,NT
```

```
 42     Y(I)=X(NZ,I)-X(1,I)
        CALL QSF(HT,Y,Z,NT)
         PX(JJ)=Z(NT)
         WRITE(6,304)GAMM
 304     FORMAT( *   GAMM=*,E16.4)
         WRITE(6,107)PX(JJ)
 107     FORMAT(/,*   PX=   *,E15.5)
        IF(KOUNT.EQ.1.AND.JJ.EQ.1)GO TO 48
         GO TO 49
 48      COMP1=PX(JJ)
        WRITE(6,103)KOUNT,COMP1
         CALL OUTPUT(LC1,LC2)
         KOUNT=2
         GO TO 51
 49     IF(KOUNT.GT.1.AND.JJ.EQ.1)GO TO 50
        GO TO 51
 50     COMP2=PX(JJ)
        KOUNT=KOUNT+1
        KKOUNT=KOUNT-1
        XXC=(COMP1-COMP2)/COMP2
        IF((ABS(XXC)).LT.PERROR)GO TO 505
         COMP1=COMP2
        WRITE(6,103)KKOUNT,COMP2
         CALL OUTPUT(LC1,LC2)
 51      CONTINUE
 103     FORMAT(*    ITER=  *,I3,5X,*  P =   *,E16.6)
        IF(JJ.EQ.1)GO TO 47
        IF(IJK1.EQ.0)GO TO 512
         IF(PX(JJ).EQ.PX(JJ-1).AND.XK0(1).EQ.XKMAX.AND.XK0(NT).EQ.XKMAX)
       1 GO TO 4521
         IF(PX(JJ).EQ.PX(JJ-1).AND.SWTCH1.EQ.1) GO TO 4521
         IF(PX(JJ).GT.PX(JJ-1))GO TO 44
        GO TO 45
 44     GAMM=GAMM*2.
        GO TO 56
 45      IF(JJ.EQ.2)GO TO 451
        GO TO 452
 451     GAM=GAM/15.
         IF(GAM.LT.1.0E-10)GO TO 507
         JJ=1
         GO TO 47
 600    GAMM=-  .005
         GAM=-GAMM/5.
        SWTCH2=1
        JJ=0
        GO TO 56
 452     IF(INTPOL.EQ.0)GO TO 4521
```

```
      GO TO 4522
4521   GAMM=0.6*GAMM/2.
      IJK1=0
      IXI=8
      GO TO 56
4522   CONTINUE
       PX1(9)=PX(JJ)
       PX1(5)=PX(JJ-1)
       PX1(1)=PX(JJ-2)
      PQ(9)=GAMM
       PQ9=PQ(9)
      PQ(5)=GAMM/2.
       PQ(1)=GAMM/4.
       FLESQ=(GAMM-GAMM/2.)
      PQ(2)=-FLESQ/2.*0.75 +GAMM/2.
      PQ(3)=-FLESQ/2.*0.50 +GAMM/2.
      PQ(4)=-FLESQ/2.*0.25 +GAMM/2.
      PQ(6)=+FLESQ*0.25 +GAMM/2.
      PQ(7)=+FLESQ*0.50 +GAMM/2.
      PQ(8)=+FLESQ*0.75 +GAMM/2.
      IJK1=0
       IJK=0
       IXI=1
       GO TO 513
512    PX1(IXI   )=PX(JJ)
       IF(IXI.EQ.4)IXI=5
       IF(IXI.EQ.8) GO TO 514
513    GAMM=PQ(IXI+1)
       GO TO 56
47    GAMM=GAM
56     CONTINUE
      IF(SWTCH3.EQ.1)GO TO 57
      IF(JJ.EQ.1)GO TO 57
      DO 700 I=1,NT
      GSTP=GAMM*B1(1,I)/TF
      IF((ABS(GSTP)).GT.XKS)GO TO 5
      GO TO 6
5     GSTP=XKS
      IF(GSTP.LT.0)GSTP=-XKS
       SWTCH1=1
6     CONTINUE
      XK0(I)=XK01(I) + GSTP
       IF(XK0(I).GE.XKMAX) XK0(I)=XKMAX
       IF(XK0(I).LE.XKMIN) XK0(I)=XKMIN
       T0(I)=-ECR/ALOG(XK0(I)/XKP)
700   CONTINUE
       GO TO 58
```

```
  57  DO  41 II1=1,NT
      DO 40 II2=1,NZ
  40  Y(II2)=DHAM(II2,II1)
      CALL QSF(HZ,Y,Z,NZ)
      GSTP=GAMM*Z(NZ)/TF
      IF((ABS(GSTP)).GT.XKS)GO TO 7
      GO TO 8
  7   GSTP=XKS
      IF(GSTP.LT.0)GSTP=-XKS
      SWTCH1=1
     8 CONTINUE
      XK0(II1)=XK01(II1)+GSTP
      IF(XK0(II1).GE.XKMAX)XK0(II1)=XKMAX
      IF(XK0(II1).LE.XKMIN)XK0(II1)=XKMIN
      T0(II1)=-EGR/ALOG(XK0(II1)/XKP)
      B1(1,II1)=Z(NZ)
      WRITE(6,1000)Z(NZ)
  1000 FORMAT(E16.5)
  41  CONTINUE
  58  IJK=0
      IF(SWTCH2.EQ.1)IJK=1
       IF(IJK1.EQ.1)GO TO 500
      IXI=IXI+1
      IF(IXI.EQ.9)GO TO 515
       GO TO 500
  514  IF(GAMM.LT.1.0.OR.GAMM.GT.100.)GO TO 516
      GO TO 518
  516  DO 517 I=1,9
  517 PQ(I)=PQ(I)/PQ(9)
      LXS=1
  518  CALL LESQ(AAX,XB,PQ,PX1,2,9)
       GAMM=-XB(2)/(2.*XB(3))  *0.70
       GAMPQ=GAMM*PQ9
      IF(LXS.EQ.1)GO TO 519
      GO TO 520
  519  GAMM=GAMPQ
      LXS=0
  520  CONTINUE
       GO TO 56
  515  JJ=0
        IJK=1
       IJK1=1
      SWTCH1=0
       GO TO 500
  505  CONTINUE
      WRITE(6,100)
  507  WRITE(6,108)KKOUNT,COMP2
```

```
  108   FORMAT(/,20X,*  ITER =*,I3,5X,* OBJECTIVE FUNCTION=*,E16.6)
         CALL OUTPUT (LC1,LC2)
        STOP
        END
```

```
C           MODIFIED  EULER  INTEGRATION  SUBROUTINES
C           =========================================


C        ****************************************
         SUBROUTINE STATE
C        ****************************************
        EXTERNAL F1,F2,F3,F4
        COMMON T0(26 ),X(17,26 ),SI(17,26 ),B1(17,26 ),B2(17,26 ),
       1 DHAM(17,26)
         COMMON /A1/P,TF,XN,XM,TZ,XJ,     XKP,XKKP,ECR,A,B ,TAV,SIMIN,
       1XMAX
        COMMON /A2/ JL2,IX2,JL1,IX1,LS2,LS1,J1,I1
         COMMON/A3/NI
        COMMON /A4/ NT,NZ,K11,LA11,LS3,LX3,LX4,LS4,L1,L2
        JL1=1
        LS1=1
        NZ1=NZ-1
        NZ11=NZ-2
         NT1=NT-1
         NT11=NT-2
         HZ=1./NZ1
          HT=1./NT1
        DO 20  I=1,NZ1
        IX1=I
        CALL ONC(F1,X1,             X(I,1),NZ,1.)
        IF(X1.GT.XMAX)X1=XMAX
 20     X(I+1,1)=X1
        JL2=1
        LS2=0
        DO 21  I=1,NT1
        IX2=I
        CALL ONC(F2,X1,              SI(1,I),NT,1.)
         IF(X1.LT.SIMIN)X1=SIMIN
 21     SI(1,I+1)=X1
        LS2=0
        LS1=1
        DO 33  J1=2,NT
        IX2=J1-1
        JL1=J1
        DO 33  I1=2,NZ
        IX1=I1-1
         JL2=I1
        CALL EUL(F1,F2,X1,X2,X(I1-1,J1),SI(I1,J1-1),1.0)
        IF(X1.GT.XMAX)X1=XMAX
         IF(X2.LT.SIMIN)X2=SIMIN
```

```
      X(I1,J1)=X1
      SI(I1,J1)=X2
 33   CONTINUE
       RETURN
      END
C      ****************************************
      SUBROUTINE ADJNT
C      ****************************************
      EXTERNAL F1,F2,F3,F4
      COMMON T0(26 ),X(17,26 ),SI(17,26 ),B1(17,26 ),B2(17,26 ),
     1 DHAM(17,26)
       COMMON /A1/P,TF,XN,XM,TZ,XJ,     XKP,XKKP,ECR,A,B ,TAV,SIMIN,
     1XMAX
      COMMON /A2/ JL2,IX2,JI1,IX1,LS2,LS1,J1,I1
       COMMON/A3/N1
      COMMON /A4/ NT,NZ,K11,LA11,LS3,LX3,LX4,LS4,L1,L2
      NZ1=NZ-1
      NZ11=NZ-2
       NT1=NT-1
       NT11=NT-2
       HZ=1./NZ1
        HT=1./NT1
      LS3=1
      K11=NT
      DO 60 I=1,NZ1
       LX3=I-1
      CALL ONC(F3,X1                  ,B1(NZ-I+1,NT),NZ,-1.)
 60    B1(NZ-I   ,NT)=X1
       LS4=0
      LA11=NZ
      DO 61 I=1,NT1
       LX4=I-1
      CALL ONC(F4,X1                  ,B2(NZ,NT-I+1),NT,-1.)
 61   B2(NZ,NT-I   )=X1
      LS3=1
       LS4=0
      DO 34 J2=2,NT
      L1=NT-J2+1
      K11=L1
      LX4=J2-2
      DO 34 I2=2,NZ
      LX3=I2-2
       L2=NZ-I2+1
       LA11=L2
      CALL EUL(F3,F4,X3,X4,B1(L2+1,L1),B2(L2,L1+1),-1.0)
       B1(L2,L1)=X3
```

```
      B2(L2,L1)=X4
   34   CONTINUE
       RETURN
      END
C      ************************************
       SUBROUTINE F4(B2I,RB2)
C      ************************************
      COMMON T0(26 ),X(17,26 ),SI(17,26 ),B1(17,26 ),B2(17,26 ),
     1 DHAM(17,26)
      COMMON /A4/ NT,NZ,K11,LA11,LS3,LX3,LX4,LS4,L1,L2
       COMMON/A3/N1
       COMMON /A1/P,TF,XN,XM,TZ,XJ,     XKP,XKKP,ECR,A,B ,TAV,SIMIN,
     1XMAX
       COMMON /A5/STOR1(17,26),LFIX
       IF(LS4.EQ.0)GO TO 11
      GO TO 12
   12  NA=NZ-N1-LX4
      R1=B1(NA,K11)
      R2=X  (NA,K11)
       R3=SI(NA,K11)
       R4=T0(K11)
      R5=X(1,K11)
      GO TO 10
   11 NB=NT-N1-LX4
      R1=B1(LA11,NB)
      R2=X(LA11, NB)
       R3=SI(LA11,NB)
      R4=T0(NB)
       R5=X(1,NB)
   10  CONTINUE
      XK0=XKP*EXP(-ECR/R4)*TF
       XKK0=XKKP*EXP(-ECR*P/R4)
      ZA1=ECR/(TAV**2*XJ)
       EX1=EXP((R2-R5)*ZA1)
       F=(A+B*R2)*EX1
       DF=B*EX1+(A+B*R2)*EX1*ZA1
       EX2=EX1**P
       ZA2=(1.-R2)**XN
      FF=         ZA2*EX2*TZ
       DFF=(XN*(1.-R2)**(XN-1.)*EX2+ZA2*EX2*P*ZA1)*TZ
       RB2=B2I*XK0*XM*R3**(XM-1.)*F        -R1*XKK0*FF
      IF(LFIX.EQ.1)GO TO 20
       U=R1*R3*FF* XKK0
      V=B2I*R3**XM*F*XK0
       IF(LS4.EQ.0)GO TO 15
      GO TO 14
```

```
15        DHAM(LA11,NB)=U*P/XK0 -V/XK0
          GO TO 13
14        DHAM(NA,K11)=U*P/XK0-V/XK0
          GO TO 13
20        IF(LS4.EQ.0)GO TO 22
         GO TO 23
22       DHAM(LA11,NB)=R3*FF*R1
         STOR1(LA11,NB)=B2I*R3**XM*F
          GO TO 13
23       DHAM(NA,K11)=R3*FF*R1
         STOR1(NA,K11)=B2I*R3**XM*F
13        RETURN
          END
C         ****************************************
          SUBROUTINE F3 (B1I,RB1)
C         ****************************************
         COMMON T0(26 ),X(17,26 ),SI(17,26 ),B1(17,26 ),B2(17,26 ),
        1 DHAM(17,26)
          COMMON/A3/N1
         COMMON /A4/ NT,NZ,K11,LA11,LS3,LX3,LX4,LS4,L1,L2
          COMMON /A1/P,TF,XN,XM,TZ,XJ,     XKP,XKKP,ECR,A,B ,TAV,SIMIN,
        1XMAX
          IF(LS3.EQ.0)GO TO 11
         GO TO 12
11       NB=NT-N1-LX3
         R1=B2(LA11,NB)
         R2=X(LA11,NB)
         R3=SI(LA11,NB)
         R4=T0(NB)
          R5=X(1,NB)
         GO TO 10
12       NA=NZ-N1-LX3
         R1=B2(NA,K11)
         R2=X(NA,K11)
          R3=SI(NA,K11)
         R4=T0(K11)
         R5=X(1,K11)
10       CONTINUE
         XK0=XKP*EXP(-ECR/R4)*TF
          XKK0=XKKP*EXP(-ECR*P/R4)
         ZA1=ECR/(TAV**2*XJ)
          EX1=EXP((R2-R5)*ZA1)
          F=(A+B*R2)*EX1
          DF=B*EX1+(A+B*R2)*EX1*ZA1
          EX2=EX1**P
          ZA2=(1.-R2)**XN
```

```
      FF=         ZA2*EX2*TZ
       DFF=(XN*(1.-R2)**(XN-1.)*EX2+ZA2*EX2*P*ZA1)*TZ
      RB1=R1*XK0*R3**XN*DF-R1I*R3*XKK0*DFF
      RETURN
       END
C      **************************************
       SUBROUTINE F2(SSI,RSI)
C      **************************************
      COMMON T0(26 ),X(17,26 ),SI(17,26 ),B1(17,26 ),B2(17,26 ),
     1 DHAM(17,26)
       COMMON /A1/P,TF,XN,XM,TZ,XJ,     XKP,XKKP,ECR,A,B ,TAV,SIMIN,
     1XMAX
      COMMON /A2/ JL2,IX2,JI1,IX1,LS2,LS1,J1,I1
       COMMON/A3/N1
      LI3=IX2+1-N1
      IF(LS2.EQ.0)GO TO 11
      GO TO 12
12     R1=T0(JL2)
      R2=X(1,JL2)
      R3=X(LI3,JL2)
       GO TO 10
11    R1=T0(LI3)
      R2=X(1,LI3)
      R3=X(JL2,LI3)
10     CONTINUE
       IF(R3.GT.XMAX)R3=XMAX
       IF(R3.LT.0.)R3=0.
       IF(SSI.GT.1.0)SSI=1.0
       IF(SSI.LT.SIMIN)SSI=SIMIN
      XK0=XKP*EXP(-ECR/R1) *TF
       XKK0=XKKP*EXP(-ECR*P/R1)
      ZA1=ECR/(TAV**2*XJ)
       EX1=EXP((R3-R2)*ZA1)
      F=(A+B*R3)*EX1
        RSI=-XK0*SSI**XM*F
       RETURN
       END
C      **************************************
       SUBROUTINE F1(XX,RX)
C      **************************************
      COMMON T0(26 ),X(17,26 ),SI(17,26 ),B1(17,26 ),B2(17,26 ),
     1 DHAM(17,26)
       COMMON /A1/P,TF,XN,XM,TZ,XJ,     XKP,XKKP,ECR,A,B ,TAV,SIMIN,
     1XMAX
      COMMON /A2/ JL2,IX2,JI1,IX1,LS2,LS1,J1,I1
```

```
       COMMON/A3/N1
      LI2=IX1+1-N1
      IF(LS1.EQ.0)GO TO 11
      GO TO 12
 11   R1=T0(LI2)
       R2=X(1,LI2)
      R3=SI(JL1,LI2)
      GO TO 10
 12   R1=T0(JL1)
      R2=X(1,JL1)
      R3=SI(LI2,JL1)
 10    CONTINUE
       IF(XX.GT.XMAX)XX=XMAX
      IF(XX.LT.0.)XX=0.
       IF(R3.LT.SIMIN)R3=SIMIN
      XK0=XKP*EXP(-ECR/R1) *TF
       XKK0=XKKP*EXP(-ECR*P/R1)
      ZA1=ECR/(TAV**2*XJ)
       EX1=EXP((XX-R2)*ZA1)
       EX2=EX1**P
       FF=(1.-XX)**XN*EX2
       RX=R3*XKK0*FF*TZ
      RETURN
      END
C      ****************************************
      SUBROUTINE FUI (FA,FB,X1,X2,P1,P2,XK)
C      ****************************************
      COMMON T0(26 ),X(17,26 ),SI(17,26 ),B1(17,26 ),B2(17,26 ),
     1 DHAM(17,26)
      COMMON /A4/ NT,NZ,K11,LA11,LS3,LX3,LX4,LS4,L1,L2
      COMMON /A2/ JL2,IX2,JL1,IX1,LS2,LS1,J1,I1
       COMMON/A3/N1
       COMMON /A1/P,TF,XN,XM,TZ,XJ,    XKP,XKKP,ECR,A,B ,TAV,SIMIN,
     1XMAX
      ER=.001
      HZ=1./(NZ-1)
      HT=1./(NT-1)
      N1=1
      IF(XK.EQ.-1.0)N1=0
      CALL FA(P1,RHA1)
      X1=P1+HZ*RHA1*XK
      IF(XK.EQ.-1.0)GO TO 1
      X(I1,J1)=X1
        GO TO 10
 1    B1(L2,L1)=X1
 10    CONTINUE
```

```
          CALL FB(P2,RHB1)
          X2=P2+HT*RHB1*XK
           IF(XK.EQ.-1.0) GO TO 2
          SI(I1,J1)=X2
           GO TO 20
 2        B2(L2,L1)=X2
 20        CONTINUE
          N1=0
           IF(XK.EQ.-1.0) N1=1
          DO 15 I=1,5
          CALL FA(X1,RHA2)
           X1=P1 + HZ/2.*(RHA1+RHA2)*XK
          IF(XK.EQ.-1.0)GO TO 4
          TEST1=ABS((X(I1,J1)-X1)/X1)
          X(I1,J1)=X1
           GO TO 40
 4         TEST1=ABS((B1(L2.L1)-X1)/X1)
          B1(L2,L1)=X1
 40        CONTINUE
          CALL FB(X2,RHB2)
          X2=P2+ HT/2.*(RHB1+RHB2)*XK
           IF(XK.EQ.-1.0) GO TO 3
          TEST2=ABS((SI(I1,J1)-X2)/X2)
          SI(I1,J1)=X2
          GO TO 30
 3         TEST2=ABS((B2(L2.L1)-X2)/X2)
          B2(L2.L1)=X2
 30        CONTINUE
          IF(TEST1.LT.ER  .AND.TEST2.LT.ER  ) GO TO 16
 15       CONTINUE
 16       CONTINUE
          RETURN
          END
C          **************************************
          SUBROUTINE ONC(F,X1,P1,N,XK)
C          **************************************
          COMMON T0(26 ),X(17,26 ),SI(17,26 ),B1(17,26 ),B2(17,26 ),
         1 DHAM(17,26)
          COMMON /A4/ NT,NZ,K11,LA11,LS3,LX3,LX4,LS4,L1,L2
          COMMON /A2/ JL2,IX2,JI1,IX1,LS2,LS1,J1,I1
           COMMON/A3/N1
           COMMON /A1/P,TF,XN,XM,TZ,XJ,     XKP,XKKP,ECR,A,B ,TAV,SIMIN,
         1XMAX
          ER=.001
          H=1./(N-1)
           N1=1
```

```
      IF(XK.EQ.-1.0)N1=0
      CALL F(P1,RH1)
      X1P=P1+H*RH1*XK
      N1=0
      IF(XK.EQ.-1.0)N1=1
      DO 15 I=1,5
      CALL F(X1P,RH2)
      X1C=P1+H/2.*(RH1+RH2)*XK
      TEST=ABS((X1P-X1C)/X1C)
      IF(TEST.LT.ER  ) GO TO 16
      IF(I.EQ.5)GO TO 16
      X1P=X1C
15     CONTINUE
16    X1=0.5*(X1P+X1C)
      RETURN
      END

C      ***************************************
       SUBROUTINE OUTPUT(LC1,LC2)
C      ***************************************
      COMMON T0(26 ),X(17,26 ),SI(17,26 ),B1(17,26 ),B2(17,26 ),
     1 DHAM(17,26)
       COMMON /A1/P,TF,XN,XM,TZ,XJ,     XKP,XKKP,ECR,A,B ,TAV,SIMIN,
     1XMAX
      COMMON /A4/ NT,NZ,K11,LA11,LS3,LX3,LX4,LS4,L1,L2
       DIMENSION TT0(51)
      NZ1=NZ-1
       NT1=NT-1
      WRITE(6,211)
211   FORMAT(//,7X,* CONVERSION X*,//)
      DO 605 J=1,NT ,LC2
      WRITE(6,200)(X(I,J),I=1,NZ1,LC1),X(NZ,J)
605    CONTINUE
       WRITE(6,100)
100    FORMAT(1H1)
       WRITE(6,212)
212    FORMAT(7X,* CAT ACTIVITY SI *,//)
      DO 606 J=1,NT ,LC2
606    WRITE(6,201)(SI(I,J),I=1,NZ1,LC1),SI(NZ,J)
       WRITE(6,202)(T0(I),I=1,NT)
200    FORMAT(    (9F14.4))
201    FORMAT(    (9F14.4))
202    FORMAT(//,7X,*  TEMPERATURE *,//,(5E15.5))
       WRITE(6,214)
214    FORMAT(//,7X,*  DERIVATIVE OF HAMILTONIAN*,/)
      DO 610 J=1,NT,LC2
610    WRITE(6,200)(DHAM(I,J),I=1,NZ1,LC1),DHAM(NZ,J)
```

```
       WRITE(6,216)
216     FORMAT(//,7X,* TEMPERATURE  DISTRIBUTED*,//)
       DO 632 I=1,NT,LC2
       DO 631 J=1,NZ
631    TT0(J)=X(J,I)/XJ+T0(I)
632     WRITE(6,200)(TT0(K),K=1,NZ1,LC1),TT0(NZ)
       WRITE(6,217)
217    FORMAT(//,7X,* ADJOINT B1*,//)
       DO 633 J=1,NT,LC2
633     WRITE(6,200)(B1(I,J),I=1,NZ1,LC1),B1(NZ,J)
       WRITE(6,218)
218     FORMAT(//,7X,* ADJOINT B2*,//)
       DO 634 J=1,NT,LC2
634     WRITE(6,200)(B2(I,J),I=1,NZ1,LC1),B2(NZ,J)
        RETURN
        END
```