ABSTRACT

CONTROL OF COMPETING CHEMICAL REACTIONS

By

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Control of chemical reactions by temperature and by distribution of reactants have been considered separately. Here we analyze the control of a simple system of parallel reactions, which are of different order with respect to one of the reactants, using both temperature and rate of addition of reactants as simultaneous control variables. It is shown by application of the necessary conditions given in Pontryagin's Maximum Principle, that the nature of the optimal policy depends, in a simple way, on the relation between the ratio of the activation energies of the competing reactions and the ratio of their orders with respect to the distributed reactant. There exists a discontinuity in the form of the optimal policy when these two quantities are equal. Numerical results are worked out for a set of parameter values which confirm the results theoretically founded.
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Nomenclature

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1. INTRODUCTION

In attempting to generate certain product(s) by chemical reaction, one is often troubled by competing side reactions which degrade the reactants into other(s) non-desired products. Where the reaction is carried out in a batch reactor one may use temperature variation or delayed addition of one or more of the reactants to inhibit the side reaction as much as possible. Reference to these techniques are made in almost every text on preparative organic chemistry. Similar methods can be used for tubular reactors by merely replacing the time coordinate by a length coordinate along the tubular reactor as the independent variable.

Both optimization by temperature regulation and by distributed addition of reactants (continuously and discretely) have already been considered separately in a number of publications. Temperature control was the first to be explored and there is a large number of publications using several techniques to optimize different reaction schemes. Among them is Horn's classical (1) treatment of optimum temperature control for a class of parallel reactions. Aris's book (2) applies dynamic programming to a number of cases; and applications to adjoint systems can be found
(2,3) as well as to more complicated reaction networks (4,5,6). A good list of publications in this area can be found in Fedotov et al (7).

Optimization by delayed addition of reactants has also been suggested and applied to several reaction mechanisms (2,8,12,16). Siebenthal and Aris treated the control of a batch reactor by delayed addition of cold feed and Jackson and Senior (10,11) developed a sufficiency criterion for non-optimality of simultaneous instantaneous addition of reactants at the beginning of a purely batch operation for any reaction network whose kinetics are known, and developed the optimal isothermal reactant distribution policy for a simple parallel reaction system.

Here we shall consider again a pair of parallel reactions of different orders with respect to the distributed reactant; but we shall use both temperature and rate of addition of one reactant as our simultaneous control variables. In spite of the apparent complexity of the resulting optimization problem, it turns out to be possible to synthesize the control policy, without detailed computation, by mere application of the necessary conditions for optimality provided by Pontryagin's Maximum Principle.
CHAPTER II

NON ISOTHERMAL DELAYED ADDITION OF REACTANTS

2.1 STATEMENT OF THE PROBLEM

We shall consider the following reaction scheme

\[ A + B \rightarrow C \quad k_1,E_1 \]

\[ A + nB \rightarrow D \quad k_2,E_2 \]

where C is the desired product and D is a waste. The kinetics are assumed to be of the mass action form and to correspond to the stoichiometry of the reactions as written. Thus, the rate of the first reaction is proportional to the mass concentration of substance B while that of the second reaction is proportional to the \( n \)th power of this concentration.

To be definite we suppose that the reactions are carried out in a well-stirred vessel immersed in a thermostatically controlled bath as indicated in Fig. 1. Heat transfer delays in the thermostat, and between the thermostat and the reactor are negligible on the time scale of the reaction, so the temperature of the reactor mixture is at all times uniform and its instantaneous value can be controlled as desired between certain limits \( T_{\text{min}} \) and \( T_{\text{max}} \). \( a_0 \) moles of substance A are present at the reaction
FIG. 1 - ILLUSTRATION OF THE PROBLEM
vessel at time zero, and substance B can be run into the vessel from a container, as shown. The instantaneous rate of addition of B can be controlled at all times between specified limits zero and \( r_m \), where the upper bound \( r_m \) is predetermined, for example, by the maximum flow rate through the tube from the reactant reservoir to the reactor. Frequently \( r_m \) will be very large but it is important that \( r \) be bounded in connection with the mathematical reasoning that follows. The total amount of B to be added is denoted by \( Q \) and is also specified in advance. By examining the reaction scheme one can see on physical grounds that there is no apparent advantage in delaying the addition of A and thus A should be added all at the beginning of the batch; this question has been discussed mathematically using Jackson and Senior's criterion for non-optimality of initial addition of reactants at the beginning of the batch (10).

To avoid unnecessary algebraic complication it is assumed that the concentration of each substance in the reaction vessel is proportional to the number of moles of that substance present, and is unaffected by the quantities of the other components of the reaction mixture in the reactor. This is exactly correct for constant volume reaction systems, and is very good approximation in several practical cases e.g.
liquid reactions carried out in dilute solution in an inert solvent.

We limit our problem to $n > 1$ because only in this case does optimal control by temperature and rate of addition of B increase the yield of C at the end. When $n \leq 1$, only temperature control should be used, and some of the policies later deduced are again applicable.

Under these conditions and assumptions our problem is to determine the temperature $T$ and the rate of addition $r$ of B, as functions of time, as to maximize the final concentration of the desired product C at the end of the batch operation, which total time length is also predetermined.

2.2 MATHEMATICAL FORMULATION OF THE PROBLEM

The problem at hand, as physically stated in the last section can be mathematically described as follows: we have a set of state variables $(a,b,c,q)$ representing the mole concentration of components A,B,C and the total number of moles of substance B added to the reactor between time zero and $t$, respectively. These physical variables are continuous functions, satisfying the following system of ordinary differential equations, except at points of discontinuity of the right hand sides, and the associated boundary conditions.
\[ \frac{da}{dt} = -k_1ab - k_2ab^n ; \quad a(0) = a_0 \]

\[ \frac{db}{dt} = -k_1ab - nk_2ab^n + r ; \quad b(0) = 0 \]

\[ \frac{dc}{dt} = k_1ab ; \quad c(0) = 0 \]

\[ \frac{dq}{dt} = r ; \quad q(0) = 0, q(T') = Q \]

where the velocity constants \( k_1 \) and \( k_2 \) are Arrhenius functions of the temperature with respective activation energies \( E_1 \) and \( E_2 \), e.g. \( k_i = k_{i0} \exp(-E_i / RT), i = 1,2 \).

Our control variables \( r \) and \( T \) should be piecewise continuous functions of time and are subject to the constraints

\[
\begin{align*}
\{ r : 0 \leq r \leq r_{\max} \} & \quad \Rightarrow \quad R \\
\{ T : 0 < T_{\min} \leq T \leq T_{\max} \} & \quad \Rightarrow \quad S
\end{align*}
\]

where \( R \) and \( S \) are defined as the sets of admissible variations of \( r \) and \( T \) respectively. Then it is required to find the piecewise continuous functions \( r(t) \) and \( T(t) \), with values
in R and S respectively, which maximize the quantity

$$C(T) = \int_0^T k_{1ab} \, dt$$

This mathematical problem falls within the class of problems for which necessary conditions are given by Pontryagin's Maximum Principle. For completeness and further reference we shall sketch those necessary conditions without any proof.

2.3 THE MAXIMUM PRINCIPLE AS NECESSARY CONDITION FOR THIS CLASS OF PROBLEM

Good expositions and proofs of this useful mathematical result, its applications and difficulties, are found in very many places. We shall mention the original source (13) and useful discussions by Rosoneor (14). Some applications and associated difficulties are found in (6,7,14). We shall merely list the conditions as they are to be used here.

We have a set of state variables $x_i$, $i = 1, \ldots, n$ which are continuous functions of an independent variable $t$ and satisfy the following differential equations at all points of continuity of the right hand sides.
\[
\frac{dx_i}{dt} = f_i(x_1, \ldots, x_n; u_1, \ldots, u_m) \quad i = 1, \ldots, n \quad (2.3-1)
\]

and the following boundary conditions

\[
x_i(0) = a_i, \quad i = 1, \ldots, n
\]

\[
x_i(T) = b_i, \quad i \in I
\]

where \( I \) is a proper subset of \( \{1, \ldots, n\} \).

The set of variables \( \{u_1, \ldots, u_m\} \) (control or decision variables) is constrained (e.g. \( u_i^{\min} \leq u_i \leq u_i^{\max} \)) and each variable \( u_i \) is to be piecewise continuous. The \( u \)'s are then to be determined as to maximize (or minimize) an objective function of the form

\[
P = \sum_{i \notin I} \alpha_i x_i(T) \quad (2.3-2)
\]

where the weighting factors \( \alpha_i \) and the value of \( T \) are specified in advance. This form of optimization problem as particular as it looks, covers many important cases which may be reduced to this form by some transformation.

To formulate the necessary conditions of Pontryagin we create an adjoint system of Lagrange multipliers \( \lambda_i \),
continuous functions of time, which satisfy the following
differential equations at all points of continuity of the
right hand sides
\[ \frac{d \lambda_i}{dt} = \sum_{j:1}^{n} \lambda_j \frac{\partial f_j}{\partial x_i} \quad i = 1, 2, \ldots, n \quad (2.3-3) \]

and the following boundary conditions

\[ \lambda_i(\tau) = -\alpha_i \] when we minimize P \\ \[ i \notin I \quad (2.3-4) \]

\[ \lambda_i(\tau) = \alpha_i \] when we maximize P

In terms of a Hamiltonian function that we can define as

\[ H(\lambda, x, u) = \sum_{i:1}^{n} \lambda_i f_i(x, u) \quad (2.3-5) \]

We can state Pontryagin's Maximum Principle as:
determine \( u_i(t) : H(\lambda, x, u) \rightarrow \max \) with respect to \( u \) at each \( t \) and such that equations (2.3-1) and (2.3-3),
together with the associated boundary conditions (2.3-2)
and (2.3-4) are satisfied. Since our system is autonomous
(the describing differential equations have no explicit
dependence on the independent variable) we can further say
that the value of the Hamiltonian which corresponds to an optimal trajectory is constant along the whole variation of the independent variable (i.e. $0 \rightarrow \tau$).

The Maximum Principle changes the originally posed problem to the solution of a two-point boundary value problem, with an optimization criterion on the Hamiltonian to choose the state variables at every point.

In applying this principle to a computer solution of a problem one usually makes a reasonable guess of the adjoint variables at zero or of the state variables at $\tau$. After integration of the set of physical and adjoint equations it is then necessary to make adjustments to the guessed values in order that the boundary conditions at the opposite end should be satisfied.

This creates some serious problems in applications where we depend on a multidimensional interaction. In addition, there are sometimes numerical difficulties of unstability in integrating the differential equations (5,15). Finally, it must be recalled that Pontryagin's Maximum Principle is only a necessary condition; it does not guarantee the existence or the uniqueness of a maximum (or minimum) for the objective function. A clear exposition of this problem can be seen in Coward and Jackson's work (6).
In the present work we develop a series of lemmas and theorems which will allow us to go systematically to the final optimal control by eliminating those forms of control which do not satisfy Pontryagin's Maximum Principle. The resulting narrowing of the class of competing functions is such that we can eventually select the whole trajectory uniquely under certain conditions on the parameters of the problem.

2.4 PONTRYAGIN'S FORMULATION OF OUR PROBLEM

As is stated in section 2.2, our problem can be solved directly by the technique explained in the last section. Namely we have to solve the following problem

\[
\frac{da}{dt} = -k_1ab - k_2ab^n ; \quad a(0) = a_0 \quad (2.4-1)
\]

\[
\frac{db}{dt} = -k_1ab - nk_2ab^n + r ; \quad b(0) = 0 \quad (2.4-2)
\]

\[
\frac{dc}{dt} = k_1ab ; \quad c(0) = 0 \quad (2.4-3)
\]

\[
\frac{dq}{dt} = r ; \quad q(0) = 0, q(T) = Q \quad (2.4-4)
\]
with all variables as denoted in section 2.2. In order to simplify manipulation we will use \( k_1 \) as control variable instead of temperature and will write

\[
k_2 = \alpha k_1^P
\]

where \( \alpha = k_{20} / k_{10}^P \) and \( p = E_2 / E_1 \), the ratio of the activation energies. It is then required to find the piecewise continuous functions \( k_1(t), r(t) \) in \([0, T]\), subject to the constraints.

\[
0 < k_1^{\text{min}} < k_1 < k_1^{\text{max}} ; 0 \leq r \leq r_m \quad (2.4-5)
\]

such that the equations and boundary conditions (2.4-1) to (2.4-4) are satisfied and \( c(\tau) \) is maximized. Such a policy is referred to here as an optimal control policy and it is assumed here that such a policy exists. It is then shown that the form of the optimal policy is determined by the necessary conditions provided by Pontryagin's Maximum Principle. Introducing continuous adjoint variables \( \lambda_a, \lambda_b, \lambda_c, \mu \) satisfying the following differential equations and boundary conditions.

\[
\frac{d\lambda_a}{dt} = k_1^b(\lambda_a + \lambda_b - 1) + k_2^b n(\lambda_a + n\lambda_b); \quad \lambda_a(T) = 0
\]

(2.4-6)
\[ \frac{d \lambda_b}{dt} = k_1a(\lambda_a + \lambda_b - 1) + nk_2ab^{n-1}(\lambda_a + n\lambda_b); \]

\[ \lambda_b(T) = 0 \quad (2.4-7) \]

\[ \frac{d \lambda_c}{dt} = 0 \quad ; \quad \lambda_c(T) = 1 \quad (2.4-8) \]

\[ \frac{d \mu}{dt} = 0 \quad ; \quad \mu(T) = \gamma \, \text{(unspecified initially)} \quad (2.4-9) \]

and constructing the Hamiltonian.

\[ H = (\lambda_b + \gamma) r + k_1ab(1 - \lambda_a - \lambda_b) - k_2ab^n \]

\[ (\lambda_a + n\lambda_b) \quad (2.4-10) \]

we have the following necessary conditions for optimality of the policy \( r(t), k_1(t) \).

a) For each \( t \in [0, T] \), if \( H \) is regarded as a function of \( r \) and \( k_1 \) in the rectangle of the \( (r, k_1) \) plane defined by (2.4-5), it takes its maximum value at the point \( (r(t), k_1(t)) \).

b) The corresponding maximum value of \( H, H_{\max} \), is independent of time.
2.5 DETERMINATION OF THE OPTIMAL POLICY

We proceed to derive a series of results which enable the form of the optimum policy to be determined without computation in certain circumstances, after assuming its existence. It is convenient to state these results as a series of lemmas and theorems, as the chain of reasoning is quite long. Results which make some statement about the form of the optimum policy will be called theorems, while auxiliary results needed in the derivation of the theorems will be referred to as lemmas.

**Lemma 1**

The total length of all intervals in which \( r = r_m \) may not exceed \( Q/r_m \).

**Proof**

This follows immediately from the fact that \( Q \) is the total amount of \( B \) added to the system.

**Lemma 2**

\( a, b, c, \lambda_a, \) and \( \lambda_b \) are continuous on \([0, \tau]\) and have piecewise continuous first derivatives in the open interval \((0, \tau)\).
Proof

The continuity follows from the definition of these variables. The first derivatives are piecewise continuous because of the postulated piecewise continuity of \(r(t)\) and \(k_1(t)\).

**Lemma 3**

In \([0, \tau]\) \(a\) is bounded above by \(a_0\), \(b\) is bounded above by \(Q\), and bounds \(\Lambda_a(Q)\) and \(\Lambda_b(Q)\) for \(|\lambda_a|\) and \(|\lambda_b|\) can be found which are independent of \(r_m\) for a given value of \(Q\).

**Proof**

The bounds \(a \leq a_0, b \leq Q\) follow immediately from equations (2.4-1), (2.4-2) and (2.4-4) and from the fact that \(a, b, k_1\) and \(k_2\) are non-negative.

The existence of the bounds \(\Lambda_a(Q)\) and \(\Lambda_b(Q)\) follows from a general result for homogeneous linear equations with continuous bounded coefficients. For equations and boundary conditions of the form

\[
\frac{dx_j}{dt} = \sum_{j=1}^{N} A_{ij}(t) x_j \quad ; \quad x_j(t_0) = x_{jo}, \quad t_0 \in [0, \tau]
\]
where \(|A_{ij}(t)| \leq A\) (all i, j, t), it can be shown that each \(|x_1(t)|\) is bounded in \([0, r]\) by a bound depending only on A. This result is clearly applicable to equations (2.4-6) and (2.4-7) defining \(\lambda_a\) and \(\lambda_b\), since \(k_1, k_2\), \(a\) and \(b\) have upper bounds according to first part of this theorem and (2.4-5). See appendix 1 for proof of the theorem.

**THEOREM 1**

(a) For an optimal policy, \(k_1(t)\) is continuous at all points where \(r < r_m\).

(b) When \(p > 1\), \(k_1(t)\) is continuous at all points of an optimum policy, provided \(r_m\) is sufficiently large.

**Proof**

For an optimal policy, \(k_1\) chosen so as to maximize the Hamiltonian at each time. But the Hamiltonian depends on \(k_1\) through the terms

\[ \tilde{H} = k_1ab(1 - \lambda_a - \lambda_b) - \alpha k_1^p ab^n(\lambda_a + n\lambda_b) \]

and the factors \(ab(1 - \lambda_a - \lambda_b)\) and \(ab^n(\lambda_a + n\lambda_b)\) are continuous functions of time, by Lemma 2. Thus, \(k_1\) can change discontinuously only if the Hamiltonian has two
equal maximum values at different points $k_1^1, k_1^2$ of the interval $[k_1^{\text{min}}, k_1^{\text{max}}]$. Examination of all possible forms of the dependence of $\tilde{H}$ on $k_1$, as sketched in Figs. 2 to 6, reveals that this is possible only in cases le, li, 2a, 2i and 3c, and in all these cases $\tilde{H}_{\text{max}} \leq 0$ at the point of discontinuity of $k_1$.

Now, if $r < r_m$ at this point, either $0 < r < r_m$, in which case $\lambda b + \gamma = 0$, or $r = 0$. Thus, in either case $(\lambda b + \gamma) r = 0$, and hence $H = \tilde{H}$ when both are evaluated on the optimal trajectory.

It follows that $H_{\text{max}} \leq 0$ at a point of discontinuity of $k_1$.

However, at $t = T$

$$H(T) = \gamma r + k_1 a(T)b(T)$$

so$$H_{\text{max}}(T) = \gamma \text{sign}'(\gamma) r_m + k_1^{\text{max}} a(T)b(T) > 0$$

where $\text{sign}'(\gamma) = 1$ for $r > 0$

$$= 0 \text{ for } r \leq 0$$

But according to the maximum principle, $H_{\text{max}}$ takes the same value for all $t$ on an optimal trajectory, so we have a contradiction and must conclude that there are no points of discontinuity of $k_1$ where $r < r_m$, proving part (a) of the theorem.
FIGURES 2, 3, 4, 5, 6

Possible forms of the Hamiltonian as a function of $k_1$

Curves 1 = $k_1 a_b (1 - \lambda_a - \lambda_b)$

Curves 2 = $- k_1 p_a b (\lambda_a + n \lambda_b)$

Curves $\tilde{H} = H - (\lambda_b + \gamma) r$
\[ I > I \]

\[ (1 - \lambda a - \lambda b) > 0 \]
\[ (\lambda a + \lambda b) > 0 \]

\[ I.b \]
\[ (1 - \lambda a - \lambda b) > 0, \]
\[ (\lambda a + \lambda b) < 0 \]

\[ I.c \]
\[ (1 - \lambda a - \lambda b) > 0 \]
\[ (\lambda a + \lambda b) = 0 \]

\[ I.d \]
\[ (1 - \lambda a - \lambda b) < 0 \]
\[ (\lambda a + \lambda b) > 0 \]

*FIG. 2*
I.e.

\((1 - \lambda a - \lambda b) < 0\)

\((\lambda a + n \lambda b) < 0\)

I. f

\((1 - \lambda a - \lambda b) < 0\)

\((\lambda a + n \lambda b) = 0\)

I. g

\((1 - \lambda a - \lambda b) = 0\)

\((\lambda a + n \lambda b) > 0\)

I. h

\((1 - \lambda a - \lambda b) = 0\)

\((\lambda a + n \lambda b) < 0\)

I. i

\((1 - \lambda a - \lambda b) = 0\)

\((\lambda a + n \lambda b) = 0\)

FIG. 3
\( p < 1 \)

2.a

\[(1 - \lambda a - \lambda b) > 0 \]
\[(\lambda a + n\lambda b) > 0 \]

2.b

\[(1 - \lambda a - \lambda b) > 0 \]
\[(\lambda a + n\lambda b) < 0 \]

2.c

\[(1 - \lambda a - \lambda b) > 0 \]
\[(\lambda a + n\lambda b) = 0 \]

2.d

\[(1 - \lambda a - \lambda b) < 0 \]
\[(\lambda a + n\lambda b) > 0 \]

FIG. 4
2.e
\[(l-\lambda a - \lambda b) < 0\]
\[(\lambda a + n\lambda b) < 0\]

2.f
\[(l-\lambda a - \lambda b) < 0\]
\[(\lambda a + n\lambda b) = 0\]

2.g
\[(l-\lambda a - \lambda b) = 0\]
\[(\lambda a + n\lambda b) > 0\]

2.h
\[(l-\lambda a - \lambda b) = 0\]
\[(\lambda a + n\lambda b) < 0\]

2.i
\[(l-\lambda a - \lambda b) = 0\]
\[(\lambda a + n\lambda b) = 0\]
3a
\[ ab(1-\lambda a-\lambda b) - \alpha ab^n (\lambda a + n\lambda b) > 0 \]

3b
\[ ab(1-\lambda a-\lambda b) - \alpha ab^n (\lambda a + n\lambda b) < 0 \]

3c
\[ ab(1-\lambda a-\lambda b) - \alpha ab^n (\lambda a + n\lambda b) = 0 \]

FIG. 6
To prove part (b) we confine our attention to those cases illustrated in Figs. 2 and 3, for which \( p > 1 \). It is seen that \( \tilde{H} \) can have two equal maximum values only in cases le and li, for which

\[
(1 - \lambda_a - \lambda_b) \leq 0 \quad \text{and} \quad (\lambda_a + n\lambda_b) \leq 0
\]

From the first of these \( (\lambda_a + \lambda_b) \geq 1 \), and using this in the second gives \( \lambda_b \leq -\frac{1}{n-1} \).

Consider now the value of \( \lambda_b + \gamma \). It is shown in Lemma 6, by arguments not depending on the present issue, that

\[
\gamma \leq \frac{QN(Q)}{rm}
\]

Thus, using this and the inequality found above for \( \lambda_b \)

\[
(\lambda_b + \gamma) \leq \left( -\frac{1}{n-1} + \frac{QN}{rm} \right) , \quad (n > 1)
\]

at any point of discontinuity of \( k_1 \), and it follows for sufficiently large \( rm \) that \( (\lambda_b + \gamma) < 0 \). Such a point can, therefore, belong to an optimal policy only if \( r = 0 \).

But this contradicts part (a) of the Theorem, already proved, so we conclude that there exist no points of discontinuity of \( k_1 \) in this case.

**Lemma 4**

For an optimal control policy \( \lambda_a \) and \( \lambda_b \) have piecewise
continuous derivatives in \((0, T)\) and bounds \(M(Q)\) and \(N(Q)\) for \(|d \lambda_a/dt|\) and \(|d \lambda_b/dt|\) can be found which are independent of \(r_m\) for a given value of \(Q\). Step discontinuities of \(d \lambda_b/dt\) and \(d \lambda_a/dt\) may occur only at points of discontinuity of \(k_1\).

**Proof**

The piecewise continuity of \(d \lambda_a/dt\) and \(d \lambda_b/dt\) follows from the defining equations (2.4-7), Lemma 2 (continuity of \(a, b, \lambda_a\) and \(\lambda_b\)) and theorem 1.

Furthermore, using Lemma 3, equations (2.4-6) and (2.4-7) yield

\[
|d \lambda_a/dt| \leq k_1^{\text{max}} Q (\Lambda_a + \Lambda_b + 1) + \alpha(k_1^{\text{max}})^p Q^n.
\]

\[
(\Lambda_a + n \Lambda_b) = M(Q)
\]

\[
|d \lambda_b/dt| \leq k_1^{\text{max}} a_0 (\Lambda_a + \Lambda_b + 1) + n \alpha(k_1^{\text{max}})^p a_0 Q^{n-1}.
\]

\[
(\Lambda_a + n \Lambda_b) = N(Q)
\]

**Theorem 2**

For an optimal policy \(k_1(t)\) has a piecewise continuous first derivative. The discontinuities in \(dk_1/dt\) occur at
points of discontinuity of $r$, at points of discontinuity of $k_1$ and at points where $k_1 = k_1^{\text{max}}$ of $k_1 = k_1^{\text{min}}$. The left and right hand limits of $dk_1/dt$ exist at the points of discontinuity.

**Proof**

$dk_1/dt$ does not exist at points of discontinuity of $k_1$, so we are concerned only with the behavior of $dk_1/dt$ at points of discontinuity of $k_1$. At interior points of intervals where $k_1 = k_1^{\text{min}}$ or $k_1^{\text{max}}$, $dk_1/dt$ is certainly continuous, as it vanishes identically. At interior points of intervals where $k_1^{\text{min}} < k_1 < k_1^{\text{max}}$, the Hamiltonian is maximized with respect to $k_1$ at a stationary value, for which $\partial H/\partial k_1 = 0$. Hence

$$k_1^{p-1} = \frac{1 - \lambda_a - \lambda_b}{\alpha p b^{n-1} (\lambda_a + n\lambda_b)} \quad (2.5-1)$$

Differentiating and noting that the denominator cannot vanish if $k_1$ is to lie in $(k_1^{\text{min}}, k_1^{\text{max}})$, and that $d\lambda_a/dt$ and $d\lambda_b/dt$ are continuous, since we are concerned with points of continuity of $k_1$, it is seen that $dk_1/dt$ is continuous except at discontinuities of $db/dt$, i.e. at discontinuities of $r$. 
Apart from discontinuities of $dk_1/dt$ at points of discontinuity of $k_1$ and of $r$, therefore, $dk_1/dt$ can have discontinuities only where an interval with $\partial H / \partial k_1 = 0$ meets an interval with $k_1 = k_1^{\text{min}}$ or $k_1 = k_1^{\text{max}}$.

It is clear that the left and right hand limits of $dk_1/dt$ exist at all the discontinuities identified above.

**Lemma 5**

For an optimal control policy $\lambda_b$ has a piecewise continuous second derivative in $(0, \tau)$. Discontinuities of $d^2 \lambda_b/dt^2$ may occur at discontinuities of $r$ and discontinuities of $dk_1/dt$. The left and right hand limits of $d^2 \lambda_b/dt^2$ exist at the points of discontinuity.

**Proof**

Direct differentialtional of equation (2.4-7) is possible at all points of continuity of $r$ and $dk_1/dt$. Thus, $d^2 \lambda_b/dt^2$ exists at all these points. It follows that discontinuities of $d^2 \lambda_b/dt^2$ must coincide with discontinuities of $r$ or $dk_1/dt$, and hence that $d^2 \lambda_b/dt^2$ is piecewise continuous. Since the left and right hand limits of both $r$ and $dk_1/dt$ exist at their points of discontinuity, it follows that the same is true for $d^2 \lambda_b/dt^2$. 
**Lemma 6**

For an optimal policy

\[ \gamma \leq QN(Q)/r_m \]  

(2.5-2)

**Proof**

We have to consider only \( \gamma > 0 \) since the result is trivially true for \( \gamma \leq 0 \). Then \( \lambda_b + \gamma > 0 \) at \( t = \tau \) and, since \( (\lambda_b + \gamma) \) is continuous and \( d/dt(\lambda_b + \gamma) \) is smaller in magnitude than \( N(Q) \), it follows that \( (\lambda_b + \gamma) > 0 \) throughout some interval \([t', \tau]\), where \( \tau - t' > \gamma/N(Q) \). But when \( \lambda_b + \gamma > 0 \), \( H \) is maximized by \( r = r_m \). Thus, \( r = r_m \) throughout this interval, and it follows from Lemma 1 that

\[ \gamma/N(Q) \leq \tau - t' < Q/r_m \text{ or } \gamma \leq QN(Q)/r_m \]

**Lemma 7**

For an optimal control policy there is no value of \( t \in (0, \tau) \) such that \( k_{1 \min} < k_1(t) < k_{1 \max} \) and \( d\lambda_b/dt = 0 \), unless \( n = p \).

**Proof**

For an optimal control policy \( k_{1 \min} < k_1(t) < k_{1 \max} \) only if \( k_1 \) corresponds to a stationary maximum value of \( H \), or

\[ ab(\lambda_a + \lambda_b - 1) + \alpha pk_1^{p-1} ab^n(\lambda_a + n\lambda_b) = 0 \]  

(2.5-3)
If $d\lambda_b/dt = 0$, on the other hand, it follows from equation (2.4-7) that

$$k_1 a(\lambda_a + \lambda_b - 1) + \alpha n k_1^p a b^{n-1}(\lambda_a + n \lambda_b) = 0 \tag{2.5-4}$$

A single value of $k_1$ satisfies both these equations only if

(i) $\lambda_a + \lambda_b - 1 = 0$, or

(ii) $n = p$

Case (i) gives $k_1 = 0$, which lies outside the specified range, so only case (ii) is relevant, and the Lemma follows.

**Lemma 8**

For an optimal policy, with $p \neq n$, and for sufficiently large values of $r_m$, the function $\lambda_b(t)$ may not have a local maximum value within a time interval in which $r = r_m$.

**Proof**

It is first necessary to dispose of the possibility that $\lambda_b$ may have a local maximum at a point of discontinuity of $k_1$. When $p > 1$, it was shown in Theorem 1 that $k_1$ is continuous, so this question does not arise, and we need only to
consider \( p \leq 1 \). As in the proof of Theorem 1, it is seen that discontinuities of \( k_1 \) may occur only when

\[
\tilde{H} = k_{1ab}(1 - \lambda_a - \lambda_b) - \kappa k_{1ab}^n(\lambda_a + n\lambda_b)
\]

has two equal maxima when regarded as a function of \( k_1 \), and of Figs. 4, 5, and 6, in which all possible forms of \( \tilde{H} \) are sketched, reveals that this can happen only in cases 2a, 2i and 3c. In case 2i, however,

\[
1 - \lambda_a - \lambda_b = 0 \quad \text{and} \quad \lambda_a + n\lambda_b = 0
\]

and, in proving part (b) of Theorem 1, it was shown that there can be no discontinuity of \( k_1 \) at a point where

\[
1 - \lambda_a - \lambda_b \leq 0 \quad \text{and} \quad \lambda_a + n\lambda_b \leq 0
\]

provided \( r_m \) is sufficiently large.

Thus, when \( p < 1 \), a discontinuity of \( k_1 \), can occur only in case 2a of Fig. 4, for which

\[
(1 - \lambda_a - \lambda_b) > 0 \quad \text{and} \quad (\lambda_a + n\lambda_b) > 0.
\]

when \( p = 1 \), \( \tilde{H} \) may have two equal maxima only in case 3c of
Fig. 6, for which the condition

\[ ab(1 - \lambda_a - \lambda_b) - \alpha ab^n(\lambda_a + n\lambda_b) = 0 \]

must be satisfied. But since \( ab \) and \( \alpha ab^n \) are both positive, \((1 - \lambda_a - \lambda_b) \) and \((\lambda_a + n\lambda_b) \) must either both vanish, or both have the same value in order to satisfy the relation. However, the cases \((1 - \lambda_a - \lambda_b) < 0, (\lambda_a + n\lambda_b) < 0 \) and \((1 - \lambda_a - \lambda_b) = 0, (\lambda_a + n\lambda_b) = 0 \) may not correspond to a discontinuity of \( k_1 \) if \( r_m \) is sufficiently large, by the argument used in proving part (b) of Theorem 1. Thus, when \( p = 1 \), a discontinuity of \( k_1 \), can occur only at a point where

\[ (1 - \lambda_a - \lambda_b) > 0 \quad \text{and} \quad (\lambda_a + n\lambda_b) > 0 \]

and we have now shown that these inequalities must be at any discontinuity of \( k_1 \), provided \( r_m \) is sufficiently large. Now suppose \( k_1 \) takes the limiting values \( k_1' \) and \( k_1'' \) on approaching the discontinuity from the left and the right respectively, and denote by \((d\lambda_b/dt)' \) and \((d\lambda_b/dt)'' \) the corresponding limiting values of \( d\lambda_b/dt \). \((\lambda_a, \lambda_b, a, \text{and } b \) are, of course, continuous at this point). Then, from equation (2.4-7)
\[ b(d \lambda_b / dt)' = - \{ k_1'ab(1- \lambda_a - \lambda_b) - k_2'ab^n(\lambda_a + n \lambda_b) \} + \]

\[ (n-1)k_2'ab^n(\lambda_a + n \lambda_b) \quad \text{and} \]

\[ b(d \lambda_b / dt)'' = - \{ k_1''ab(1- \lambda_a - \lambda_b) - k_2''ab^n(\lambda_a + n \lambda_b) \} + \]

\[ (n-1)k_2''ab^n(\lambda_a + n \lambda_b) \]

But the quantity in braces in the right hand side in each case is the value of \( \tilde{H} \), and examination of Fig. 4 case 2a and Fig. 6 case 3a shows that \( \tilde{H}' = \tilde{H}'' \leq 0 \). Furthermore, \( n > 1 \) and \( (\lambda_a + n \lambda_b) > 0 \) at a point of discontinuity of \( k_1 \), as already shown. It therefore follows that

\[ (d\lambda_b / dt)' > 0 \quad \text{and} \quad (d\lambda_b / dt)'' > 0 \]

and hence the point of discontinuity of \( k_1 \) is not extremum of \( \lambda_b \).

Any local maximum at an interior point of a time interval in which \( r = r_m \) must therefore be a stationary point. Then, by Lemma 7, \( k_1 = k_1^{\text{min}} \) or \( k_1 = k_1^{\text{max}} \) at this point, provided \( p \neq n \). But at any such point \( dk_1/dt \) vanishes, or, if the point coincided with an end point of an interval
in which \( k_1 = k_1^{\min} \) or \( k_1 = k_1^{\max} \), the limit of \( dk_1/dt \) on approaching the point from within this interval vanishes.

Consider the value of \( d^2 \lambda_b/dt^2 \) at the stationary point, or, when appropriate as above, the limit of \( d^2 \lambda_b/dt^2 \) on approaching the stationary point from within an adjacent interval of constant \( k_1 \). This derivative can be found by differentiation of equation (2.4-7)

\[
\left( \frac{d^2 \lambda_b}{dt^2} \right)_s = a(k_1 + nk_2 b^{n-1}) \frac{d \lambda_a}{dt} + n(n-1) k_2 ab^{n-2}.
\]

\[
(\lambda_a + n \lambda_b) \frac{db}{dt}
\]

(2.5-5)

after using the condition \( d \lambda_b/dt = 0 \) at the stationary point. Again, the left hand side is to be interpreted as a limit if necessary. From equations (2.4-6) and (2.4-7) it also follows that

\[
d \lambda_a/dt = -k_2(n-1) b^n(\lambda_a + n \lambda_b)
\]

(2.5-6)

where \( d \lambda_b/dt = 0 \). Thus
\[
\left( \frac{d^2 \lambda_b}{dt^2} \right)_s = (n-1)k_2 a^n b^{n-2} \left( \lambda_a + n \lambda_b \right) \left\{ nr_m - nk_1 a b - n^2 k_2 a b^n \right. \\
- k_1 b^2 - nk_2 b^{n+1} \right\} \quad (2.5-7)
\]

For sufficiently large values of \( r_m \), for example

\[
r_m > k_1 \text{max} a_0 Q + nk_2 \text{max} a_0 Q^n + \frac{k \text{max} Q^2}{n} + k_2 \text{max} n+1 Q
\]

(2.5-8)

The term in braces in (2.5-7) is positive. Since \( n > 1 \) and \( k_2 > 0 \), it follows that \( \left( \frac{d^2 \lambda_b}{dt^2} \right)_s \) has the sign of \( \left( \lambda_a + n \lambda_b \right) \), which we now consider.

Since the stationary point lies within an interval where \( r = r_m \) and the control policy is optimal, \( \left( \lambda_b + \gamma \right) > 0 \) at the stationary point. (Otherwise \( r = r_m \) would not maximize \( H \).) Thus, using Lemma 6

\[
\lambda_b \gg -\gamma \gg -Q N/r_m
\]

Now suppose \( \left( \lambda_a + n \lambda_b \right) \leq 0 \). Then \( \lambda_a + \lambda_b \leq - (n-1) \lambda_b \) or, using the above inequality

\[
\lambda_a + \lambda_b \leq (n-1) \frac{Q N}{r_m}
\]
Thus,

\[ 1 - \lambda_a - \lambda_b \geq 1 - (n-1) Q N/r_m \]

Recalling that \( N \) does not depend on \( r_m \) (by Lemma 3), it follows that \( 1 - \lambda_a - \lambda_b > 0 \), provided

\[ r_m > (n-1) Q N \quad (2.5-9) \]

But at a stationary point of \( \lambda_b \), equation (2.4-7) shows that either

\[ 1 - \lambda_a - \lambda_b = \alpha nk_1 p^{-1} b^{n-1} (\lambda_a + n\lambda_b), (k_1 \neq 0) \quad (2.5-10) \]

or \( k_1 = 0 \). But \( k_1 = 0 \) does not lie in the permitted interval, so we need only consider (2.5-10) which shows that \( (\lambda_a + n\lambda_b) \) has the same sign as \( (1 - \lambda_a - \lambda_b) \), and hence that \( (\lambda_a + n\lambda_b) > 0 \), which contradicts our initial hypothesis that \( (\lambda_a + n\lambda_b) \leq 0 \).

We conclude that \( (\lambda_a + n\lambda_b) > 0 \) and hence, from (2.5-7) that \( (d^2 \lambda_b/dt^2)_s > 0 \). Thus, the stationary value of \( \lambda_b(t) \) cannot be a local maximum.

**Lemma 9**

For an optimal policy, with \( p \neq n \), the function \( \lambda_b(t) \)
may not have a local minimum value within a time interval in which \( r = 0 \).

**Proof**

According to Theorem 1 (a), there are no discontinuities of \( k_1 \) in an interval where \( r = 0 \). Thus, the reasoning leading to equation (2.5-7) in Lemma 8 is still valid in this case, except that \( r = r_m \) must be replaced by \( r = 0 \) in equation (2.5-7), giving

\[
\left( \frac{d^2 \lambda_b}{dt^2} \right)_s = -(n-1)k_2a^n b^{n-1}(\lambda_a + n\lambda_b) \left\{ nk_1a + n^2k_2a b^{n-1} + k_1b + nk_2 b^n \right\} \tag{2.5-11}
\]

The term in braces is clearly positive so, since \( n > 1 \) and \( k_2 > 0 \), \( (d^2 \lambda_b/dt^2)_s \) has the opposite sign to \( (\lambda_a + n\lambda_b) \).

At \( t = T \) the Hamiltonian becomes

\[
H = \gamma r + k_1 a(T) b(T)
\]

and it is clear that its maximum value, \( H_{\text{max}}(T) \), with respect to \( r \) and \( k_1 \), is positive, irrespective of the sign of \( \gamma \). Furthermore, from the maximum principle (condition 2), \( H_{\text{max}} \) has the same value at all points of an optimum trajectory and, in particular, equating its value at a point where \( r = 0 \) to its final value
\[ H_{\text{max}}(T) = k_1 \; ab(1 - \lambda_a - \lambda_b) - k_2 \; ab^n(\lambda_a + n \lambda_b) \]

at a stationary point of \( \lambda_b \), using equation (2.4-7), this reduces to

\[ H_{\text{max}}(T) = (n-1) \; k_2 \; ab^n(\lambda_a + n \lambda_b) > 0 \]

whence it follows that \( (\lambda_a + n \lambda_b) > 0 \). Thus, \( (d^2 \lambda_b/dt^2)_s < 0 \) and the stationary point cannot be a minimum.

**THEOREM 3**

When \( p \neq n \):

(i) For an optimal control policy there exists no interval \((t_1, t_2), 0 < t_1, t_2 < T\), such that \( r = 0 \) for all \( t \in (t_1, t_2) \) and \( \lambda_b(t_1) + \gamma = \lambda_b(t_2) + \gamma = 0 \).

(ii) For an optimal control policy provided \( r_m \) is sufficiently large, there exists no interval \((t_1, t_2), 0 < t_1, t_2 < T\), such that \( r = r_m \) for all \( t \in (t_1, t_2) \) and \( \lambda_b(t_1) + \gamma = \lambda_b(t_2) + \gamma = 0 \).

**Proof**

(i) \( (\lambda_b + \gamma) \) is continuous in \([t_1, t_2]\), so it attains its relative minimum value in this interval. Furthermore, this minimum value is negative, since
a) \( \lambda_b + \gamma \) is nowhere positive in \((t_1, t_2)\), otherwise \( r \) would take the value \( r_m \) in some neighborhood of such a point.

b) \( \lambda_b + \gamma \) does not vanish identically in \([t_1, t_2]\), otherwise \( r \) would take values appropriate to a singular segment, as given in Theorem 6 below, rather than the specified value zero.

Since \((\lambda_b + \gamma) = 0 \) at \( t = t_1, t_2 \), the minimum occurs at an interior point. But this contradicts Lemma 9, and we conclude that no interval of the type described may exist.

(ii) The proof of the second part follows exactly similar lines, within "minimum" replaced by "maximum," the sign of \((\lambda_b + \gamma) \) reversed, and \( r = 0 \) replaced by \( r = r_m \). Thus, one is led to the existence of a stationary minimum of \( \lambda_b \) at an interior point, and this contradicts the result of Lemma 8 for sufficiently large \( r_m \).

**THEOREM 4**

For an optimal policy, provided \( r_m \) is sufficiently large, there exists no interval \((t_1, \tau]\), \( t_1 > 0 \), such that \( r = r_m \) for all \( t \in (t_1, \tau] \).
Proof

If there exists such an interval at all, there exists such an interval with $\lambda_b(t_1) + \gamma = 0$, since the interval with $r = r_m$ cannot have length $\tau$, for sufficiently large $r_m$ (Lemma 1), and $(\lambda_b + \gamma)$ must vanish at its left terminal point.

$(\lambda_b + \gamma)$ is continuous in $[t_1, \tau]$, so it attains its maximum value and, as in Theorem 3, the fact that $r = r_m$ throughout $[t, \tau]$ implies that this maximum value is positive. It cannot therefore occur at $t_1$. Furthermore, $d/dt (\lambda_b + \gamma) = d\lambda_b/dt = -k_1 a < 0$ at $t = \tau$, so the maximum cannot occur at $t = \tau$. It must, therefore, occur at an interior point; which again contradicts Lemma 8.

COROLLARY

For sufficiently large $r_m$, $\gamma \leq 0$ for an optimal policy

Proof

From Theorem 4 there exists a closed interval with $\tau$ as its right hand end point on which $\lambda_b + \gamma \leq 0$. Since $\lambda_b(\tau) = 0$ and $|d\lambda_b/dt|$ is bounded by $N$, with a value independent of $r_m$, it follows that $\gamma \leq 0$. 
**Lemma 10**

For given values of $Q$, $r_m$, $k_1^{\min}$ and $k_1^{\max}$, the maximum value of $c(\tau)$ is a monotone increasing function of $\tau$.

**Proof**

Suppose $r$ is chosen optimally in $[0, \tau]$, with

$$\int_0^\tau r \, dt = Q.$$  

In $(\tau, \tau_1)$, $\tau_1 > \tau$, set $r = 0$. $dc/dt > 0$ everywhere in this interval, as seen from equation (2.4-3), so $c(\tau_1) > c(\tau)$, while $Q$ and $r_m$ are unchanged. Thus, there exists a policy in $[0, \tau_1]$ such that $c(\tau_1) > \max c(\tau)$ when $\tau_1 > \tau$, and it follows a fortiori that $\max (c(\tau_1)) > \max (c(\tau))$.

**Theorem 5**

For an optimal policy there exists no interval $(0, t_1)$, $0 < t_1 < \tau$, such that $r = 0$ for all $t \in (0, t_1)$.

**Proof**

In such an interval $b = 0$, so $a(t_1) = a_0$ and $b(t_1) = 0$. Thus, the initial conditions are simply transferred to $t = t_1$, and the control policy, which is constrained by the same values of $Q$, $r_m$, $k_1^{\min}$, and $k_1^{\max}$, must now operate during the time interval $t \to t_1 < \tau$. It follows from Lemma 10 that the final value of $c$ is less than $\max(c(\tau))$, with the policy freely available over the whole interval $[0, \tau]$. 
Thus, a policy with an initial interval $r = 0$ cannot be an optimal policy.

**THEOREM 6**

If an optimal policy includes an interval of non-zero length in which $0 < r < r_m$ everywhere, then

(a) $\lambda_b = -y$, $\lambda_a = \frac{k_1 + y(k_1 + n^2_k_2 b^{n-1})}{k_1 + nk_2 b^{n-1}}$

(b) $\frac{(n-1)k_1 k_2 a b^n}{k_1 + n k_2 b^{n-1}} \left[ 1 - y(n-1) \right]$

$$k_1 \max_{\tau} a(\tau) b(\tau) + r_m y \text{sgn}'(y)$$

where

$$\text{sgn}'(y) = 1 \quad \text{for } y > 0$$

$$= 0 \quad \text{for } y \leq 0$$

and

(c) $r = (k_1 + n k_2 b^{n-1}) b(a + b/n)$

(The part of the optimum trajectory corresponding to such an interval will be called a singular segment.)
Proof

\[ \lambda_b \equiv -\gamma \] implies that \( d\lambda_b/dt = 0 \), and substituting these into equation (2.4-7) and solving for \( \lambda_a \) establishes result (a) above.

Using these values of \( \lambda_a \) and \( \lambda_b \) on equation (2.4-10) an expression for the Hamiltonian can be found in terms of the physical variables only. Equating the value of this on the trajectory to the maximum value of the Hamiltonian at \( t = T \), as required by the maximum principle, result (b) follows.

To prove part (c) we need to refer to the proofs of Theorems 9 and 10 below, where it is shown that \( k_1 \) takes the constant value \( k_1^{\min} \) of \( k_1^{\max} \) on a singular segment, depending on the sign of \( (n-p) \), and this is shown without reference to the result we are at present attempting to prove.

We may thus differentiate with respect to time the expression given for \( \lambda_a \) in result (a), treating \( k_1 \) and \( k_2 \) as constants. Substituting for \( d\lambda_a/dt \) in the result from equation (2.4-6), and for \( db/dt \) from equation (2.4-2), and using the values of \( \lambda_a \) and \( \lambda_b \) already found, the desired expression for \( r \) is obtained.
THEOREM 7

(i) The initial point $t = 0$ may not belong to a singular segment.

(ii) The final point $t = \tau$ may not belong to a singular segment.

Proof

(i) At the initial point $a = a_0$ and $b = 0$. But examination of Theorem 6(b) shows that the curve representing the singular segment parametrically in the $(a,b)$-plane does not pass through $(a_0,0)$.

(ii) $d\lambda_b/dt = -k_1 a(\tau)$ at $t = \tau$. Thus, $d\lambda_b/dt < 0$ at $t = \tau$ and, since $d\lambda_b/dt$ is continuous, there exists a non-zero interval adjacent to $t = \tau$ in which $d\lambda_b/dt < 0$. But it is necessary that $d\lambda_b/dt = 0$ on a singular segment, so this interval may not be part of such a segment.

THEOREM 8

For an optimal policy, provided $r_m$ is sufficiently large, the function $r(t)$ must take one of the two forms indicated in Figure 7.

Proof

By Theorems 5 and 7(i), an optimal policy must start
FIG. 7 - OPTIMUM r-POLICY
with an interval in which \( r = r_m \). This cannot continue to \( t = T \), provided \( r_m T > Q \). Suppose, therefore, that it terminates at \( t = t_1 < T \). Then \( \lambda_b(t_1) + \gamma = 0 \) if the maximum principle is to be satisfied. Adjacent to the above interval in \( t > t_1 \) must be either an interval with \( r = 0 \), or an interval occupied by a singular segment. In the former case, the interval with \( r = 0 \) must extend to \( t = T \), for if it terminated at some \( t_2 < T \), \( \lambda_b(t_2) + \gamma = 0 \), and Theorem 3(i) would be violated. Thus, we have the control policy shown in Figure (7,a).

In the latter case, the singular segment must terminate at some \( t_2 < T \), or Theorem 7(ii) would be violated. It cannot be followed by an interval in which \( r = r_m \), for if this interval terminated at some \( t_3 < T \), Theorem 3(ii) would be violated, while if it continued to \( t = T \), Theorem 4 would be violated. Thus, the singular segment must be followed by an interval with \( r = 0 \) and, if Theorem 3(i) is not to be violated, this must extend to \( t = T \), giving the policy shown in Figure (7,b).

**Theorem 9**

For an optimal policy, when \( r_m \) is sufficiently large and \( p > n \), \( k_1 = k_1^{\max} \) for all \( t > t_1 \), where \( t_1 \) is the terminus of
the initial interval with \( r = r_m \). (See Figure 7.)

**Proof**

In the general expression for \( \partial H / \partial k_1 \) obtained by differentiating equation (2.4-10), substitute the values of \( \lambda_a \) and \( \lambda_b \) on the singular segment, as given by Theorem 6(a). Then

\[
\frac{\partial H}{\partial k_1} = \frac{k_2 ab^n \cdot [1 - \gamma(n-1)] \cdot (n-p)}{(k_1 + n k_2 b^{n-1})}
\]

But \( n > 1 \), and for sufficiently large \( r_m \) we know that \( \gamma \leq 0 \), so \( \partial H / \partial k_1 > 0 \) when \( p < n \). It follows that the singular segment can form part of an optimal policy only if \( k_1 = k_1^{\text{max}} \) everywhere on it.

Consider now the final interval with \( r = 0 \), i.e., the interval \((t_1, T]\) in Figure (7,a) or in the interval \((t_2, T]\) in Figure (7,b). Denote the initial point of this interval by \( t' \), where \( t' = t_1 \) or \( t_2 \) in the cases represented by Figures (7,a) and (7,b), respectively. We know that

\[
\lambda_b(t') + \gamma = 0; \quad \lambda_b(t) + \gamma \leq 0, \quad t \in [t', T]; \quad \lambda_b(T) = 0
\]

and that \( \gamma \leq 0 \) for sufficiently large \( r_m \). Since \( \lambda_b \) is continuously differentiable, for \( p > n > 1 \), it follows that
\[ \frac{d A}{dt} \leq 0 \text{ at } t = t', \text{ and } t' \text{ may not be the left hand end point of an interval in which } \frac{d \lambda}{dt} = 0, \text{ or this interval would correspond to a singular segment, contrary to the hypothesis that } r = 0 \text{ in } (t', T] . \] 
Thus, recalling that \( \frac{d \lambda}{dt} \) is continuous, there exists some interval \((t', t' + \epsilon)\) in which \( \frac{d \lambda}{dt} < 0 \). Then, if \( \frac{d \lambda}{dt} \geq 0 \) at any point \( t'' \) of \((t', T)\), there exists a value \( t''' \) of \( t, t''' \in (t', t'') \), such that \( \lambda(t) \) has a stationary minimum value at \( t''' \). But this violates Lemma 9, so we conclude that \( \frac{d \lambda}{dt} < 0 \) for all \( t \in (t', T) \). This implies that \( 0 < \lambda < -\gamma \) for all \( t \in (t', T] \).

Since the interval \((t', T] \) is part of an optimal policy, 

\[ H_{\text{max}}(t) = H_{\text{max}} > 0 \text{ for all } t \in (t', T] \] 
and, since \( r = 0 \),
this gives

\[ k_1 b(\lambda_a + \lambda_b - 1) + k_2 b^n(\lambda_a + n \lambda_b) < 0 \text{ for all } t \in (t', T] \]

Hence, from equation (2.4-6), \( \frac{d \lambda}{dt} < 0 \) for all \( t \in (t', T) \),
so

\[ \lambda_a(t) > \lambda_a(T) = 0 \text{ for all } t \in (t', T) . \]

From this inequality, and the corresponding inequality previously found for \( \lambda_b(t) \), it is seen that

\[ (\lambda_a + n \lambda_b) > 0 \text{ for all } t \in (t', T) \]
and, incidentally, $\lambda_a + n \lambda_b$ decreases monotonically to zero in this interval.

Since $d \lambda_b/dt < 0$ in $(t', T)$, equation (2.4-7) shows that

$$ab(1 - \lambda_a - \lambda_b) > \frac{nk_2}{k_1} ab^n(\lambda_a + n \lambda_b)$$

for all $t \in (t', T)$ \hspace{1cm} (2.5-12)

From equation (2.4-10)

$$\frac{\partial H}{\partial k_1} = ab(1 - \lambda_a - \lambda_b) - \frac{pk_2}{k_1} ab^n(\lambda_a + n \lambda_b)$$

and, using (2.5-12) above

$$\frac{\partial H}{\partial k_1} > \frac{(n-p)k_2}{k_1} 2 ab^n(\lambda_a + n \lambda_b)$$ for all $t \in (t', T)$

But we have shown that $(\lambda_a + n \lambda_b) > 0$, so $\partial H/\partial k_1 > 0$ when $p < n$, for all $t \in (t', T)$. Thus, this interval can form part of an optimal policy only if $k_1 = k_1^{\text{max}}$ everywhere on it. This completes the proof.
THEOREM 10

When \( p > n \), for sufficiently large \( r_m \) and sufficiently small \( k_1^{\min} \), the optimal policy contains no singular segment.

Proof

On a singular segment it has already been shown that

\[
\frac{\partial H}{\partial k_1} = \frac{k_2 a b^n [1 - \gamma(n-1)] (n-p)}{(k_1 + n k_2 a b^{n-1})}
\]

For sufficiently large \( r_m \), \( \gamma \leq 0 \) (Corollary to Theorem 4), so for \( p > n > 1 \), \( \frac{\partial H}{\partial k_1} < 0 \) on the singular segment, which can therefore form part of an optimal policy only if \( k_1 = k_1^{\min} \) everywhere on it.

The equation of the singular segment in the \((a,b)\)-plane can be written (Theorem 6(b))

\[
\frac{(n-1) a b^n [1 - \gamma(n-1)]}{k_1^{\max} a(\tau)b(\tau)} = \frac{k_1^{\min} + n k_2^{\min} b^{n-1}}{k_1^{\min} k_2^{\min}} = \frac{1 + n a(k_1^{\min}) p^{-1} b^{n-1}}{k_1^{\min} p^{\min}} \tag{2.5-13}
\]

We now establish a contradiction by showing that the left hand side is bounded above by a bound independent of
\(k_1^{min}\), while the right hand side increases without bound as \(k_1^{min} \to 0\).

It is easy to show (see Appendix 2) that \(b^{n-1}, b/b(T)\) and \(a/a(T)\) are bounded above by bounds independent of \(k_1^{min}\). Now we consider the factors \([1 - \gamma(n-1)]\). Since \(\gamma \leq 0\) for sufficiently large \(r_m\) (Corollary to Theorem 4), this factor is equal to \([1 + |\gamma| \cdot (n-1)]\), and we need to seek a bound for \(|\gamma|\). Since we consider points on a singular segment, however, \(\lambda_b + \gamma = 0\), so \(|\gamma| = |\lambda_b|\).

But it was shown in Lemma 3 that \(|\lambda_b|\) is bounded above by a bound independent of \(r_m\) for a given value of \(Q\), and the same proof also establishes the existence of a bound independent of \(k_1^{min}\) for a given value of \(Q\). This is also a bound for \(|\gamma|\), so the left hand side of equation (2.5-13) is indeed bounded above by a bound independent of \(k_1^{min}\).

For sufficiently small values of \(k_1^{min}\), therefore, equation (2.5-13) leads to a contradiction, and we conclude that a singular segment may not then form part of an optimal policy.

2.6 SYNTHESIS OF THE OPTIMAL POLICY

Summarizing our previous results we can say this much about the optimal simultaneous \(r\) and \(T\) control.
The nature of the optimal policy depends on the relative values of the activation energies \( p \) and the ratio of the orders of reaction \( n \) with respect to the distributed reactant. There is a sudden change in the nature of the control policy on passing from \( p < n \) to \( p > n \).

When \( p < n \), we know that, in the case of \( r_m \) large, we shall start with \( r = r_m \) over some interval \( (0, t_1) \); after which we shall have the temperature of its maximum permissible value and control by variation of \( r \), giving one of the two possibilities shown in Fig. 7. As we increase \( r_m \), \( t_1 \) goes to zero, and in the asymptotic case \( r_m \to \infty \) we shall have isothermal control at the maximum temperature (Theorem 9). Some fraction of \( Q \) is then dumped into the reactor, and further control is by \( r \) regulation.

When \( p > n \), we still have one of the two possibilities shown in Fig. 7, if \( r_m \) is large enough. Furthermore, if \( k_1^{\text{min}} \) is sufficiently small we eliminate the singular segment by Theorem 10; so that we are left only with policies like those in Fig. 7,a, comprising a segment in which the total amount \( Q \) of \( B \) is dumped at \( r_{\text{max}} \) in the interval \( (0, t_1) \), followed by zero addition of \( B \) in \( (t_1, \tau] \). Again as we let \( r_{\text{max}} \to \infty \), still keeping \( k_1^{\text{min}} \) small and retaining the same value of \( Q \), we make \( t_1 \to 0 \). Thus we pass, in the limit, to pure batch operation with optimization by controlling the
temperature only. As is common for this case, we get a non-decreasing temperature profile, ending in $T = T_{\text{max}}$ at $t = \tau$. (This can be proved; see Appendix 3).

We still have some cases not covered by this analysis, namely: $n = p$, or $r_{\text{max}}$ not large, or $k_1^{\text{min}}$ not small. Some of them are very particular (i.e., $n = p$) and may not need a complete analysis; others are quite important but general reasoning leading to the optimal control policy is less easy to obtain.
3.1 NUMERICAL PROCEDURES AND SOME RESULTS

As was seen in Chapter II, the form of the optimal control policy depends on the relative values of $p$ and $n$, and changes suddenly as the ratio $p/n$ passes across 1.

For the case $p < n$ and $r_{\text{max}} = \infty$ the temperature is at its maximum value, and a typical optimum $r$ profile can be seen in Fig. 11 taken from Senior's work (11). (The values of the problem parameters are given in the caption to Fig. 11). We notice here that the optimum $r(t)$ is independent of $p$, and consists of three parts, namely a delta function at $t = 0$, giving $b(0) = 0.1857$, a singular segment in which the rest of $Q$ is added and a final coasting segment with $r = 0$.

Curve (a) in Fig. 12 shows the value of $c(\tau)$ for isothermal operation with $r$-control, and may be compared with curve (b) showing $c(\tau)$ for pure batch operation with optimum temperature control. The superiority of $r$-control when $p < n$ is clear; indeed the two curves cross at $p = n$.

Notice that $c(\tau)$ is independent of $p$, as previously remarked, when $p < n$. A second example with $Q = 1.2$ is shown
in Fig. 23.

For \( p > n \), we have the following optimization problem as posed in section 2.4 i.e.: solution of the following differential system with the given optimization criteria

\[
\begin{align*}
\frac{d\lambda_a}{dt} &= k_1 b (\lambda_a + \lambda_b - 1) + k_2 b^n (\lambda_a + n \lambda_b), \\
\lambda_a(\tau) &= 0 \\
\frac{d\lambda_b}{dt} &= k_1 a (\lambda_a + \lambda_b - 1) + nk_2 ab^{n-1} \\
(\lambda_a + n \lambda_b), \quad \lambda_b(\tau) &= 0 \\
\frac{d\mu}{dt} &= 0; \quad \mu(\tau) = \gamma \text{ (unspecified initially)}
\end{align*}
\]

with \( k_1 \) and \( r \) to be chosen as to maximize
\[ H = (\lambda_b + \gamma) r + k_{1ab}(1 - \lambda_a - \lambda_b) - k_{2ab^n}(\lambda_a + n\lambda_b) \]  

(3.1-7)

with respect to \( r \) and \( k_1 \).

For our case at hand, \( p > n, k_1^{\text{min}} \) small and \( r_{\text{max}} \) large we proved in Chapter II that all \( Q \) has to be added at the beginning and \( r = 0 \) in \( (0, \tau) \). Consequently we eliminate equations (3.1-3) and (3.1-6), make \( b(0) = Q \) in (3.1-2) and eliminate the first term of (3.1-7). So we are left with

\[
\frac{da}{dt} = -k_{1ab} - k_{2ab^n}; \quad a(0) = a_0 \quad (3.1-8)
\]

\[
\frac{db}{dt} = -k_{1ab} - nk_{2ab^n}; \quad b(0) = Q \quad (3.1-9)
\]

\[
\frac{d\lambda_a}{dt} = k_{1b}(\lambda_a + \lambda_b - 1) + k_{2b^n}(\lambda_a + n\lambda_b); \quad \lambda_a(\tau) = 0 \quad (3.1-10)
\]

\[
\frac{d\lambda_b}{dt} = k_{1a}(\lambda_a + \lambda_b - 1) + nk_{2ab^{n-1}}(\lambda_a + n\lambda_b); \quad \lambda_b(\tau) = 0 \quad (3.1-11)
\]

with \( k_1 \) to be chosen as to maximize at every point in \([0, \tau]\)
The straightforward manner to solve this two-point boundary value problem is to guess the unknown variables at one end i.e.: \( \lambda_a(0) \) and \( \lambda_b(0) \) or \( a(T) \) and \( b(T) \) and integrate the state and adjoint equations with \( k_b \) chosen in \([ k_b^{\text{min}}, k_b^{\text{max}} ]\) so as to maximize \( H \) at each point. We will not match in general the boundary conditions given at the other end (i.e. \( \lambda_a(T) \) and \( \lambda_b(T) \) or \( a(0) \) and \( b(0) \) and an iterative procedure to improve the guessed values will be necessary.

For our problem that procedure would involve a two dimensional search that we can avoid by the procedure now to be described. Since the optimum \( k_1(t) \) is continuous (Theorem 1) and provided \( k_1^{\text{min}} \) is small and \( r_{\text{max}} \) is large, we shall have a \( k_1 \) policy comprising, at most, a segment with \( k_1 \equiv k_1^{\text{min}} \) followed by a segment of monotone increasing \( k_1 \), on which \( H \) has a stationary maximum with respect to \( k_1 \), followed by \( k_1 \equiv k_1^{\text{max}} \) up to \( t = T \).

During the stationary segment of \( H \) with respect to \( k_1 \), \( \partial H / \partial k_1 = 0 \) so that \( d/dt( \partial H / \partial k_1 ) = 0 \)

\[
\frac{d}{dt} \left[ k_1ab(\lambda_a + \lambda_b - 1) + k_2ab^n \right] \left( \lambda_a + n \lambda_b \right) = 0
\]
which after differentiation, replacement of the expressions for \( \frac{da}{dt}, \frac{db}{dt}, \frac{d\lambda_a}{dt}, \) and \( \frac{d\lambda_b}{dt} \) and some algebraic cancellations give an expression for \( \frac{dk_1}{dt} \) along the optimal trajectory if a stationary segment of \( H \) with respect to \( k_1 \) occurs, namely

\[
(\frac{dk_1}{dt})_S = k_1(b + na)(k_1 + pk_2b^{n-1})/p \quad (3.1-13)
\]

Thus, once \( k_1(0) \) is known, we can find the optimal policy by direct integration of (3.1-8), (3.1-9) with

\[
k_1 = k_1^{\min} \text{ in } (0, t_1)
\]

\[
k_1 = k_1 \text{ stationary in } (t_1, t_2) \text{ and }
\]

\[
k_1 = k_1^{\max} \text{ in } (t_2, T)
\]

But if \( k_1^{\min} \) is small enough we eliminate the segment with \( k = k_1^{\min} \) in \( (0, t_1) \). We can then integrate (3.1-8), (3.1-9) and (3.1-13) with a guessed value for \( k_1(0) \). The integration terminates where \( k_1 \) reaches the value \( k_1^{\max} \), and the trajectory is completed by integrating (3.1-8) and (3.1-9) on to \( t = T \) with \( k_1 = k_1^{\max} \).
It is then possible to guess $k_1(0)$ only and find the value for $k_1(0)$ which maximizes $c(T)$ by a one-dimensional search. Since we do not need the adjoint variables for this search, we integrate equations (3.1-10) and (3.1-11) backwards only after the optimal $k_1(0)$ (and optimal $k_1(t)$) is known. The resulting $\lambda_a$ and $\lambda_b$ trajectories may be used to check the constancy of $H_{\text{max}}$ along the solution and to check if Jackson and Senior's necessary condition for optimality of pure batch operation is satisfied with the optimal temperature profile.

In the computations we used a fifth order Runge-Kutta-Merson technique with automatic stepsizing; but because the integrated functions were reasonably well behaved and the automatic stepsizing was very time consuming we eliminated it after some initial calculations and used two different but fixed stepsizes, a small one for the segment of $H$ stationary with respect to $k_1$ and a bigger one for the segment with $k_1 = k_1^{\text{max}}$.

To determine $k_1(0)$ we used a Fibonacci search with an uncertainty in $k_1(0)$ optimum no greater than $10^{-6}$. As we made the backwards integration of the adjoint variables we checked the constancy of $H_{\text{max}}$ along the optimal trajectory within 1%, and the value of $|\partial H/\partial k_1|$ along the stationary region was nowhere greater then $10^{-3}$. 
To make a comparison with some existing results in Senior's work \(11\) we used the same parameters i.e.:
\[
\begin{align*}
a(0) &= 1.0, \\
Q &= 1.2 \text{ and } 2.5, \\
k_1^{\max} &= 1.0, \\
k_2^{\max} &= 2.0, \\
T &= 4.0 \text{ and } n = 2.
\end{align*}
\]
We made calculations for values of \(p = 1.0, 1.9, 2.0, 2.1, \text{ and } 3.0; Q = 2.5\) and the other parameters as shown above. The \(k_1\) profiles and adjoint variable trajectories are shown in Figs. 13 to 17, and the corresponding values of \(c(T)\) vs. \(p\) are shown in Fig. 12, curve (b).

We will emphasize again how the optimal policy breaks suddenly from \(p < n\) to \(p > n\), as can be seen in Fig. 12. Isothermic control at \(T^{\max}\) is better than pure batch operation with temperature control when \(p < n\) and vice versa for \(p > n\).

We can also check the satisfaction of Jackson and Senior's necessary condition on the \(\lambda\)'s for the optimality of the simultaneous addition of reactants at \(t = 0\) when \(p > n\) (Figs. 16, 17), namely \(\lambda_i(0) \geq \lambda_i(t)\) for all reactants and for all \(t \in [0, T]\), (reactants = all substances added to the reactor, here A and B). We notice that, for cases in which \(p < n\), the necessary condition is not satisfied and those cases are indeed non-optimal as seen in Fig. 12.

It is interesting to notice that the same necessary condition is satisfied for \(p = n\); in fact \(d\lambda_i/dt = 0\) along the stationary segment of \(H\) with respect to \(k_1\); but the
crossing of the two curves on Fig. 12 indicates the limiting nature of this case.

The same kind of results are found for $Q = 1.2$ as is shown in Figs. 18 to 23, where $p = 1.0, 1.9, 2.0, 2.1$ and 3.0; and the same conclusions can be drawn from them.

Finally, the optimum control policies found here should be compared with simple non-optimal operation. For pure batch operation, with all the available quantities of substances A and B added to the reactor at $t = 0$, and subsequent isothermal operation at $k_1 = k_1^{\text{max}}$, the value of $c(T)$ is 0.2475 for $Q = 2.5$ and the other problem parameters as given previously. This should be compared with the values of $c(T)$ shown in Fig. 12, using whichever curve is higher. For $Q = 1.2$, the simple pure batch isothermal policy gives a value of $c(T) = 0.3811$, and the higher value of $c(T)$ in Fig. 22 is used for the comparison. The relative improvements of $c(T)$ with respect to these simple policies are shown in Table 1.
### TABLE I
Relative Improvements of the Optimal Policies With Respect to Simple Policies

<table>
<thead>
<tr>
<th>Q</th>
<th>p</th>
<th>c(T) Optimal</th>
<th>% Improvement With Respect to Isothermal Batch at T^{max}</th>
<th>% Improvement with Respect to Isothermal Batch at T^{max} Using Optimum b(0)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.2</td>
<td>1.0</td>
<td>0.5185</td>
<td>36.05</td>
<td>26.86</td>
</tr>
<tr>
<td>1.9</td>
<td>0.5185</td>
<td>36.05</td>
<td>26.86</td>
<td></td>
</tr>
<tr>
<td>2.0</td>
<td>0.5185</td>
<td>36.05</td>
<td>26.86</td>
<td></td>
</tr>
<tr>
<td>2.1</td>
<td>0.5319</td>
<td>39.57</td>
<td>31.33</td>
<td></td>
</tr>
<tr>
<td>3.0</td>
<td>0.6244</td>
<td>63.84</td>
<td>54.17</td>
<td></td>
</tr>
<tr>
<td>2.5</td>
<td>1.0</td>
<td>0.5729</td>
<td>131.47</td>
<td>41.46</td>
</tr>
<tr>
<td>1.9</td>
<td>0.5729</td>
<td>131.47</td>
<td>41.46</td>
<td></td>
</tr>
<tr>
<td>2.0</td>
<td>0.5729</td>
<td>131.47</td>
<td>41.46</td>
<td></td>
</tr>
<tr>
<td>2.1</td>
<td>0.5991</td>
<td>142.06</td>
<td>47.93</td>
<td></td>
</tr>
<tr>
<td>3.0</td>
<td>0.7651</td>
<td>209.13</td>
<td>88.91</td>
<td></td>
</tr>
</tbody>
</table>

In the case Q = 2.5 a considerable stoichiometric excess of B has been used, and optimal operation has enabled us to make effective use of this, whereas the use of such an excess in isothermal batch operation leads to undue consumption of A in the side reaction. Another interesting comparison
is provided by the maximum value of $c(T)$ obtainable in isothermal operation at $T^{\text{max}}$, with all the B added at $t = 0$, regarding the amount of B to be added as available to be chosen. Simple computations shown in Fig. 24 indicate that $c(T)$ is maximized by a value of Q approximately equal to 1.4 and the corresponding maximum value of $c(T)$ is 0.403. A second column of relative improvements with respect to this policy is shown also in Table 1. $Q = 1.2$ is a relatively small excess of A with respect to B, but again the optimal policy allows a better use of the available B without undue encouragement of the side reaction.

3.2 CONCLUSIONS

The most striking conclusions concern the discontinuity of the optimal policy according to the relative values of $p$ and $n$, and the semi-independency of the two controls, in the sense that it is unnecessary to consider simultaneous variations of $r$ and $T$, but optimize with respect to only one of them at a time, while the other is kept constant at a "proper" value, namely $k_1 = k_1^{\text{max}}$ with $r$ variation for $p < n$ or $r \equiv 0$ with $k_1$ variation for $p > n$.

The case $p = n$ is not analysed here, but it seems that multiple equivalent optimal control policies may exist for it (11).
The fact that under certain circumstances, namely a large value of $r_{\text{max}}$ and a small value of $k_1^{\text{min}}$, the whole form of the trajectory can be determined uniquely by simple reasoning is also remarkable.

Our policies here are optimal with respect to the objective function we have chosen. It is important to notice that in a more realistic situation we should include the relative costs of the several components as well as the cost of implementing the controlling policies.

We will notice finally that this, as an introductory study, is necessarily simple and such reasoning may not determine optimal trajectories in more realistic cases. An approximate method of solution is hence in order, and gradients in function space is generally easy enough to implement and still gives good answers. For example, Senior (11) found convergence to within 1% of the optimal value of the objective function, even though the approximation to the optimal trajectory was not very accurate. Fortunately in many practical situations all we need is the optimal value of the objective function; the precise form of the optimal policy is unimportant if we can easily find near-optimal policies.
FIG. 8 - $r(t)$ FOR $n=2, \alpha_0=1.0, Q=2.5, k_1=k_1^{\text{max}}=1.0, \tau = 4.0$
AND $r_m = 1.0$
FIG. 9 - $r(t)$ FOR $n = 2$, $a_0 = 1.0$, $Q = 2.5$, $k_1 = k_1^{\text{max}} = 1.0$, $\tau = 4.0$ AND $r_m = 2.0$
FIG. 10 - \( r(t) \) FOR \( n = 2, c_0 = 1.0, Q = 2.5, k_1 = k_{1,\text{max}} = 1.0, \tau = 4.0 \) AND \( r_m = 5.0 \)
FIGURE 11

Optimum rate of addition of B for isothermal operation at $T = T^{\text{max}}$. $n = 2$, $a(0) = a_0 = 1.0$, $b(0) = 0.1857$, $k_1 = k_1^{\text{max}} = 1.0$, $k_2 = k_2^{\text{max}} = 2.0$, $Q = 2.5$, $T = 4.0$, $r_m = \infty$

The form of $r(t)$ is independent of $p$. 
$b_0 = 0.1857$
Optimum $c(\tau)$. $n = 2$, $a_o = 1.0$, $Q = 2.5$, $k_1^{\text{max}} = 1.0$, $k_2^{\text{max}} = 2.0$, $k_1^{\text{min}} = k_2^{\text{min}} = 0$, $\tau = 4.0$, $r_m = \infty$

**Curve (a)** Isothermal operation at $T^{\text{max}}$, optimized with respect to distributed addition of B

**Curve (b)** Pure batch operation with all B added at $t = 0$, optimized with respect to temperature variation.
FIGURE 13

(i) Optimum temperature policy with all $B$ added at $t = 0$

(ii) Corresponding adjoint variables

$n = 2$, $a(0) = a_0 = 1.0$, $b(0) = Q = 2.5$, $k_1^{\max} = 1.0$,

$k_2^{\max} = 2.0$, $k_1^{\min} = k_2^{\min} = 0$, $\tau = 4.0$, $p = 1.0$. 
(i) Optimum temperature policy with all B added at \( t = 0 \)

(ii) Corresponding adjoint variables

\[ n = 2, \quad a(0) = a_0 = 1.0, \quad b(0) = Q = 2.5, \quad k_1^{\text{max}} = 1.0, \]
\[ k_2^{\text{max}} = 2.0, \quad k_1^{\text{min}} = k_2^{\text{min}} = 0, \quad T = 4.0, \quad p = 1.9. \]
\[ \frac{t}{\tau} \]

\[ k_1 \]

\[ p = 1.9 \]

\[ \lambda_a \]

\[ \lambda_b \times 10^2 \]

\[ F1G.14 \]
(i) Optimum temperature policy with all B added at $t = 0$

(ii) Corresponding adjoint variables

$n = 2$, $a(0) = a_0 = 1.0$, $b(0) = Q = 2.5$, $k_1^{\text{max}} = 1.0$, $k_2^{\text{max}} = 2.0$, $k_1^{\text{min}} = k_2^{\text{min}} = 0$, $\tau = 4.0$, $p = 2.0$. 
\[ t / \tau \rightarrow \infty \]

\[ \lambda_a \]

\[ \lambda_b \times 10^2 \]

FIG. 15
(i) Optimum temperature policy with all B added at $t = 0$

(ii) Corresponding adjoint variables

$n = 2, a(0) - a_0 = 1.0, b(0) = Q = 2.5, k_1^{\text{max}} = 1.0,$
$k_2^{\text{max}} = 2.0, k_1^{\text{min}} = k_2^{\text{min}} = 0, \quad \tau = 4.0, \quad p = 2.1.$
$p = 2.1$

FIG. 16
FIGURE 17

(i) Optimum temperature policy with all $B$ added at $t = 0$

(ii) Corresponding adjoint variables

$n = 2$, $a(0) = a_0 = 1.0$, $b(0) = Q = 2.5$, $k_1^{\text{max}} = 1.0$,

$k_2^{\text{max}} = 2.0$, $k_1^{\text{min}} = k_2^{\text{min}} = 0$, $\tau = 4.0$, $p = 3.0$. 
(i) $p = 3.0$

(ii) $f_1(t)$

FIG. 17
FIGURE 18

(i) Optimum temperature policy with all $B$ added at $t = 0$

(ii) Corresponding adjoint variables

$n = 2$, $a(0) = a_0 = 1.0$, $b(0) = Q = 1.2$, $k_1^{\text{max}} = 1.0$, $k_2^{\text{max}} = 2.0$, $k_1^{\text{min}} = k_2^{\text{min}} = 0$, $\tau = 4.0$, $p = 1.0$. 
FIGURE 19

(i) Optimum temperature policy with all B added at $t = 0$

(ii) Corresponding adjoint variables

$n = 2$, $a(0) = a_0 = 1.0$, $b(0) = Q = 1.2$, $k_1^{\text{max}} = 1.0$,

$k_2^{\text{max}} = 2.0$, $k_1^{\text{min}} = k_2^{\text{min}} = 0$, $\tau = 4.0$, $p = 1.9$. 
FIGURE 20

(i) Optimum temperature policy with all $B$ added at $t = 0$

(ii) Corresponding adjoint variables

$n = 2$, $a(0) = a_0 = 1.0$, $b(0) = Q = 1.2$, $k_1^{\text{max}} = 1.0$,
    $k_2^{\text{max}} = 2.0$, $k_1^{\text{min}} = k_2^{\text{min}} = 0$, $\tau = 4.0$, $p = 2.0$. 
FIGURE 21

(i) Optimum temperature policy with all B added at t = 0

(ii) Corresponding adjoint variables

\[ n = 2, \ a(0) = a_0 = 1.0, \ b(0) = Q = 1.2, \ k_1^{\text{max}} = 1.0, \]
\[ k_2^{\text{max}} = 2.0, \ k_1^{\text{min}} = k_2^{\text{min}} = 0, \ T = 4.0, \ p = 2.1. \]
(i) Optimum temperature policy with all B added at \( t = 0 \)

(ii) Corresponding adjoint variables

\( n = 2, \ a(0) = a_0 = 1.0, \ b(0) = Q = 1.2, \ k_1^{\text{max}} = 1.0, \)
\( k_2^{\text{max}} = 2.0, \ k_1^{\text{min}} = k_2^{\text{min}} = 0, \ \tau = 4.0, \ p = 3.0 \)
FIG. 22
FIGURE 23

Optimum $c(T)$. $n = 2$, $a_0 = 1.0$, $Q = 1.2$, $k_1^{\text{max}} = 1.0$, $k_2^{\text{max}} = 2.0$, $k_1^{\text{min}} = k_2^{\text{min}} = 0$, $T = 4.0$, $r_m = \infty$

Curve (a) Isothermal operation at $T^{\text{max}}$, optimized with respect to distributed addition of B

Curve (b) Pure batch operation with all B added at $t = 0$, optimized with respect to temperature variation
FIGURE 24

c(τ) vs b(0) for isothermal pure batch operation at $T_{\text{max}}$.

$n = 2$, $a(0) = a_0 = 1.0$, $k_1^{\text{max}} = 1.0$, $k_2^{\text{max}} = 2.0$, $\tau = 4.0$
APPENDIX I

BOUNDEDNESS OF SOLUTIONS OF A SYSTEM OF ORDINARY LINEAR HOMOGENEOUS DIFFERENTIAL EQUATIONS

WITH BOUNDED COEFFICIENTS

Consider the following linear homogeneous differential equation system with the associated boundary conditions

\[ \frac{dx_i}{dt} = \sum_{j=1}^{n} A_{ij}(t) x_j ; \quad x_j(t_0) = x_{j0} \quad \text{to} \in [0, \tau] \]

then we can premultiply by a row vector \( \{x_1 \ldots x_n\} \) obtaining

\[ \sum_{i=1}^{n} x_i \frac{dx_i}{dt} = \sum_{i=1}^{n} \sum_{j=1}^{n} x_i A_{ij} x_j \]

or

\[ \frac{1}{2} \frac{d}{dt} \sum_{i=1}^{n} x_i^2 = \sum_{i=1}^{n} \sum_{j=1}^{n} x_i A_{ij} x_i \]

thus

\[ \left| \frac{d}{dt} \sum_{i=1}^{n} x_i^2 \right| \leq \sum_{i=1}^{n} \sum_{j=1}^{n} |x_i| \cdot |x_j| \cdot |A_{ij}| \]

2A \[ \sum_{i=1}^{n} \sum_{j=1}^{n} |x_i| \cdot |x_j| \]
where
\[ A = \max_{t, i, j} |A_{ij}| \]

but
\[ |x_i| |x_j| \leq |x_i|^2 \quad (|x_i| > |x_j|) \]
or
\[ |x_i| |x_j| \leq |x_j|^2 \quad (|x_j| > |x_i|) \]

thus
\[ A \sum_{i=1}^{n} \sum_{j=1}^{n} |x_i| |x_j| \leq 2nA \sum_{i=1}^{n} |x_i|^2 \]

as can be seen by replacing each \(|x_i| |x_j|\) on the left hand side by \(|x_i|^2\) or \(|x_j|^2\), whichever is larger.

Thus
\[ \left| \frac{d}{dt} \sum_{i=1}^{n} x_i^2 \right| \leq 4nA \sum_{i=1}^{n} |x_i|^2 = 4nA \sum_{i=1}^{n} x_i^2 \]

and defining \( y = \sum_{i=1}^{n} x_i^2 \) we obtain
\[ \left| \frac{dy}{dt} \right| \leq 4ny \]
or \(-4\text{An} \leq \frac{dy}{dt} \leq 4\text{An}\)

or \(-4\text{An} \leq \frac{d}{dt} (\ln y) \leq 4\text{An}\)

which, integrated with respect to t gives

\[-4\text{An}(t-t_0) \leq \ln(y(t)/y(t_0)) \leq 4\text{An}(t-t_0)\]

whence

\[-4\text{An}\tau \leq \ln \left(\frac{y(t)}{y(t_0)}\right) \leq 4\text{An}\tau, \text{ all } t \in [0, \tau]\]

or

\[0 \leq y_0 \exp (-4\text{An}\tau) \leq y(t) \leq y_0 \exp (4\text{An}\tau)\]

but

\[|x_i|^2 \leq \sum_{j=1}^{n} x_j^2 = y \text{ for all } i\]

so

\[|x_i|^2 \leq y_0 \exp (4\text{An}\tau)\]

or

\[|x_i| \leq \sqrt{y_0} \exp (2\text{An}\tau)\]
which shows the boundedness of the moduli of $x_i$ for every $i$. 
APPENDIX II

BOUNDEDNESS OF $b^{n-1}$, $a(t)/a(T)$ AND $b(t)/b(T)$

**Boundedness of $b^{n-1}$**

We proved in Lemma 3 that at any time $b \leq Q$, and it follows that $b^{n-1} \leq Q^{n-1}$ and provided $n$ is finite that gives a finite upper bound for $b^{n-1}$.

**Boundedness of $a/a(T)$**

$$
\frac{da}{dt} = -k_1ab - k_2ab^n
$$

or

$$
-da/a = -(k_1b + k_2b^n)dt
$$

and integrating

$$
a/a(T) = \exp \int_t^T (k_1b + k_2b^n)dt
$$

which is indeed bounded because all $k_1$, $k_2$, $b$ and $b^n$ are.

In fact we can say

$$
a(t)/a(T) \leq \exp \left[ (k_1^{\max}Q + k_2^{\max}Q^n)(T - t) \right]
$$

**Boundedness of $b/b(T)$**

$$
\frac{db}{dt} = -k_1ab - k_2ab^n + r
$$
or 
\[-db/b = (k_1a + k_2ab^{n-1} - r/b) \, dt\]

which integrated between \(t\) and \(T\) gives

\[b(t)/b(T) = \exp \left( \int_t^T (k_1a + k_2ab^{n-1} - r/b) \, dt \right)\]

\[= \exp \left[ \int_t^T (k_1a + k_2ab^{n-1}) \, dt \right] \exp \left[ \int_t^T -r/b \, dt \right]\]

but \(r, b \geq 0\) so \(\exp \left[ \int_t^T -r/b \, dt \right] \leq 1\)

and \(b(t)/b(T) \leq \exp \left[ \int_t^T (k_1a + k_2ab^{n-1}) \, dt \right]\) for \(t > 0\)

\[b(t)/b(T) \leq \exp (k_1^{\text{max}} a_0 + k_2^{\text{max}} a_0 q^{n-1}) (T-t), \quad t > 0\]

which proves boundedness of \(b(t)/b(T)\) for \(t \leq T\).
APPENDIX III

MONOTONICITY OF THE OPTIMAL TEMPERATURE PROFILE

We have proved in Theorem 1(b) that the optimum 
k_1(t) policy is continuous (for any r policy, provided 
r_m is sufficiently large and p > 1) and thus is only 
necessary to look at the temperature profile during the 
time interval in which the maximum of H with respect to 
k_1 is a stationary value.

Along that subinterval of \([0, \tau']\), \((t_1', t_2')\), \(t_1' > 0\), 
t_2' < \tau we have \(\partial H/\partial k_1 = 0\) and \(k_1 \in \left[k_1^{\min}, k_1^{\max}\right]\)

or 
\[k_1^{p-1} = \frac{(1 - \lambda_a - \lambda_b)}{p \alpha b^{n-1}(\lambda_a + n \lambda_b)}\]

which can be written as

\[k_1(1 - \lambda_a - \lambda_b) = pk_2b^{n-1}(\lambda_a + n \lambda_b), \ t \in (t_1', t_2')\]

and substitution in the expression for the Hamiltonian gives

\[H_s = (\lambda_b + \gamma) r + k_2 ab^n(\lambda_a + n \lambda_b)(p-1)\]

where \(H_s = \) partial stationary maximum of the Hamiltonian.
with respect to $k_1$. All the state, control and multiplier variables are evaluated along the trajectory.

$H_s$ therefore depends on the simultaneous $r$-policy and differentiating with respect to $t$ along the trajectory we will get

$$\frac{d}{dt} H_s = \frac{d}{dt} \left[ (\lambda_b + \gamma) \right] \frac{d}{dt} + \frac{dk_2}{dt} ab^n$$

$$(\lambda_a + n\lambda_b) \frac{(p-1)}{(p-1)} + k_2 \left( -k_1ab - k_2ab^n \right) b^n.$$ 

$$(\lambda_a + n\lambda_b) + (p-1) k_2an b^{n-1} \left( -k_1ab - nk_2ab^n + r \right)$$

$$(\lambda_a + n\lambda_b) + (p-1) k_2ab^n(k_2b^n - pk_2b^n + n^2k_2ab^{n-1} - npk_2ab^{n-1})(\lambda_a + n\lambda_b)$$

or

$$\frac{d}{dt} H_s = \frac{d}{dt} \left[ (\lambda_b + \gamma) \right] \frac{d}{dt} + \frac{dk_2}{dt} ab^n$$

$$(\lambda_a + n\lambda_b)(p-1) + (p-1) k_2ab^n(\lambda_a + n\lambda_b)$$

$$(nr/b - (na + b)(k_1 + pk_2b^{n-1}))$$
From Theorem 10, if \( r_m \) is large enough and \( k_{1\text{min}} \) is small enough we should have an \( r \)-policy without singular segment; furthermore by letting \( r_{\text{max}} \to \infty \) we push \( t_1^* \) on Fig. 7 to zero. Therefore we have to prove only that \( \frac{dk_2}{dt} > 0 \) for all \( t \in (t_1', t_2') \) if \( r = 0 \).

Obviously \( \frac{d}{dt} [(\lambda_b + \gamma) r] \equiv 0 \) over \((t_1, \tau)\) because \((\lambda_b + \gamma) r \equiv 0\) and \( \frac{d}{dt} H_s \equiv 0 \) over \((t_1', t_2')\) to satisfy Pontryagin's condition along the segment of stationary maximum of \( H \) with respect to \( k_1 \). We thus have, provided \( \lambda_a + n \lambda_b \neq 0 \)

\[
\frac{dk_2}{dt} = k_2(na + b) (k_1 + pk_2b^{n-1}) > 0 \text{ for } (t_1', t_2')
\]

which proves that the \( k_1 \) policy is monotonically nondecreasing over \((t_1, \tau)\).
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a)</td>
<td>mole concentration of substance A</td>
</tr>
<tr>
<td>(a_0)</td>
<td>mole concentration of substance A at time zero</td>
</tr>
<tr>
<td>(b)</td>
<td>mole concentration of substance B</td>
</tr>
<tr>
<td>(b_0)</td>
<td>mole concentration of substance B at time zero</td>
</tr>
<tr>
<td>(c)</td>
<td>mole concentration of substance C</td>
</tr>
<tr>
<td>(E_i)</td>
<td>Arrhenius activation energy for reaction (i; i = 1,2)</td>
</tr>
<tr>
<td>(H)</td>
<td>Hamiltonian function, Equation (2.4-10)</td>
</tr>
<tr>
<td>(H_{\text{max}})</td>
<td>maximum value of the Hamiltonian with respect to (r) and (k_l) for fixed values of the state variables</td>
</tr>
<tr>
<td>(k_i)</td>
<td>velocity constant for reaction (i; i = 1,2)</td>
</tr>
<tr>
<td>(k_{i0})</td>
<td>frequency factor for velocity constant (k_i; i = 1,2)</td>
</tr>
<tr>
<td>(k_{i\text{max}})</td>
<td>maximum permissible value of (k_i)</td>
</tr>
<tr>
<td>(k_{i\text{min}})</td>
<td>minimum permissible value of (k_i)</td>
</tr>
<tr>
<td>(M(Q))</td>
<td>upper bound for (</td>
</tr>
<tr>
<td>(n)</td>
<td>order of the reaction rate with respect to distributed reactant B</td>
</tr>
<tr>
<td>(N(Q))</td>
<td>upper bound for (</td>
</tr>
<tr>
<td>(p)</td>
<td>ratio of the activation energies, (E_2/E_1)</td>
</tr>
<tr>
<td>(q)</td>
<td>amount of B added to the mixture from (t = 0) to time (t)</td>
</tr>
<tr>
<td>(Q)</td>
<td>total amount of B added to the mixture during the total reaction time</td>
</tr>
<tr>
<td>(r)</td>
<td>instantaneous rate of addition of B to the mixture</td>
</tr>
<tr>
<td>(R)</td>
<td>ideal gas constant</td>
</tr>
</tbody>
</table>
\( t \) time coordinate

\( T \) uniform temperature in reactor at time \( t \)

\( T^{\text{max}} \) maximum permissible value of the reactor temperature

\( T^{\text{min}} \) minimum permissible value of the reactor temperature

**Greek Symbols**

\[ \alpha = \frac{k_{20}}{k_{10}} \]

\( \gamma \) final value of the adjoint variable \( \mu \)

\( \lambda_a \) adjoint variable corresponding to physical variable \( a \)

\( \lambda_a(Q) \) upper bound for \( |\lambda_a| \)

\( \lambda_b \) adjoint variable corresponding to physical variable \( b \)

\( \lambda_b(Q) \) upper bound for \( |\lambda_b| \)

\( \lambda_c \) adjoint variable corresponding to physical variable \( c \)

\( \mu \) adjoint variable corresponding to physical variable \( q \)

\( \tau \) total length of time for the batch operation
BIBLIOGRAPHY


