

OPTIMIZATION OF A TUBULAR REACTOR
FOR PARALLEL REACTIONS WITH CATALYST DECAY

OPTIMIZATION OF A TUBULAR REACTOR
FOR PARALLEL REACTIONS WITH CATALYST DECAY

BY

ROBERT STANSFELD ROWBOTTOM, B.Eng.

A PROJECT REPORT
SUBMITTED TO THE SCHOOL OF GRADUATE STUDIES
IN PARTIAL FULFILMENT OF THE REQUIREMENTS
FOR THE DEGREE
MASTER OF ENGINEERING

McMASTER UNIVERSITY

October, 1970

MASTER OF ENGINEERING
(Chemical Engineering)

McMASTER UNIVERSITY
Hamilton, Ontario

TITLE: Optimization of a Tubular Reactor for Parallel Reactions
with Catalyst Decay

AUTHOR: Robert StansfeldRowbottom, B.Eng. (Nova Scotia Technical
College)

SUPERVISOR: Dr. C.M. Crowe

NUMBER OF PAGES: vii, 68

SCOPE AND CONTENTS:

The temperature policy with time is sought which maximizes a performance index for a fixed time in a tubular reactor with uniform temperature, decaying catalyst, and two first-order irreversible parallel reactions.

For the case where the performance index is the total amount of desired product produced, an analogy between the optimization problems for a first-order reversible reaction and a parallel reaction first-order in both paths is developed.

A numerical procedure together with theoretical developments is used to solve the problem for a more general performance index which takes into account the cost of the reactant as well as the value of the desired product. The problem is treated in the format of Pontryagin's Maximum Principle.

ACKNOWLEDGEMENTS

The author wishes to express his gratitude to Professor C.M. Crowe, the research supervisor, and to Mr. N. Therien for their valuable advice and assistance.

The author also wishes to acknowledge the financial support received from the National Research Council of Canada and from McMaster University.

TABLE OF CONTENTS

	<u>PAGE</u>
ACKNOWLEDGEMENTS	iv
LIST OF FIGURES	vii
CHAPTER 1 <u>INTRODUCTION</u>	1
CHAPTER 2 <u>STATEMENT OF THE PROBLEM</u>	3
CHAPTER 3 <u>THEORETICAL DERIVATIONS</u>	7
3.1 KINETICS	7
3.2 THE MAXIMUM PRINCIPLE	9
3.3 PROPERTIES OF OPTIMAL POLICIES	11
3.3.1 Stationary Curve S	11
3.3.2 Initial Temperature Limitations	17
3.3.3 Behaviour of the Optimal Temperature Policy as $t \rightarrow \tau$	18
3.4 ANALOGY BETWEEN OPTIMAL POLICIES FOR FIRST ORDER REVERSIBLE AND PARALLEL REACTIONS WITH CATALYST DECAY	20
CHAPTER 4 <u>NUMERICAL SOLUTIONS</u>	24
4.2 RESULTS	25
4.2.1 Classification of Results	25
4.2.2 Definition of the Reaction System: Numerical Values	26
4.2.3 Unconstrained Optimal Policies	27
4.2.4 Constrained Optimal Policies	37
4.2.5 Effect of α on Constrained Optimal Policies	44

	<u>PAGE</u>
4.2.6 Sensitivity of a Constrained Optimal Policy	48
CHAPTER 5 <u>GENERAL CONCLUSIONS AND HYPOTHESES</u>	51
NOMENCLATURE	52
BIBLIOGRAPHY	54
APPENDIX A1 ANALOGY BETWEEN FIRST ORDER REVERSIBLE AND PARALLEL REACTIONS	55
APPENDIX A2 BEHAVIOUR OF THE HAMILTONIAN WITH TIME ALONG AN OPTIMAL POLICY	58
APPENDIX A3 PROOF THAT THE ADJOINT IS POSITIVE FOR $t < \tau$	59
APPENDIX B OPTIMAL POLICY FOR A PARALLEL REACTION FIRST ORDER IN BOTH PATHS (FORTRAN LISTING)	60

LIST OF FIGURES

<u>FIGURE NUMBER</u>		<u>PAGE</u>
1	UNCONSTRAINED OPTIMAL POLICY FOR $p_1 = p_2 = p$	30
2	UNCONSTRAINED OPTIMAL POLICY FOR $1 > p_1 > p_2$	31
3	UNCONSTRAINED OPTIMAL POLICY FOR $p_1 \geq 1 > p_2$	32
4	UNCONSTRAINED OPTIMAL POLICY FOR $p_1 > p_2 \geq 1$	33
5	UNCONSTRAINED OPTIMAL POLICY FOR $1 > p_2 > p_1$	34
6	UNCONSTRAINED OPTIMAL POLICY FOR $p_2 \geq 1 > p_1$	35
7	UNCONSTRAINED OPTIMAL POLICY FOR $p_2 > p_1 \geq 1$	36
8	CONSTRAINED OPTIMAL POLICIES FOR $p_1 > p_2$	40
9	A^+ , B^+ , ψ^+ VERSUS TIME FOR A CONSTRAINED OPTIMAL POLICY $p_1 > p_2$	41
10	CONSTRAINED OPTIMAL POLICIES FOR $p_1 < p_2$	42
11	A^+ , B^+ , ψ^+ VERSUS TIME FOR A CONSTRAINED OPTIMAL POLICY $p_1 < p_2$	43
12	EFFECT OF α ON A CONSTRAINED OPTIMAL POLICY FOR $p_1 > p_2$	46
13	EFFECT OF α ON A CONSTRAINED OPTIMAL POLICY FOR $p_1 < p_2$	47
14	PERFORMANCE INDEX VERSUS INITIAL REACTOR TEMPERATURE FOR ISOTHERMAL POLICIES AND OPTIMAL POLICIES	50

CHAPTER 1

INTRODUCTION

Commercial reactions which involve catalyst decay are numerous and as such the determination of optimal operating policies for reaction schemes of this type is of considerable interest. The problem of optimizing such a system is not a simple one; catalyst activity at any instant depends on the entire previous history of the operating variables and thus the control variable must be chosen at every instant with regard to both its instantaneous and long term effect on the system.

For all but the simplest reaction schemes complete analytical solutions have not been found. For simple irreversible reactions (i.e. $A \rightarrow B$) the solution is well known and many workers [Jackson (1965, 1967), Szepe (1966), Crowe (1969)] have emphasized different aspects of it.

Jackson (1965, 1967) has considered the optimal temperature profile in a tubular reactor with a reversible exothermic reaction. The problem is easily formulated, but as yet no analytical solutions are available.

Drouin (1969) has studied the reversible reaction, deriving the necessary conditions for an optimal policy and using a numerical method together with the analytical developments to obtain a complete solution.

The present study examines a parallel reaction scheme and follows essentially the approach used by Drouin(1969)

to obtain a complete solution. An analogy is developed between the optimization problem for the reversible reaction and the problem for a parallel reaction. Using this analogy the results of Drouin's work can be used as the solution to a similarly stated problem for a parallel reaction scheme.

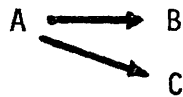
CHAPTER 2

STATEMENT OF THE PROBLEM

For a single tubular reactor at uniform temperature and fulfilling the further conditions and assumptions described herein, it is required to maximize the performance index, as represented by the objective function, over a fixed total reaction time, τ , by choosing the temperature at every instant.

The reactor system is further defined by the following conditions and assumptions:

- (1) There is a parallel reaction irreversible in both paths and represented schematically by:



A material balance on B, assuming plug flow, is a function of catalyst activity ψ , temperature T , and concentration of A.

$$\frac{\partial B}{\partial t} + \frac{\partial B}{\partial z} = f_1(\psi, T, A) \quad (2.1)$$

where $f_1(\psi, T, A)$ is the rate of formation of B, z is the space-time through the bed, t is the time on stream and $B = B_i(t)$ at $z = 0$ (B_i is the inlet concentration of B)

Similarly a material balance on A gives

$$\frac{\partial A}{\partial t} + \frac{\partial A}{\partial z} = f_2(\psi, T, A) \quad (2.2)$$

(2) The catalyst activity ψ is defined [Anderson (1968), Kunii and Levenspiel (1969)] as the ratio of the rate of reaction with decayed catalyst to that with fresh catalyst. For the present study it is assumed that this ratio is independent of the temperature at which the reaction rates are measured.

(3) The rate of decay of catalyst activity is assumed to depend on the temperature and on activity itself but not on concentration of products or reactant, as follows:

$$\frac{d\psi}{dt} = -k(T)g(\psi) = \phi \quad (2.3)$$

$\psi = \psi_0$ at $t=0$ for all z

with $0 \leq g(\psi) \leq 1$. Since the reactor has uniform temperature at any time, equation (2.3) implies that ψ is uniform over the distance z .

The decay rate described by equation (2.3) could represent a catalyst which loses activity by evaporation of active species, by sintering, or by deposition of a poison at a rate unaffected by position in the bed.

(4) It is required that temperature and inlet conditions be essentially constant over a time period equal to the space time in order that activity can be assumed constant for integration over z , and it can be

assumed that

$$\frac{\partial B}{\partial t} \ll \frac{\partial B}{\partial z} \quad \text{and} \quad \frac{\partial A}{\partial t} \ll \frac{\partial A}{\partial z}$$

(5) K_1 and K_2 are the rate constants of A to B and A to C respectively and are related to the catalyst decay rate constant by

$$K_1 \propto k^{p_1}$$

$$K_2 \propto k^{p_2}$$

If K_1 , K_2 and k are of the Arrhenius form then $p_{1,2}$ are the ratios of the respective activation energies $E_{1,2}$ to E_c with $0 \leq p = \frac{E}{E_c} < \infty$.

Since, for $E_c > 0$ $k(T)$ is a strictly monotonic increasing function of T , the temperature may be replaced as a decision variable by k . If $E_c = 0$ $k(T)$ is constant, the choice of T does not affect the activity and the optimal policy is then the same as without catalyst decay.

The performance index, P , is defined by:

$$P \equiv \int_0^T [\beta(B - B_i) + \alpha(A - A_i)] dt \quad (2.4)$$

where

$\beta \equiv$ value per unit of B

$\alpha \equiv$ value per unit of A

and

$$\beta > \alpha \geq 0.$$

The performance index may be visualized as the integral of the instantaneous profit over the operating period, for the case of negligible relative value of product C, activity, and time.

The problem now consists of maximizing the objective function over a fixed total reaction time, τ , by choosing the rate coefficient k (and thence T) at every instant.

That is,

$$P^+ = \text{MAX}_{k(t)} P \quad (2.5)$$

subject to

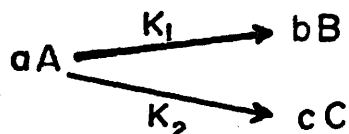
$$0 \leq k_* \leq k \leq k^* \quad (2.6)$$

CHAPTER 3

THEORETICAL DERIVATIONS

3.1 KINETICS:

For the general parallel reaction



the rate per unit volume of reacting fluid at which substance B is being formed is defined by the expression

$$r = \frac{1}{bV} \frac{dn_B}{dt} = \frac{1}{bV} \frac{d(VB)}{dt}$$

which for a reaction m^{th} order in A is also given by

$$r = K_1 A^m \psi$$

or

$$\frac{1}{bV} \frac{d(VB)}{dt} = K_1 A^m \psi \quad (3.1.1)$$

For the case of:

(1) a first order reaction $m = 1$

(2) $b = 1$

(3) constant volume of reacting fluid, equation

(3.1.1) reduces to

$$\frac{dB}{dt} = K_1 A \psi = f_1(\psi, T, A) \quad (3.1.2)$$

Similarly for $a = 1$, $c = 1$ and first order

reaction A to C the rate per unit volume or reacting fluid at which A is being formed is given by

$$\begin{aligned} \frac{dA}{dt} &= - (K_1 + K_2) A \psi \\ &= f_2(\psi, T, A) \end{aligned} \quad (3.1.3)$$

Combining equations (2.1) and (2.2) with (3.1.2) and

and (3.1.3) gives the following equations describing the reaction system

$$\frac{\partial B}{\partial t} + \frac{\partial B}{\partial z} = K_1 A \psi \quad (3.1.4)$$

$$\frac{\partial A}{\partial t} + \frac{\partial A}{\partial z} = -A \psi (K_1 + K_2) \quad (3.1.5)$$

$$B(t,0) = B_i \quad A(t,0) = A_i$$

Under assumption (4) equations (3.1.4) and (3.1.5) reduce to

$$\frac{dB}{dz} = K_1 \psi A \quad (3.1.6)$$

$$\frac{dA}{dz} = - (K_1 + K_2) \psi A \quad (3.1.7)$$

Equations (3.1.6) and (3.1.7) can now be solved analytically to give the exit concentrations of A and B at time t:

$$A(t,\theta) = A_i e^{-\psi \theta (K_1 + K_2)} \quad (3.1.8)$$

$$B(t,\theta) = B_i + \frac{K_1 A_i}{K_1 + K_2} (1 - e^{-\psi \theta (K_1 + K_2)}) \quad (3.1.9)$$

For convenience the time unit is defined such that the space time θ equals 1, so that τ in equation (2.4) is the number of space times.

Equations (3.1.8) and (3.1.9) may be used to alter the form of equation (2.4) to:

$$P = \int_0^{\tau} \left(\frac{\beta K_1}{K_1 + K_2} - \alpha \right) (A_i - A) dt \quad (3.1.10)$$

3.2 THE MAXIMUM PRINCIPLE

The problem as stated by equations (2.3), (2.5), (2.6), (3.1.8) and (3.1.10) may be conveniently treated in the format of Pontryagin's Maximum Principle [Pontryagin et. al. (1962)].

The Hamiltonian H is defined by

$$H(\psi, \lambda, k, t) = \left(\frac{\beta K_1}{K_1 + K_2} - \alpha \right) (A_i - A) + \lambda \phi \quad (3.2.1)$$

where λ , the adjoint variable, is defined by

$$\frac{d\lambda}{dt} = \left(\frac{\beta K_1}{K_1 + K_2} - \alpha \right) \frac{\partial A}{\partial \psi} - \lambda \frac{\partial \phi}{\partial \psi} \quad (3.2.2)$$

with

$$\begin{aligned} \lambda(\tau) &= 0 & \text{if } \psi(\tau) > 0 \\ \lambda(\tau) &\geq 0 & \text{if } \psi(\tau) = 0 \end{aligned}$$

The maximization of P in equation (3.1.10) is then equivalent, according to Pontryagin's maximum principle [Pontryagin et al (1962), Halkin (1966)], to requiring of an optimal policy $k^+(t)$ that it satisfy

$$H(\psi^+, \lambda^+, k^+, t) = \underset{k(t)}{\text{MAX}} H(\psi^+, \lambda^+, k, t) \quad (3.2.3)$$

at almost all t and for all admissible values of k .

If $k^+(t)$ is the optimal policy then one of the following three conditions is necessary at any time $t \leq \tau$:

(a) Stationary curve:

$$\frac{\partial H(k^+)}{\partial k} = 0 \quad \text{and} \quad \frac{\partial^2 H}{\partial k^2} \leq 0 \quad \text{if} \quad k_* < k^+ < k^*$$

(b) Upper constraint

$$\frac{\partial H(k^+)}{\partial k} \geq 0 \quad \text{if} \quad k^+ = k^* \quad (3.2.4)$$

(c) Lower constraint

$$\frac{\partial H(k^+)}{\partial k} \leq 0 \quad \text{if} \quad k^+ = k_*$$

3.3 PROPERTIES OF OPTIMAL POLICIES

3.3.1 Stationary Curve S

From condition (3.2.4a) and Equations (3.2.1) and (3.1.8) along a sub-policy S

$$\begin{aligned} \frac{\partial H}{\partial k} \Big|_{\psi, \lambda, A_i, t} &= \frac{\beta K_1 K_2 (p_1 - p_2)}{k (K_1 + K_2)^2} (A_i - A) \\ &+ \left[\frac{\beta K_1}{K_1 + K_2} - \alpha \right] \frac{A_i \psi}{k} (p_1 K_1 + p_2 K_2) e^{-\psi(K_1 + K_2)} \\ &+ \frac{\lambda \phi}{k} = 0 \end{aligned}$$

OR

$$\begin{aligned} \lambda \phi &= - \frac{\beta K_1 K_2 (p_1 - p_2) (A_i - A)}{(K_1 + K_2)^2} \\ &- \left[\frac{\beta K_1}{K_1 + K_2} - \alpha \right] A_i \psi (p_1 K_1 + p_2 K_2) e^{-\psi(K_1 + K_2)} \end{aligned} \quad (3.3.1)$$

From Equations (3.2.1) and (3.3.1) the expression for the Hamiltonian on the sub-policy S is

$$\begin{aligned} H_S &= \left[\frac{\beta K_1}{K_1 + K_2} - \alpha \right] [A_i - A - A\psi(p_1 K_1 + p_2 K_2)] \\ &- \frac{\beta K_1 K_2}{(K_1 + K_2)^2} (p_1 - p_2) (A_i - A) \end{aligned} \quad (3.3.2)$$

with $A = A(B, A_i, B_i, k)$

$$\psi = \psi(B, A_i, B_i, k)$$

from Equations (3.1.8) and (3.1.9).

Then

$$H_s = f(B, A_i, B_i, k).$$

Consider the case of constant inlet concentrations

$$\frac{dA_i}{dt} = \frac{dB_i}{dt} = 0$$

then

$$\frac{dH_s}{dt} = \frac{\partial H_s}{\partial B} \frac{dB}{dt} + \frac{\partial H_s}{\partial k} \frac{dk}{dt} \quad (3.3.3)$$

However

$$\frac{dH_s}{dt} = \frac{dH}{dt} \quad (\text{general})$$

and for

$$\frac{dA_i}{dt} = 0, \quad \frac{dB_i}{dt} = 0 \quad (\text{see Appendix A2})$$

therefore

$$\frac{dH_s}{dt} = 0.$$

Evaluating the partial derivatives of H_s , Equation (3.3.3)

becomes

$$\frac{dH_s}{dt} = \left[\left(\frac{\beta K_1}{K_1 + K_2} - \alpha \right) \frac{K_1(1 - p_1) + K_2(1 - p_2)}{K_1} \right]$$

(Cont'd.)

$$\begin{aligned}
& - \frac{\beta K_2 (p_1 - p_2)}{K_1 + K_2} - \left(\frac{\beta K_1}{K_1 + K_2} - \alpha \right) \frac{p_1 K_1 + p_2 K_2}{K_1} \ln \left(1 - \frac{(B - B_i)(K_1 + K_2)}{K_1 A_i} \right) \Big] \frac{dB}{dt} \\
& + \frac{K_2 (p_1 - p_2)}{k} \text{ [many terms] } \frac{dk}{dt} = 0 \tag{3.3.4}
\end{aligned}$$

When $p_1 = p_2 = p$, Equation (3.3.4) reduces to

$$\begin{aligned}
& \left[\left(\frac{\beta K_1}{K_1 + K_2} - \alpha \right) (1-p)(K_1 + K_2) \right. \\
& \left. - \left(\frac{\beta K_1}{K_1 + K_2} - \alpha \right) \frac{p(K_1 + K_2)}{K_1} \ln \left(1 - \frac{(B - B_i)(K_1 + K_2)}{K_1 A_i} \right) \right] \frac{dB}{dt} = 0 \tag{3.3.5}
\end{aligned}$$

Equation (3.3.5) has two solutions:

(1) $\frac{dB}{dt} = 0$ which implies $B = \text{a constant}$

(2) $\left[\frac{\beta K_1}{K_1 + K_2} - \alpha \right] \frac{K_1 + K_2}{K_1} \left[1 - p - p \ln \left[1 - \frac{(B - B_i)(K_1 + K_2)}{K_1 A_i} \right] \right] = 0$

OR $B = B_i + \frac{K_1 A_i}{K_1 + K_2} \left[1 - e^{\frac{1-p}{p}} \right]$

for $\frac{\beta K_1}{K_1 + K_2} - \alpha \neq 0$

It is shown in Appendix A3 that $\frac{\beta K_1}{K_1 + K_2} - \alpha$ cannot be negative or zero on an optimal policy.

For $p_1 = p_2$, $\frac{K_1}{K_1 + K_2} = \text{a constant}$, and therefore the second solution is also

$B = \text{a constant}$

Hence for the special case where $p_1 = p_2$ the stationary temperature policy is one which maintains a constant outlet concentration of B for constant A_i and B_i .

From Equation (3.1.9) where

$$K_1 = \frac{a_1}{a_c^p} k^p$$

and

$$K_2 = \frac{a_2}{a_c^p} k^p$$

(a_1 , a_2 and a_c are the frequency factors for the two reactions and the catalyst decay respectively) the stationary policy for $p_1 = p_2 = p$ is given by

$$k(t) = \frac{1}{a_c} \sqrt[p]{\frac{\ln \left(\frac{a_1 A_i}{a_1 A_i + (B_i - B)(a_1 + a_2)} \right)}{\psi(a_1 + a_2)}} \quad (3.3.6)$$

For the general case $p_1 \neq p_2$, the complexity of Equation (3.3.4) makes a complete analytical solution impractical.

In order that the Hamiltonian along the stationary curve be locally maximum at any t , it is necessary that

$$\frac{\partial^2 H}{\partial k^2} \leq 0.$$

From Equation (3.2.1) we have

$$\frac{\partial^2 H}{\partial k^2} = \frac{\partial^2}{\partial k^2} \left[\left[\frac{\beta K_1}{K_1 + K_2} - \alpha \right] (A_i - A) + \lambda \phi \right] \quad (\text{Cont'd.})$$

$$\begin{aligned}
&= \beta A_1 K_1 K_2 (p_1 - p_2) (1 - e^{-\psi(K_1 + K_2)}) \frac{K_1(p_2 - 1 - p_1) + K_2(p_1 - 1 - p_2)}{k^2(K_1 + K_2)^3} \\
&+ \frac{2\beta A_1 K_1 K_2 \psi(p_1 - p_2)(p_1 K_1 + p_2 K_2)}{k^2(K_1 + K_2)^2} e^{-\psi(K_1 + K_2)} \\
&+ A_1 \psi \left[\frac{\beta K_1}{K_1 + K_2} - \alpha \right] \frac{p_1^2 K_1 + p_2^2 K_2 - p_1 K_1 - p_2 K_2 - \psi(p_1 K_1 + p_2 K_2)^2}{k^2} \\
&e^{-\psi(K_1 + K_2)}
\end{aligned}$$

$$\leq 0$$

Again consider the special case $p_1 = p_2 = p$. $\frac{\beta K_1}{K_1 + K_2} - \alpha$ is constant and always positive on an optimal policy (A3), and the sign of $\frac{\partial^2 H}{\partial k^2}$ is given by

$$(p-1) - \psi p(K_1 + K_2).$$

for $p \leq 1$ $\frac{\partial^2 H}{\partial k^2} < 0$ and the stationary policy is optimal.

for $p > 1$ $\frac{\partial^2 H}{\partial k^2}$ may be positive, negative or zero.

For the general case $p_1 \neq p_2$ the sign of $\frac{\partial^2 H}{\partial k^2}$ must be evaluated numerically to determine whether the Hamiltonian is a maximum on the stationary policy.

At $t = \tau$, $\lambda = 0$ and from Equation (3.2.1) the Hamiltonian is

$$H = \left[\frac{\beta K_1}{K_1 + K_2} - \alpha \right] (A_1 - A) \quad (3.3.7)$$

$A_1 - A \geq 0$ since the reaction is irreversible.

From the Maximum Principle

$$H(\psi^+, \lambda^+, k^+, t) \geq H(\psi^+, \lambda^+, k, t)$$

therefore if there exists a feasible k such that $\frac{\beta K_1}{K_1 + K_2} - \alpha \geq 0$, then at $t = \tau$, $\frac{\beta K_1}{K_1 + K_2} - \alpha$ must be positive or zero on the optimal policy. If there is no feasible k such that $\frac{\beta K_1}{K_1 + K_2} - \alpha \geq 0$ the process is not economical to operate since the value of A consumed will always be greater than the value of B produced. The optimal policy for such a problem would be the trivial case of not operating. It will therefore be assumed that $\frac{\beta K_1}{K_1 + K_2} - \alpha \geq 0$ for at least one feasible k .

From Equation (3.3.7) on an optimal policy at $t = \tau$

$$H \geq 0$$

For constant inlet concentration of A it has been shown that

$$\frac{dH}{dt} = 0 \quad (A2)$$

\therefore for $\frac{dA_1}{dt} = 0$, on an optimal policy

$$H \geq 0 \quad \text{for } 0 \leq t \leq \tau \quad (3.3.8)$$

On an optimal policy

$$\lambda > 0 \quad \forall \quad t < \tau \quad (\text{see Appendix A3})$$

and therefore from Equation (3.2.1)

$$H \leq \left[\frac{\beta K_1}{K_1 + K_2} - \alpha \right] (A_i - A) \quad (3.3.9)$$

on an optimal policy.

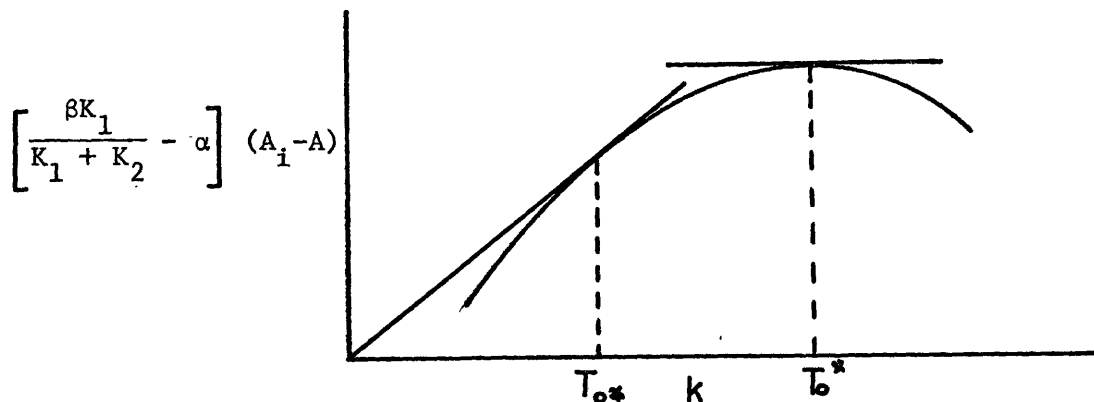
3.3.2 Initial Temperature Limitations

Some regions of initial temperature will not have any stationary policies associated with them which satisfy the Maximum Principle; initial temperatures in such regions will violate conditions 3.3.8 or 3.3.9.

The Hamiltonian on a stationary policy may be written as

$$H_s = \left[\frac{\beta K_1}{K_1 + K_2} - \alpha \right] (A_i - A) - k \frac{\partial \left[\frac{\beta K_1}{K_1 + K_2} - \alpha \right] (A_i - A)}{\partial k}$$

If we consider a graph of $\left[\frac{\beta K_1}{K_1 + K_2} - \alpha \right] (A_i - A)$ vs k then condition 3.3.8 limits initial temperatures (or k) to those above a tangent from the origin. While condition 3.3.9 limits initial temperatures to regions of positive or zero slope



For $p_1 \geq p_2$ condition 3.3.9 is always satisfied ($k \geq 0$) and therefore there is no upperbound on the initial temperature.

For $p_1 < p_2$ there will be an upperbound on the initial temperature which may or may not be in the region of physically permissible temperatures, $k_* \leq k \leq k^*$.

If at $t = 0$, we permit only those starting temperatures which satisfy condition 3.3.8 then

$$\frac{\partial^2 \left[\frac{\beta K_1}{K_1 + K_2} - \alpha \right] (A_i - A)}{\partial k^2} < 0$$

in the permissible region, since the tangent point from the origin will be above the inflection point. Also from Equation (3.2.1) with

$$\phi = -k\psi$$

$$\frac{\partial^2 H}{\partial k^2} = \frac{\partial^2 \left[\frac{\beta K_1}{K_1 + K_2} - \alpha \right] (A_i - A)}{\partial k^2}$$

$\therefore \frac{\partial^2 H}{\partial k^2} < 0$ for a starting temperature which satisfies condition 3.3.8, and hence the stationary policy is optimal at $t = 0$ (condition 3.2.4a).⁽¹⁾

3.3.3 Behaviour of the Optimal Temperature Policy as $t \rightarrow \tau$.

At the end of the process ($t = \tau$) since the activity is free the adjoint is fixed and by definition is zero, then from Equation (3.3.1)

1. Constrained policies starting at such temperatures can also be optimal, however the period of operation will be different from the optimal policy which is initially stationary.

$$\left. \frac{\partial H}{\partial k} \right|_{\psi, t=\tau} = \frac{A_1 \beta K_1 K_2 (p_1 - p_2)}{k(K_1 + K_2)^2} (1 - e^{-\psi(K_1 + K_2)}) + \left[\frac{\beta K_1}{K_1 + K_2} - \alpha \right] \frac{A_1 \psi}{k} (p_1 K_1 + p_2 K_2) e^{-\psi(K_1 + K_2)} \quad (3.3.10)$$

The second term is always positive, and for $p_1 \geq p_2$ the first term is positive or zero, \therefore for $p_1 \geq p_2$

$$\left. \frac{\partial H}{\partial k} \right|_{t=\tau} > 0$$

which implies that the optimal policy ends on the upper constraint.

For $p_1 < p_2$ Equation (3.3.10) may be positive, negative or zero and the policy may end respectively on the upper constraint, lower constraint or in the unconstrained region.

3.4 ANALOGY BETWEEN OPTIMAL POLICIES FOR FIRST ORDER REVERSIBLE
AND PARALLEL REACTIONS WITH CATALYST DECAY

For the case without catalyst decay Horn (1961) was able to show that the optimization problems of maximizing product concentration for a first order reversible and for one product of a first order parallel reaction were analogous after a suitable transformation of variables. If a similar analogy could be found between first order reversible and first order parallel reactions with catalyst decay, then the optimal policies as reported by Drouin (1969) for a reversible reaction with catalyst decay could be applied to the parallel reaction system.

The optimization problem as solved by Drouin (1969) for first order reversible reactions can be stated in the following manner:

$$\text{with } \frac{d\psi}{dt} = \phi \quad \psi(0) = 1 \quad (3.4.1)$$

it is required to

$$\text{MAX}_k \quad P = \int_0^T B(t, \theta) dt \quad (3.4.2)$$

subject to

$$0 \leq k_* \leq k \leq k^*$$

An optimization problem for a first order parallel reaction could be stated in the same manner as for the reversible reaction (equations 3.4.1, 3.4.2) with the exception that the expression for $B(t, \theta)$ will

be different in the general case for the two reactions.

In Appendix A1 a general analogy is developed between first order reversible and parallel reactions. The analogy is as follows:

<u>REVERSIBLE</u>	<u>PARALLEL</u>
$A - A_{eq}$	$\frac{K_1}{K_1 + K_2} A$
B	B
A_i	$A_i + \frac{K_2}{K_1} B_i$
B_i	B_i

The optimization problems for the reversible and parallel reactions are the same if the corresponding expressions for the Hamiltonian are identical. The Hamiltonian on a stationary policy, for the problem as stated by equations 3.4.1 and 3.4.2 is

$$H_s = B - k \frac{\partial B}{\partial k} \quad (3.4.3)$$

If B and $\frac{\partial B}{\partial k}$ are identical for the two cases then the two optimization problems may be considered as one.

Consider the following cases:

(1) $\underline{B_i = 0, 0 \leq t \leq t}$

then $B = \frac{K_1 A_i}{K_1 + K_2} \left[1 - e^{-\psi \theta (K_1 + K_2)} \right]$

for both parallel and reversible reactions (see Equations A1.4 and 3.1.9). Also for $B_i = 0$, A_i reverse is analogous to A_i parallel and therefore the expressions for B and $\frac{\partial B}{\partial k}$ are identical and the optimal temperature policies for first order reversible reactions can be directly applied to first order parallel reactions.

The optimal policies reported by Drouin (1969) were for cases where $B_i = 0$, $0 \leq t \leq \tau$, and these policies may therefore be used as the solution to the optimization problem as stated by equations 3.4.1 and 3.4.2 for a parallel reaction first order in both paths.

$$(2) \quad \underline{B_i \neq 0; A_i, B_i \text{ constant for } 0 \leq t \leq \tau}$$

on substituting,

$$A_i' = A_i + \frac{B_i K_2}{K_1}$$

for the parallel reaction, the expressions for B reduce to the same form for reversible and parallel reactions with B reverse corresponding to B parallel and A_i reverse corresponding to A_i' parallel.

However, A_i' is a function of k while A_i is not, therefore the expressions for $\frac{\partial B}{\partial k}$ are not the same, from which it may be concluded that H_s (reversible) and H_s (parallel) are not identical expressions.

However if A_i' is constrained to be a constant value equal to A_i reverse, by varying A_i parallel, then the optimal policy as found for one case could be used to extract an optimal policy for the other reaction system.

For Example if the optimization problem for the reverse

reaction is solved with

$$A_i = \text{a constant } c_1$$

$$B_i = \text{a constant } c_2$$

the resulting optimal policy is $k^+(t)$. This solution will correspond to the optimal control policy for the parallel reaction problem where

$$B_i = c_2$$

$$A_i' = c_1$$

However for A_i' to be constant A_i parallel must vary such that

$$A_i = c_1 - c_2 \frac{K_2}{K_1}. \quad (3.4.4)$$

Therefore for $k^+(t)$ other than a constant, A_i for the parallel system must vary with time according to Equation 3.4.4.

CHAPTER 4

NUMERICAL SOLUTIONS

4.1 CALCULATION METHOD

The properties of an optimal policy, developed in sections 3.2 and 3.3, are used as the basis for the computational algorithm embodied in the FORTRAN program listed in Appendix B. The main features of the algorithm are as follows.

Given a definition of the reaction system (i.e., $p_1, p_2, E_c/R, a_c, T^*, T_*$) and a set of initial conditions, the outlet concentration of A and B and the initial Hamiltonian are calculated from Equations (3.1.8), (3.1.9) and (3.3.2). The Hamiltonian is then checked against conditions (3.3.8) and (3.3.9); if it fails to fulfil either of these conditions the initial temperature has no optimal policy associated with it. If the Hamiltonian fulfils both condition (3.3.8) and (3.3.9) the optimal policy begins as a stationary policy.

The calculations now enter a repetitive phase. For a small time increment the same temperature is assumed and the activity concentration of A and B, and the Hamiltonian are evaluated. If the constancy of the Hamiltonian is respected, the time is incremented and the procedure repeated, if not, a searching procedure is implemented to find the new temperature which will keep the Hamiltonian constant. Before each time increment $\frac{\partial^2 H}{\partial k^2}$ is evaluated and checked for the sign required by condition 3.2.4a.

When the policy reaches a temperature constraint calculations are switched to another section of the algorithm. On the constrained

policy $\frac{\partial H}{\partial k}$ is no longer zero and the adjoint is evaluated by integrating the adjoint equation. For each time increment activity and concentration of A and B are updated, and the adjoint is evaluated from an integrated form of Equation (3.2.2), the Hamiltonian is then calculated from Equation (3.2.1) and tested for constancy. $\frac{\partial H}{\partial k}$ is checked for the appropriate sign required by condition 3.2.4b or 3.2.4c. The optimal policy terminates when the adjoint becomes zero.

An alternative method for calculating the constrained policy is to evaluate the adjoint from Equation (3.2.1) using the value of the stationary Hamiltonian for H. Then a sufficient check for the policy to be optimal is that $\frac{\partial H}{\partial k}$ have the sign required by condition 3.2.4 b or c.

4.2 RESULTS

4.2.1 Classification of Results

A parallel reaction can be conveniently classified according to the relative magnitudes of the activation energies of its two paths. Parallel reactions in general may be divided into three classes:

$$(1) \quad p_1 = p_2$$

$$(2) \quad p_1 > p_2$$

$$(3) \quad p_1 < p_2$$

A further classification may be made by considering the relative size of the reaction activation energy to the catalyst decay

activation energy. For instance, class 2 may then be considered as the following group of sub-classes:

$$(a) \quad p_1 > p_2 \geq 1$$

$$(b) \quad p_1 \geq 1 > p_2$$

$$(c) \quad 1 > p_1 > p_2$$

4.2.2 Definition of the Reaction System: Numerical Values

Numerical solutions were calculated for the following hypothetical reaction system:

$$g(\psi) = \psi$$

$$\text{Catalyst decay frequency factor: } a_c = 100 \text{ s}^{-1}$$

$$\text{Catalyst decay temperature factor: } \frac{E_c}{R} = 15,000^\circ\text{K}$$

$$\text{Reactor temperature constraints: } T^* = 900^\circ\text{K}$$

$$T_* = 800^\circ\text{K}$$

$$\text{Ratio of reactor length to linear velocity: } \theta = 1\text{s}$$

$$\text{Initial catalyst activity: } \psi_0 = 1.00$$

$$\text{Inlet concentrations: } A_i = 1.0, \quad B_i = 0$$

$$\text{Value coefficients: } \alpha = 0.25, \quad \beta = 1.0$$

In order to compare reactions with different values of p_1 and p_2 the following criterion was used: at maximum temperature (900°K) and maximum activity (1.00) the conversion of A is 90%, 45% to B and 45%

to C. Or

$$B^* = C^* = 0.45 \quad (\text{at } T^* \text{ and } \psi_0)$$

The criterion was satisfied for each set of p_1 and p_2 by setting the frequency factors for the two reaction paths.

4.2.3 Unconstrained Optimal Policies

(a) $p_1 = p_2 = p$

For this type of reaction one numerical solution has been calculated for $p = 1.0$; the results are shown in Figure 1.

As determined in section 3.3 the optimal control policy is one of constant conversion and $k^+(t)$ is given by Equation (3.3.6). The unconstrained solution has no finite operating time associated with it although temperature rises very sharply after 118 hours of operation.

The reaction rates A to B and A to C are equal for $p_1 = p_2$ and changing temperature has no effect on the ratio of B to C which is 1. The reaction then behaves identically to a first order irreversible reaction ($A \rightarrow D$). Hence the constrained solutions for this type of reaction will be of the same form as those calculated by Crowe (1969) for a first order irreversible reaction.

(b) $p_1 > p_2$

For this class of reactions numerical solutions have been calculated for the following cases:

(1) $1 \geq p_1 > p_2$ ($p_1 = 0.8, p_2 = 0.5$)

(Cont'd)

$$(2) \quad p_1 \geq 1 > p_2 \quad (p_1 = 1.1, \quad p_2 = 0.9)$$

$$(3) \quad p_1 > p_2 \geq 1 \quad (p_1 = 1.5, \quad p_2 = 1.3)$$

The results for these 3 cases are presented in Figures 2 to 4 respectively.

All of the calculated policies exhibit increasing concentrations of A and consist of rising temperature curves which do not end at finite temperatures. The concentration of B is observed in the 3 cases to be respectively decreasing, decreasing and increasing, and increasing.

It was shown in section 3.3. that, for $p_1 \geq p_2$, at the end of the optimal policy $\frac{\partial H}{\partial k} > 0$. However for the case of no temperature constraint the optimal policy is stationary ($\frac{\partial H}{\partial k} = 0$) and hence continues indefinitely. As activity approaches zero the temperature must rise with increasing rapidity to keep up the production of B; thus the behaviour exhibited in Figures 2 to 4 where temperature approaches a vertical asymptotic behaviour as activity approaches zero.

For $p_1 > p_2$ an increase in temperature increases the ratio of B produced to C produced. The optimal policy strives to prevent a sharp decrease in B; for $p_1 > p_2$ by increasing temperature one is able to maintain a favourable production of B and at the same time increase the B to C ratio and thereby require the consumption of less A for the same result in B.

In cases where B^+ is decreasing or essentially constant, the above implies that A^+ will increase, this behaviour is observed in Figures 2 and 3. In cases where B^+ is rising while temperature is increased the behaviour of A^+ will depend on the sensitivity of the

ratio B to C to temperature increase. In Figure 4, B^+ is increasing while at the same time A^+ increases, this behaviour indicates that the B to C ratio is highly sensitive to the increasing temperature and C is being reduced rapidly enough to increase both A and B.

$$(c) \underline{p_1 < p_2}$$

For this class of reactions numerical solutions have been calculated for the following cases:

$$(1) \quad 1 \geq p_2 > p_1 \quad (p_1 = 0.5, \quad p_2 = 0.8)$$

$$(2) \quad p_2 \geq 1 > p_1 \quad (p_1 = 0.5, \quad p_2 = 1.5)$$

$$(3) \quad p_2 > p_1 > 1 \quad (p_1 = 1.3, \quad p_2 = 1.5)$$

The results for these three cases are presented in Figures 5 to 7 respectively. All of the calculated policies exhibit falling concentrations of A and B and consist of rising temperature curves ending at finite temperatures.

For $p_1 < p_2$ an increase in temperature decreases the ratio of B to C produced. An optimal policy will tend to slow the decline in B^+ caused by falling activity by raising the temperature. Raising the temperature causes a decrease in the ratio of B to C produced and thereby necessitates the consumption of more A to produce the same amount of B. Even for a slightly decreasing B^+ the decrease in the ratio of B to C caused by increasing temperature is likely to be great enough to require the consumption of more A to produce even the lower amount of B.

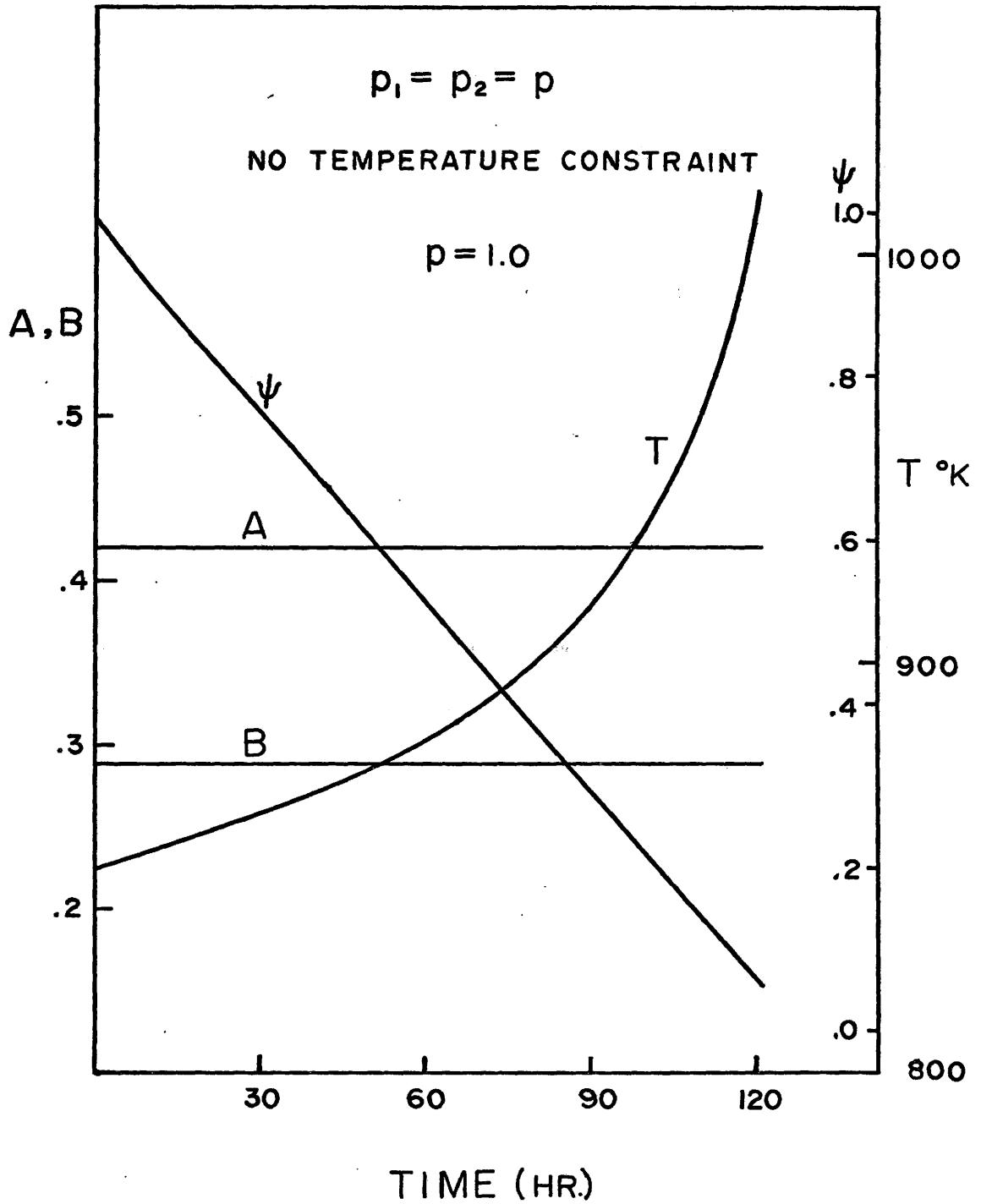


FIGURE I

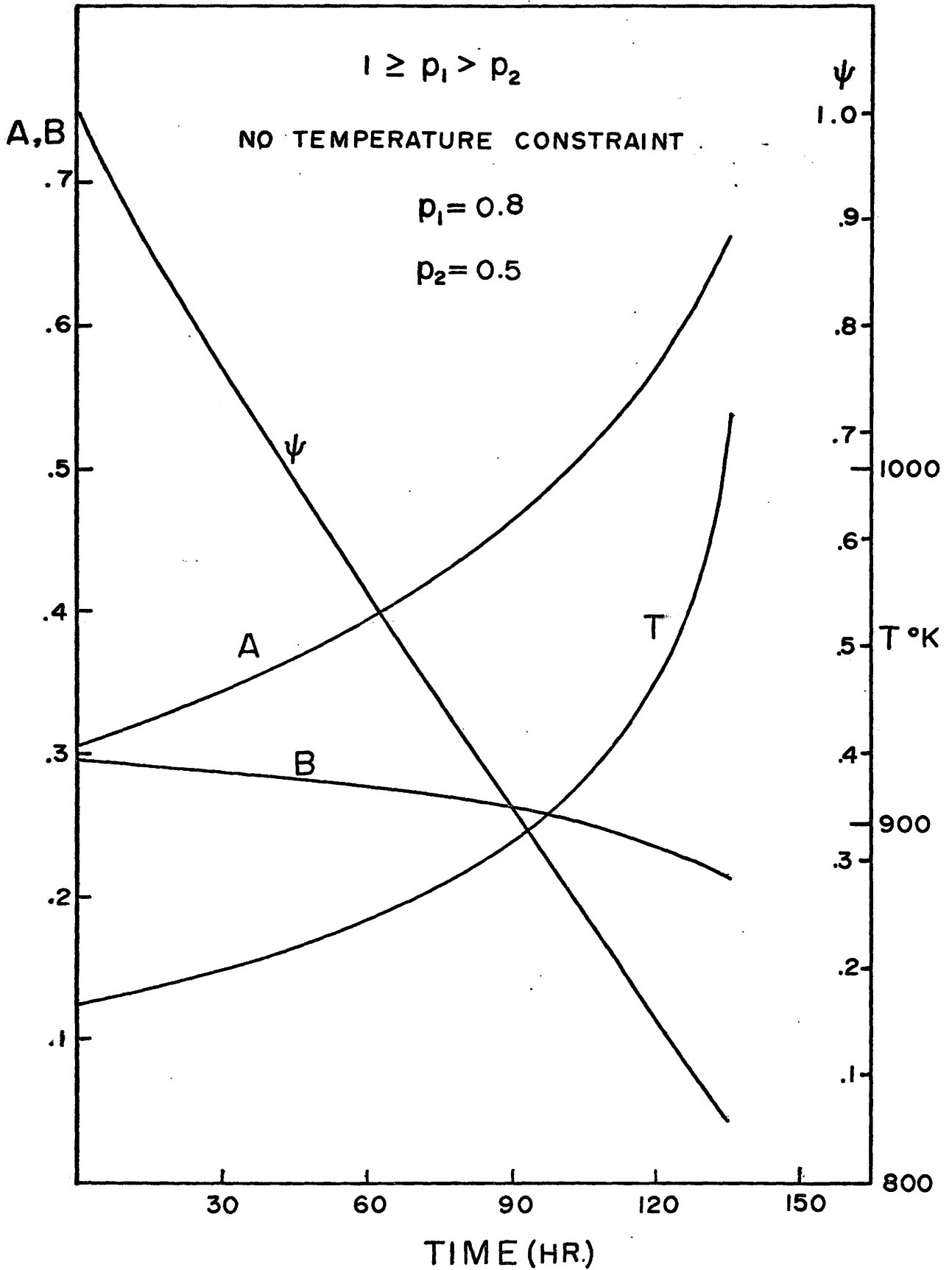


FIGURE 2

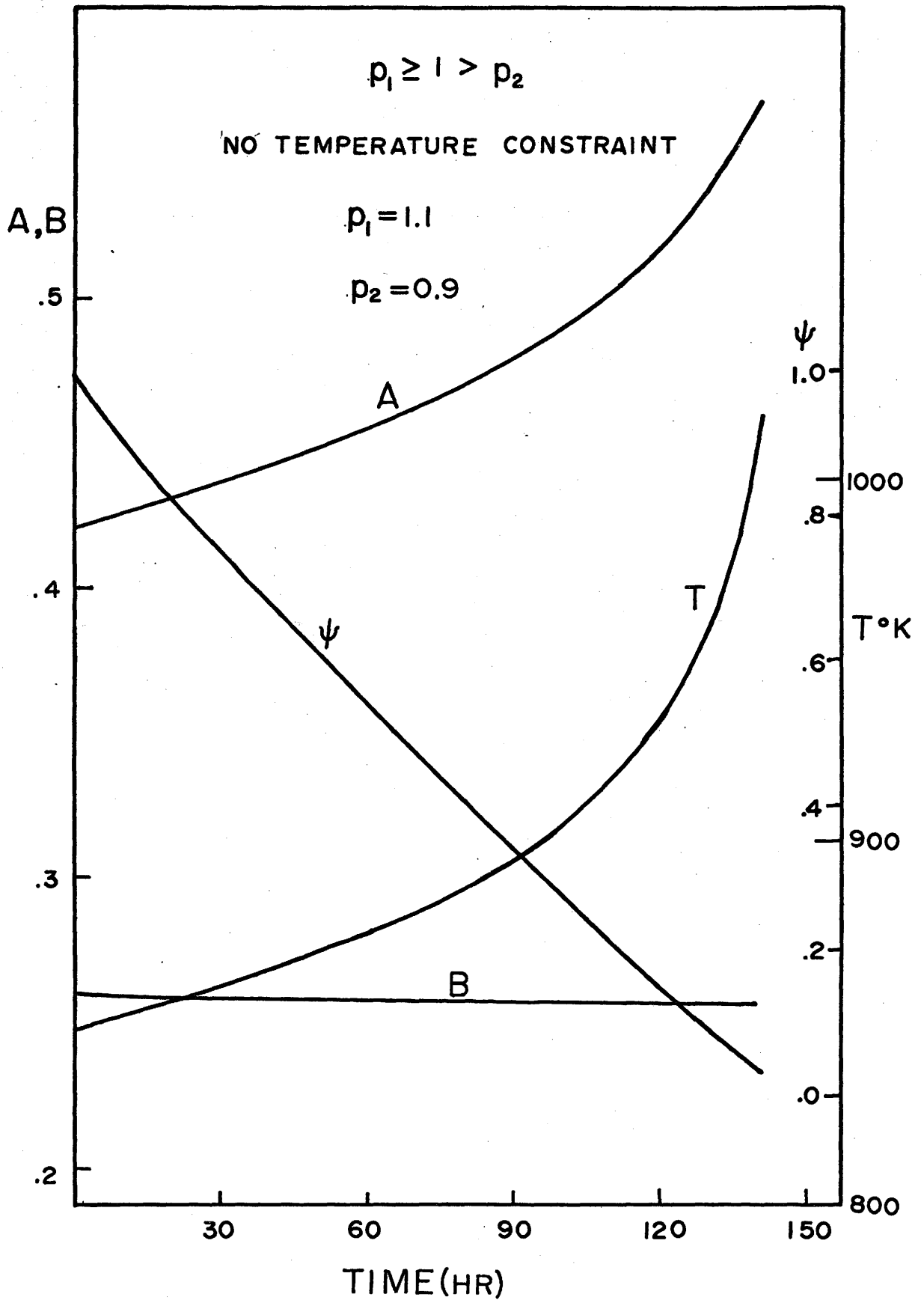


FIGURE 3

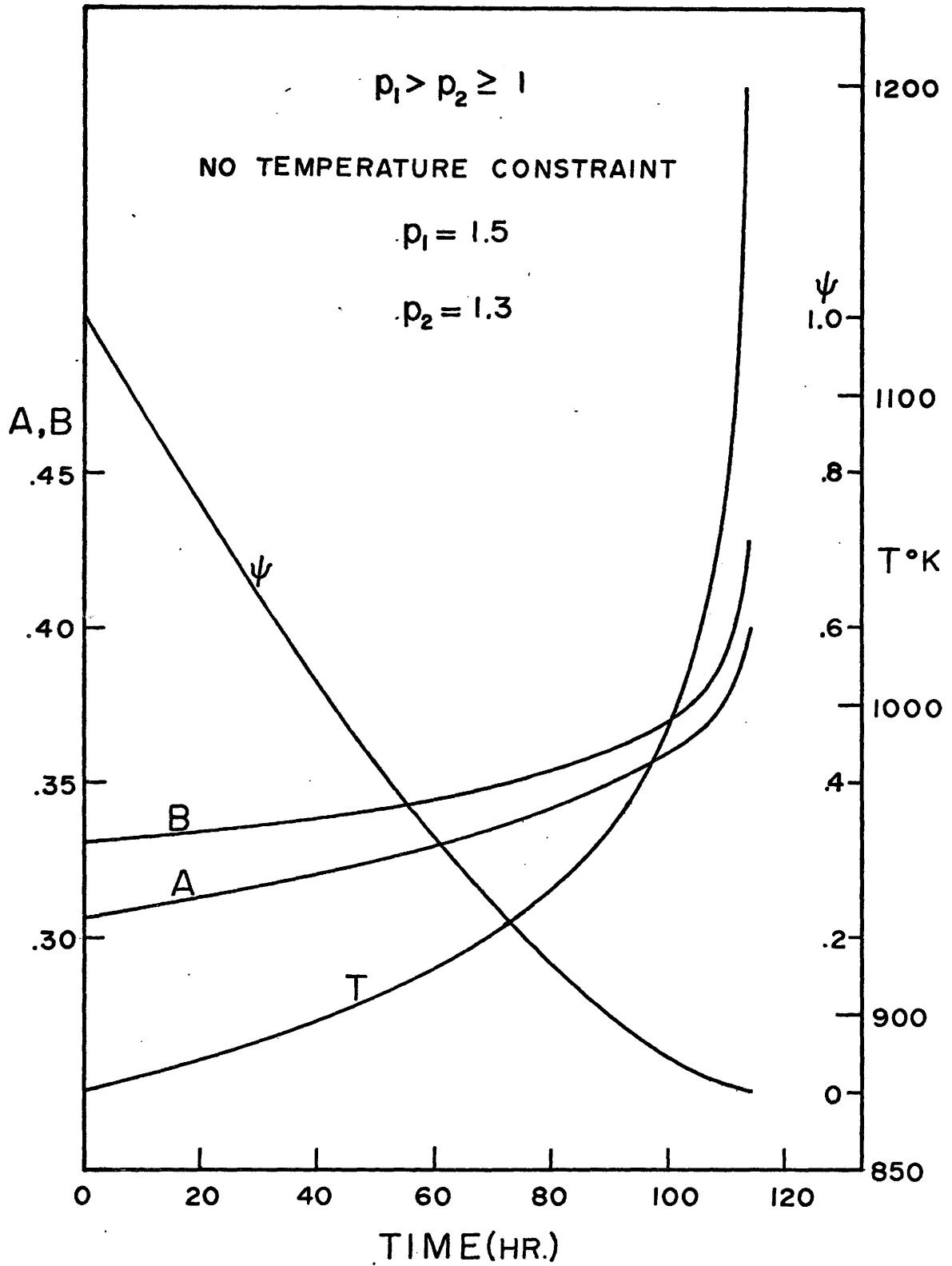


FIGURE 4

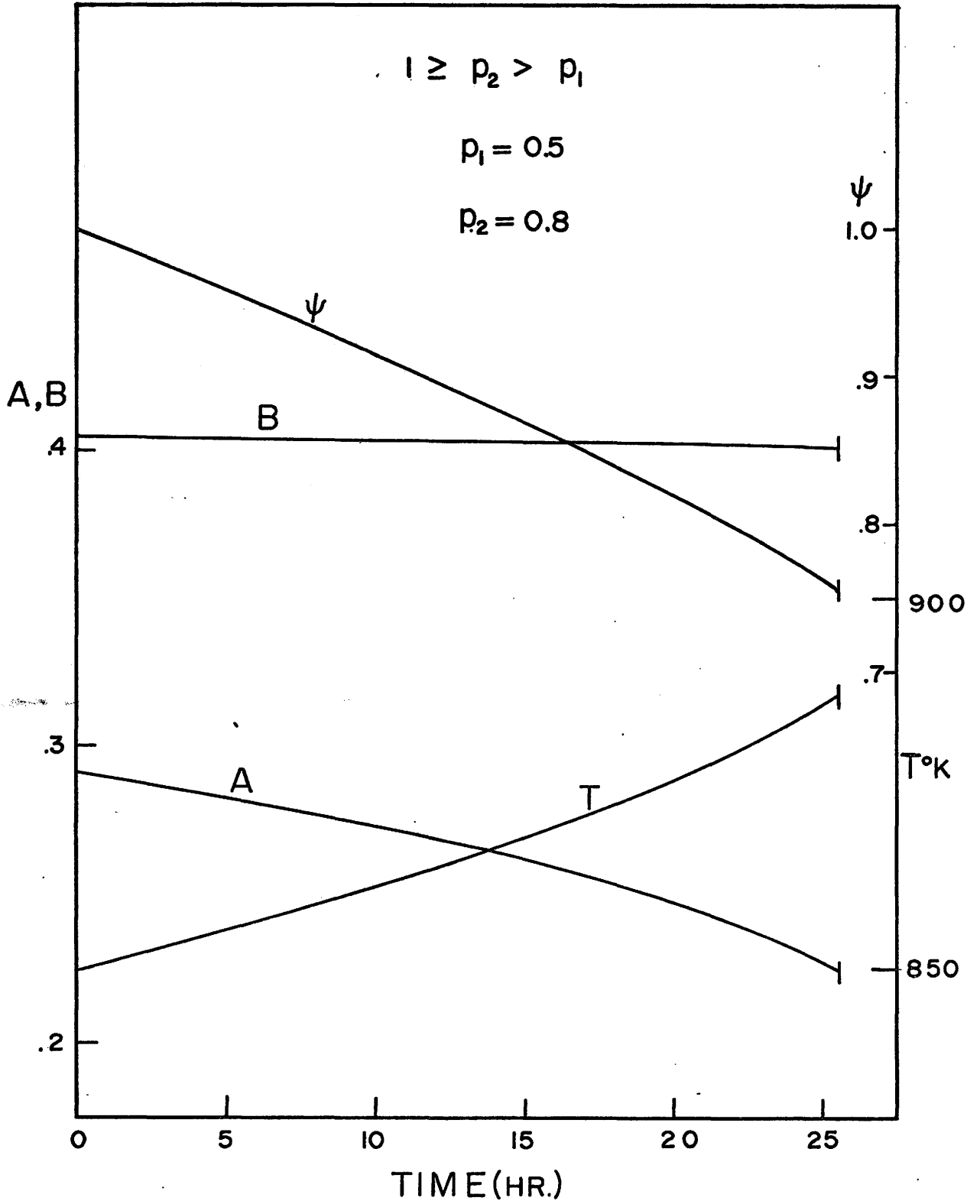


FIGURE 5

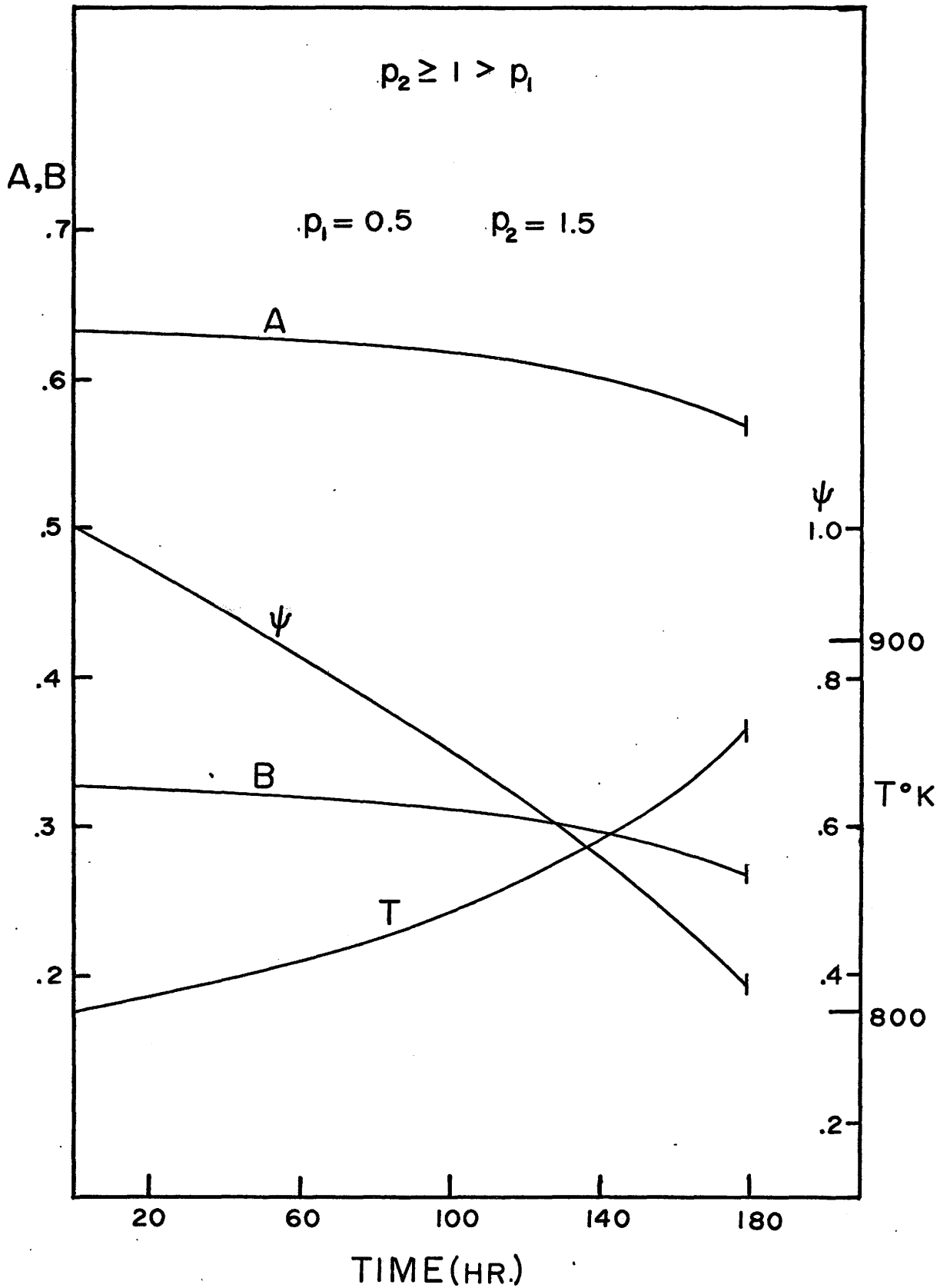


FIGURE 6

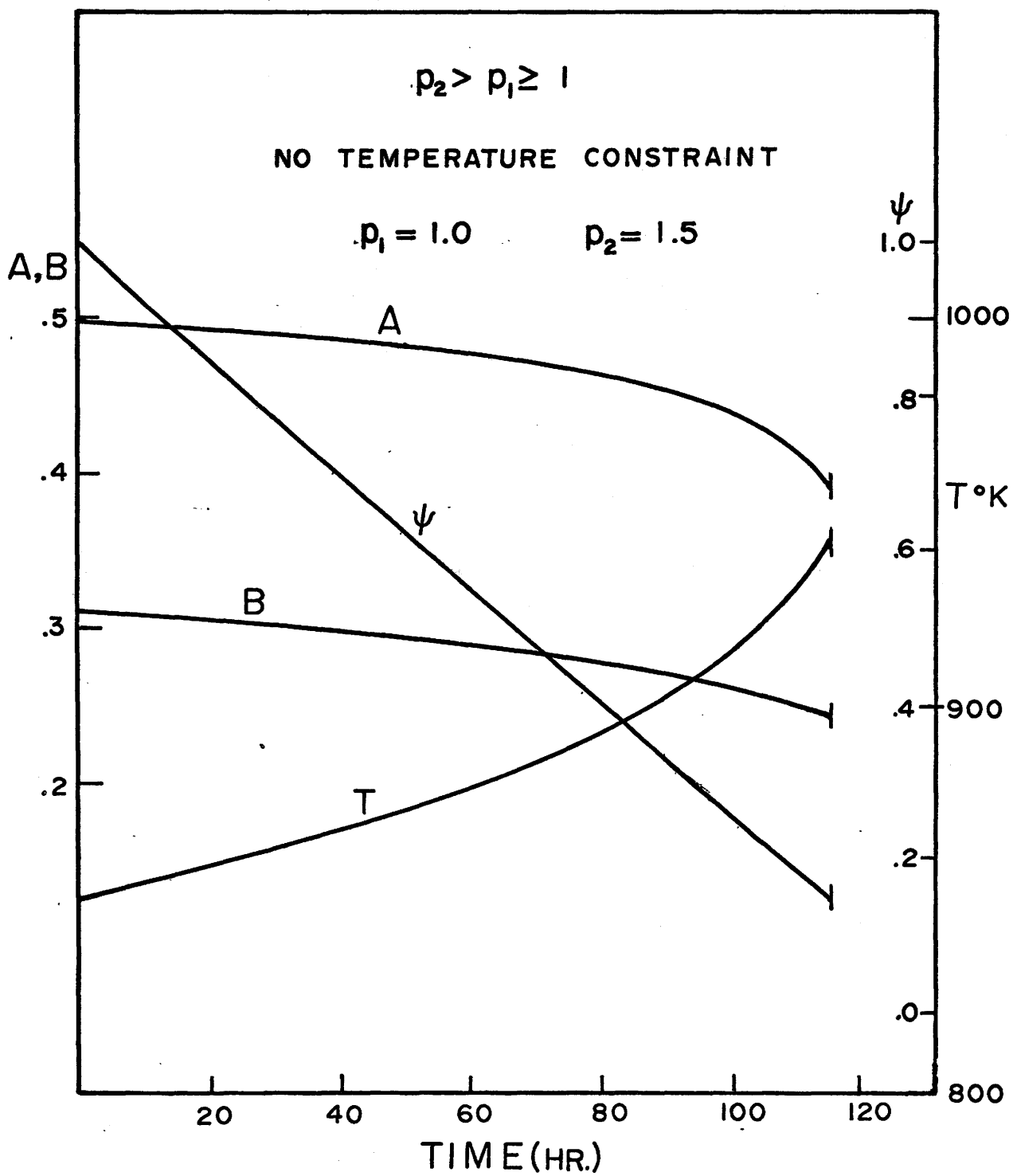


FIGURE 7

4.2.4 Constrained Optimal Policies

(a) $p_1 > p_2$

Figure 8 shows the constrained optimal policies associated with various fixed operating periods, for $p_1 = 1.1$ and $p_2 = 0.9$.

As the initial temperature is increased the operating period of the respective optimal policies decreases. The shortest optimal policy is 59.15 hours and has as an initial temperature the upper constraint (900°K). The longest possible optimal policy has a starting temperature of 830.58°K. Below this temperature the Hamiltonian is negative violating condition (3.3.9), and hence policies with initial temperatures in this range cannot be optimal in the sense of Pontryagin's Maximum Principle.

As determined in section 3.3. for $p_1 > p_2$ all optimal policies end on the upper temperature constraint. The four policies shown in Figure 8 verify this property and in addition are observed to consist only of increasing temperature curves and or T^* .

Using a down-time of 12 hours for replenishing the catalyst, the performance index per hour has been calculated for each policy. The maximum average performance index is realized for the policy starting on the upper temperature constraint.

Figure 9 shows the behaviour of catalyst activity and outlet concentrations of A and B along the optimal policy for $\tau = 211.48$ (curve 3 in Figure 8). The behaviour of the variables is much as one would expect. On reaching the temperature constraint:

- (1) The rate of decline of the catalyst activity slows appreciably, reflecting the stop in the increase of the catalyst decay rate constant.
- (2) The concentration of A increases very rapidly due to the decreasing activity and constant temperature.
- (3) The concentration of B decreases rapidly due to the decreasing catalyst activity and the constant temperature.

(b) $p_1 < p_2$

Figure 10 shows the constrained optimal policies associated with various fixed operating periods for $p_1 = 1.0$ and $p_2 = 1.5$.

As was the case for $p_1 > p_2$, increasing the initial temperature decreases the operating period. The longest optimal policy is 458.08 hours and has as its initial temperature the lower constant (800°K). The shortest optimal policy operates for zero time beginning at 888.62°K . At initial temperatures above 888.62K no optimal policies exist as condition 3.9 is violated in this region.

For $p_1 < p_2$ an optimal policy does not have to end on the upper temperature constraint. Of the policies calculated only one ended on the stationary curve, the remainder ended on T^* . Each of the optimal policies consists only of rising temperature curves and or T^* .

As for $p_1 > p_2$, the average performance index has been calculated for each optimal policy. The largest average performance index was found for $T_0 = 875$ and the maximum will be for a policy with an initial temperature in the range of $850 < T_0 < 885$.

Figure 11 shows the behaviour of A, B and ψ along the optimal policy for $\tau = 113.89$ hours. The behaviour along the stationary policy has been discussed previously (Figures 5,6,7) and that along the constraint is very similar to Figure 9.

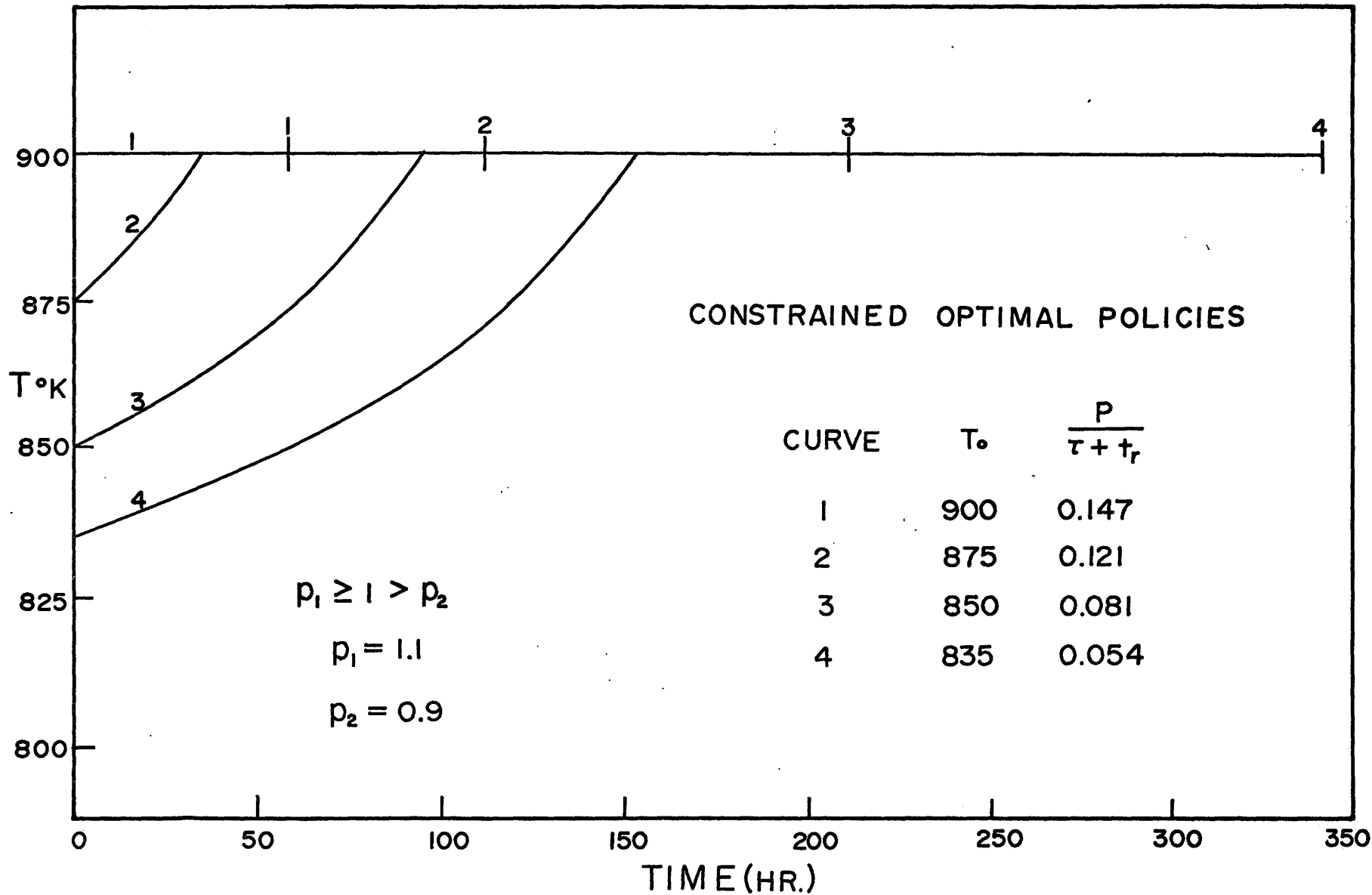


FIGURE 8

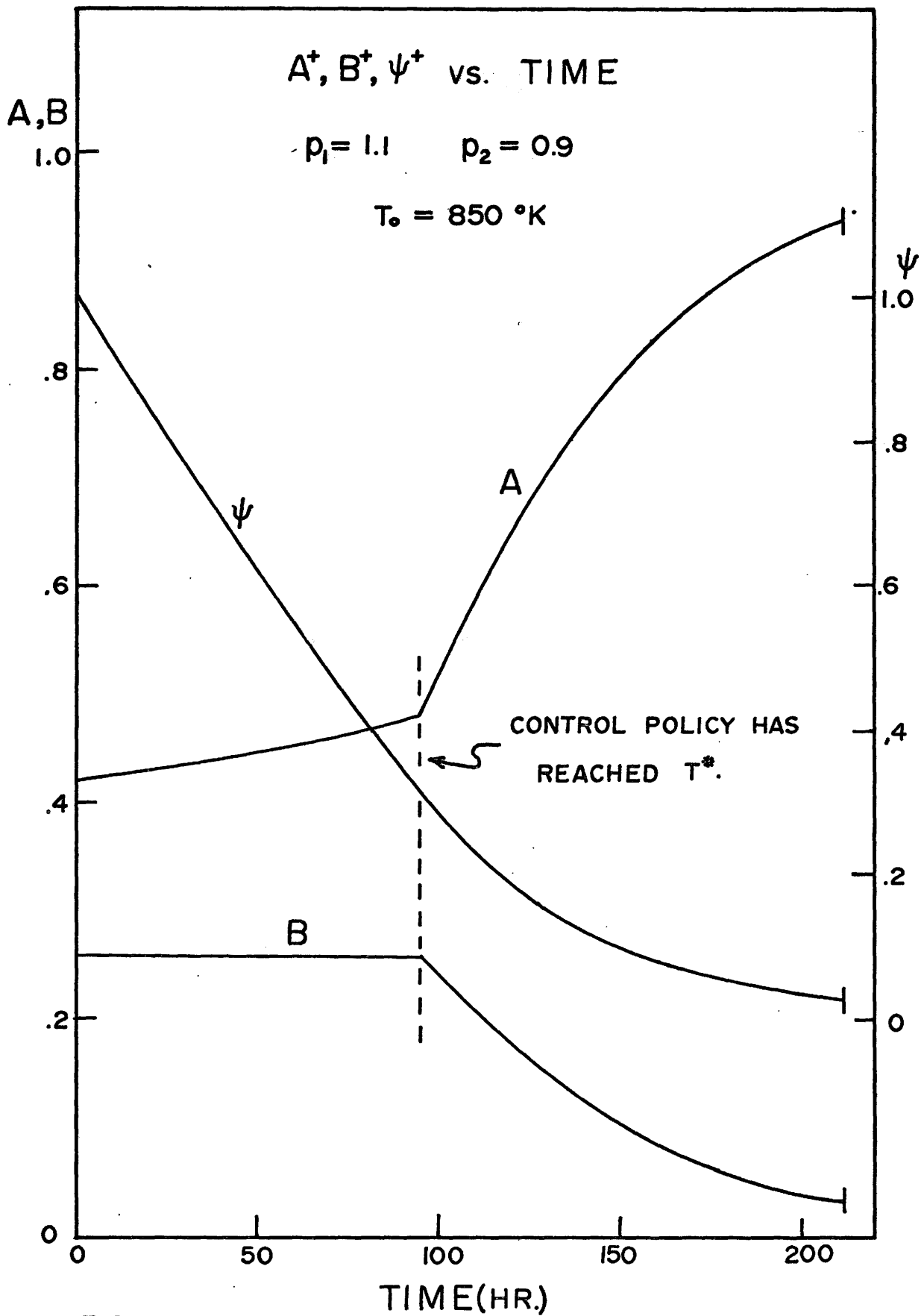


FIGURE 9

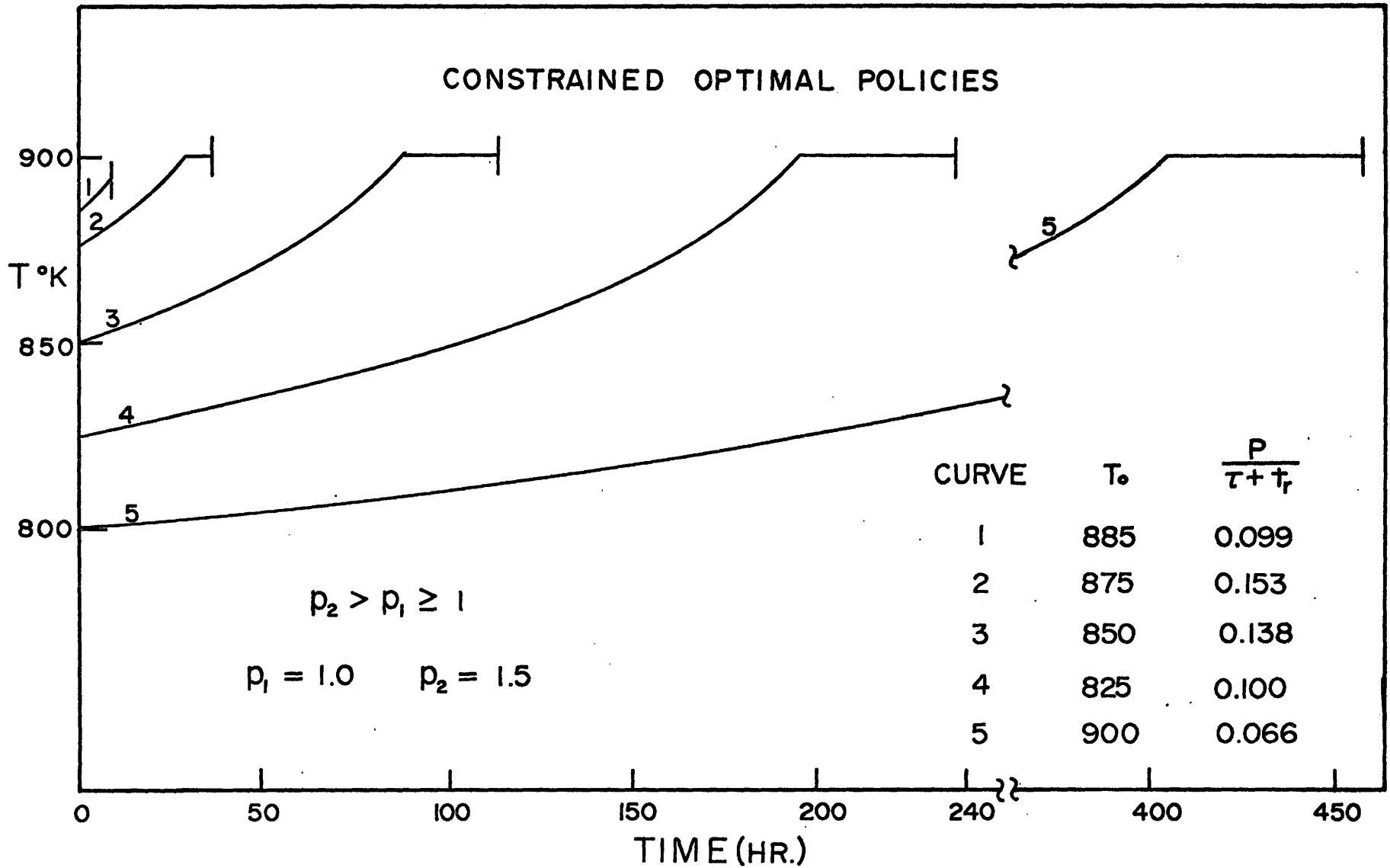


FIGURE 10

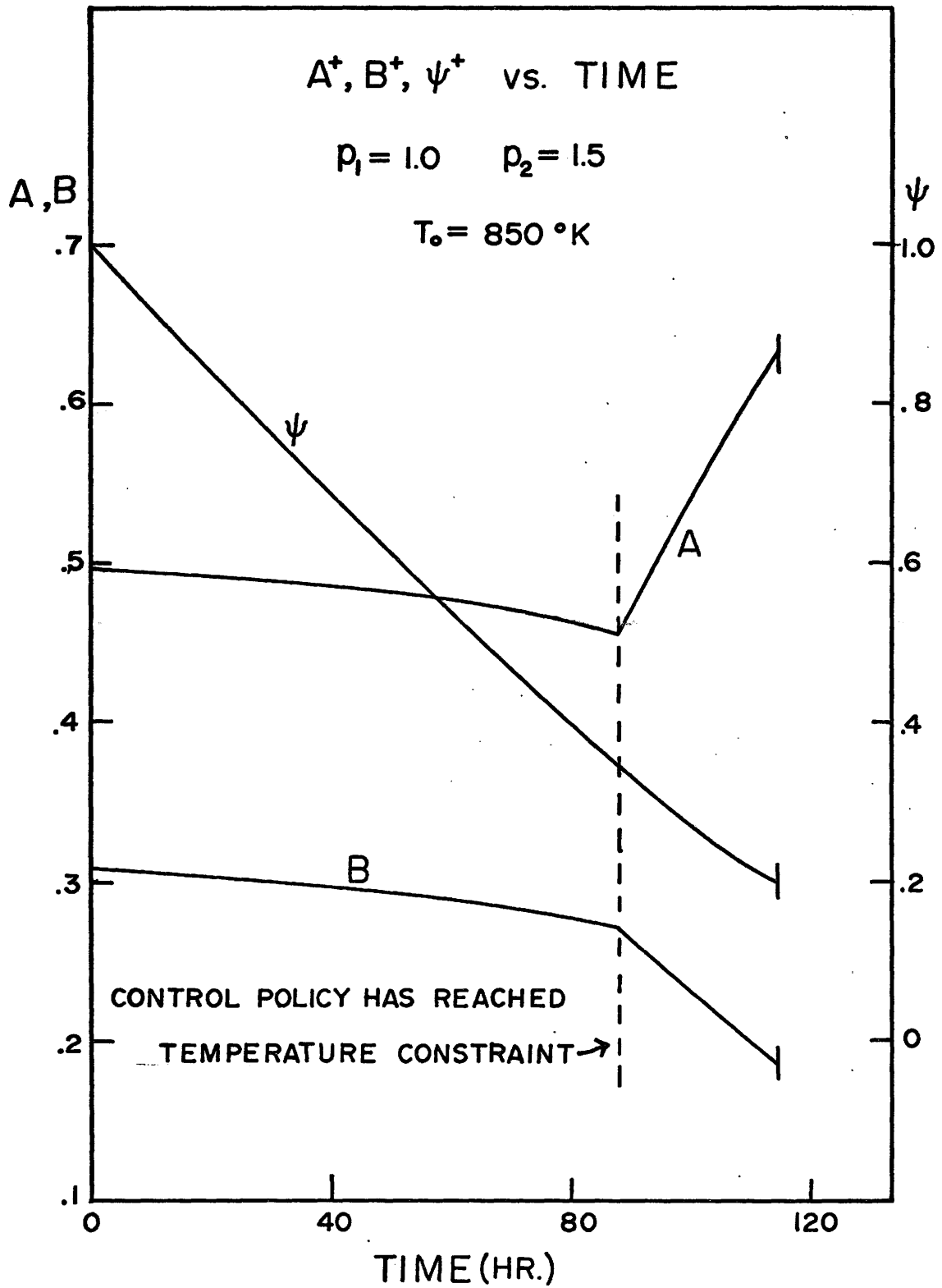


FIGURE II

4.2.5 Effect of α on Constrained Optimal Policies

Figures 12 and 13 show the effect of the relative value of the reactant (α) on a constrained optimal policy for $p_1 > p_2$ and $p_1 < p_2$ respectively.

For $p_1 > p_2$ increasing the value of the reactant lengthens the optimal policy and significantly lowers the optimal temperature along the stationary curve. Figure 12 shows this behaviour for $p_1 = 1.1$, $p_2 = 0.9$, $T_0 = 850^\circ\text{K}$ and $\alpha = 0, .25, .30$.

As α is increased the optimal policy becomes more sensitive to the efficient use of A, that is, it tends to reduce the amount of C produced while trying to maintain the production level of B. For $p_1 > p_2$, as α is increased, the optimal policy achieves this goal by first operating at lower temperatures on the stationary curve and thus increasing A along this section, and then by operating along T^* for a longer period of time. On T^* the ratio of B to C produced is highest and hence A is being used most efficiently along this section.

For $p_1 < p_2$ increasing the value of the reactant lengthens the optimal policy and causes a slight temperature increase along the stationary curve. Figure 13 shows this behaviour for $p_1 = 1.0$, $p_2 = 1.5$, $T_0 = 850^\circ\text{K}$ and $\alpha = 0, .1, .25, .35, .45$.

The temperature variation along the stationary curve was very small in comparison with the case for $p_1 > p_2$. The maximum temperature deviation observed for $p_1 < p_2$ was -0.5°K between policies for $\alpha = .25$ and $\alpha = 0$, while the maximum deviation for $p_1 > p_2$ between $\alpha = .25$ and $\alpha = 0$ was $+ 8.0^\circ\text{K}$.

For $p_1 < p_2$, decreasing temperature would improve the ratio of B to C produced. However, decreasing temperature also substantially decreases the amount of B produced. Hence to counter falling catalyst activity the stationary policy is one of increasing temperature, despite the attendant decreasing ratio of B to C produced. As α is increased, the tendency then is to terminate the optimal policy earlier due to the increasingly unfavourable ratio of B to C produced. On T^* the ratio of B to C produced is at its lowest and thus the higher α the less time the policy will operate on T^* .

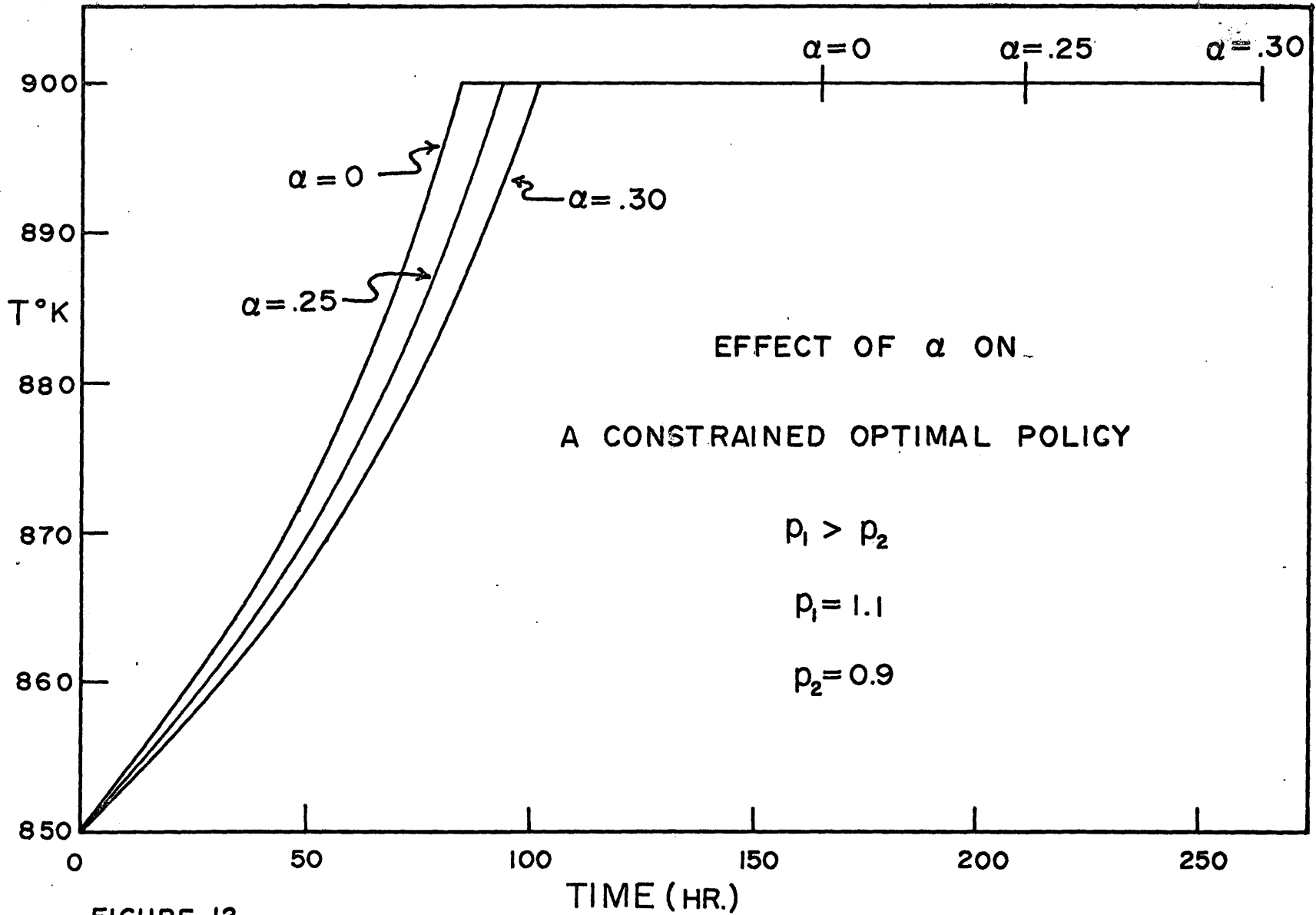


FIGURE 12

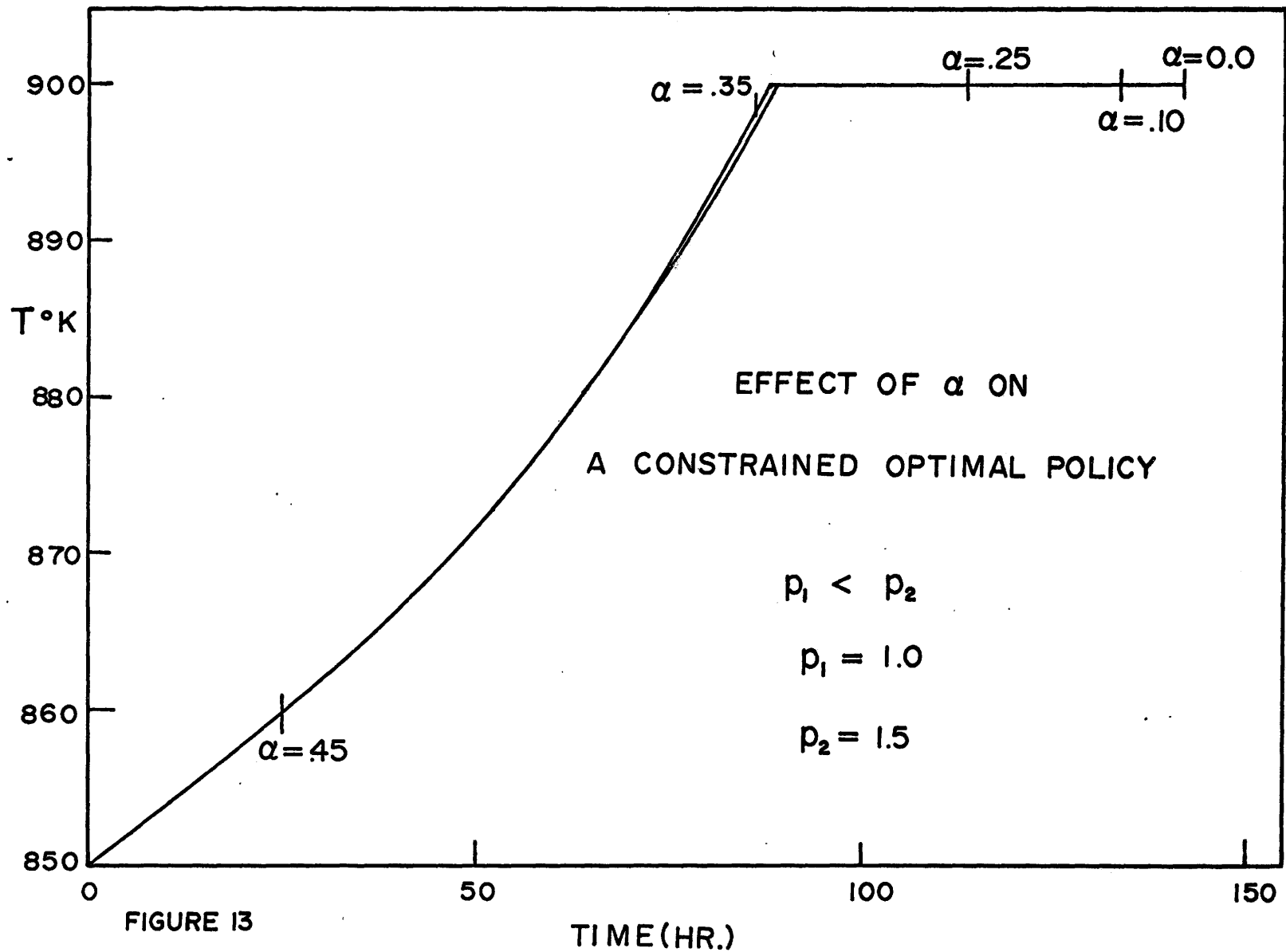


FIGURE 13

4.2.6 Sensitivity of a Constrained Optimal Policy

The sensitivity of the performance index to variations in the system parameters was examined for the case of $p_1 = 1.0$, $p_2 = 1.5$, and $\tau = 113.89$ hours ($T_0 = 850^\circ\text{K}$).

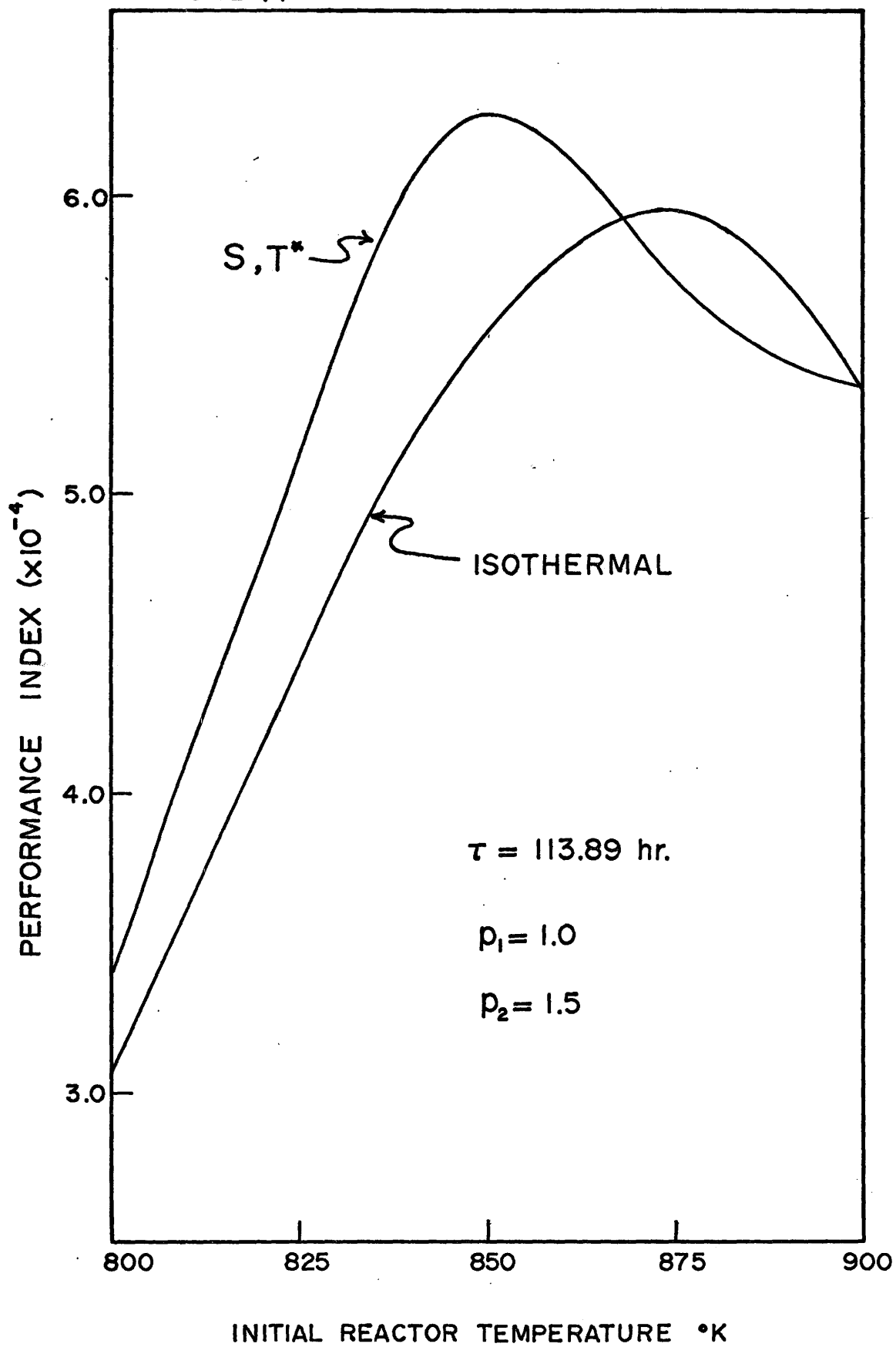
A perturbation of +1%, -1% on the initial temperature resulted in a decrease in the performance index of 1.5%, 2.4% respectively, when the optimal policies for these initial temperatures were terminated at $\tau = 113.89$ hours. These percentages may be regarded as an indication of the sensitivity of the performance index to the accuracy of the temperature control along the optimal policy. In the case of -1% perturbation the temperature policy is below the optimal policy until it reaches T^* , hence 2.4% of the performance index would be lost if the control system kept the temperature slightly below $T^+(t)$ during the period of increasing temperature .

Perturbing the catalyst decay activation energy + 10% and - 10% resulted in decreases in the performance index of 12.2% and 76% respectively. The large percentage decrease in performance index for a - 10% change in E_c (also changes E_1 and E_2) indicates that the activation energies must be accurately known before a computed optimal policy can be relied upon.

Perturbing $T^* + 1\%$, $- 1\%$ resulted in changes in the performance index of + 0.7% and - 0.7% respectively. Since the optimal policy is one of increasing temperature, it is necessary that T^* be as high as possible in order to achieve the best reactor performance.

A convenient method of assessing the optimal policy is to compare it with the best isothermal policy. For the case chosen, Figure 14 shows the performance index versus initial temperature for isothermal policies and policies of constant $H(S, T^*)$. The best isothermal policy is 873°K and realizes a performance index of 5.947×10^4 , 5.2% less than the optimal policy. Hence the optimal policy is a significant improvement over the best isothermal policy.

FIGURE 14



CHAPTER 5

GENERAL CONCLUSIONS AND HYPOTHESES

Conclusions

From the theoretical derivations in Chapter 3 the following conclusions have been made about the optimal control policy:

- (1) For $p_1 = p_2$ the optimal stationary policy is one of constant A and B, and is given by Equation (3.3.6).
- (2) For $p_1 \geq p_2$ the optimal policy must end on T^* (section 3.3.2).

Hypotheses

From numerical study the results of which are presented and discussed in Chapter 4 the following hypotheses have been made:

- I. In General
 - Optimal policies starting as stationary policies consist only of S and or T^* .
- II. For Stationary Sections of Optimal Policies
 - Only rising temperature policies occur
 - For $p_1 > p_2$ A^+ always increases with time
 - For $p_1 < p_2$ A^+ always decreases with time
 - For $p_1 < p_2$ B^+ always decreases with time
- III. For Constrained Optimal Policies
 - As T_0 is increased, τ decreases
 - For $p_1 > p_2$ as α is increased τ increases
 - For $p_1 < p_2$ as α is increased, τ decreases

NOMENCLATURE

- a - Arrhenius frequency factor
- A - Reactant concentration, also used schematically to represent the reactant.
- B - Desired product concentration
- c - A constant
- C - The undesired product
- E - Arrhenius activation energy
- g - Activity-dependent factor in catalyst decay rate
- H - Hamiltonian function
- k - Catalyst decay rate constant, also the decision variable
- K - Reaction rate constant
- p - Ratio of reaction activation energy to catalyst decay activation energy
- P - The performance index
- S - Stationary policy
- t - Time on stream
- t_r - Reactor down time between runs
- T - Temperature
- Z - Space time through reactor $0 \leq z \leq \theta$ ($\theta \equiv 1$)
- α - Value, per unit concentration x reactor volume, of A
- β - Value, per unit concentration x reactor volume, of B.
- θ - Space time of reactor $\equiv 1$
- λ - Adjoint variable to ψ
- τ - Total reaction time

- ϕ - Rate of catalyst decay
 ψ - Catalyst activity

Subscripts

- c - Catalyst
eq - Equilibrium
i - inlet, $z = 0$
o - $t = 0$
s - Stationary policy
1 - Reaction A to B
2 - Reaction A to C
* - Minimum attainable value

Superscripts

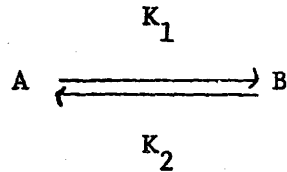
- + - Value along optimal policy
* - Maximum attainable value

BIBLIOGRAPHY

- ANDERSON, R.B., ed.,
Experimental Methods in Catalytic Research,
Academic Press, 1968.
- CROWE, C.M.,
Preprint 34 c, 65th National Meeting AIChE, Cleveland,
May 1969.
- DROUIN, J.G.,
M.Eng. Project Report, McMaster University, Hamilton, 1969.
- HALKIN, H., in Leitmann, G., ed.,
Topics in Optimization, Chapter 6, Academic Press, New York,
1967.
- HORN, F.,
Chem. Eng. Sci., 14, (Jan. 1961), 77-88.
- JACKSON, R.,
The Application of Mathematical Models in Chemical Engineering,
Research, Design and Production
Institute of Chemical Engineers, London, 1965, p. 32.
- KUNII, D., and LEVENSPIEL, O.,
Fluidization Engineering, Wiley, New York, 1969, p. 355.
- PONTRYAGIN, L.S., BOLTYANSKII, V.G., GAMKRELIDZE, R.V. and MISHCHENKO, E.F.
The Mathematical Theory of Optimal Processes, John Wiley,
New York, 1962.
- SZEPE, S.,
Ph.D. Thesis, Illinois Institute of Technology, 1966.

APPENDIX A1ANALOGY BETWEEN FIRST ORDER REVERSIBLE AND
PARALLEL REACTIONS

For the reversible reaction



first order in both paths, material balances on A and B, assuming plug flow give

$$\frac{\partial B}{\partial t} + \frac{\partial B}{\partial Z} = \psi(K_1 A - K_2 B) \quad A1.1$$

$$\frac{\partial A}{\partial t} + \frac{\partial A}{\partial Z} = \psi(K_2 B - K_1 A) \quad A1.2$$

for $\frac{\partial B}{\partial t} \ll \frac{\partial B}{\partial Z}$ and $\frac{\partial A}{\partial t} \ll \frac{\partial A}{\partial Z}$ the above equations may be considered as ordinary differential equations in space-time. Dividing A1.1 by A1.2 then gives

$$\frac{\dot{B}}{A} = -1$$

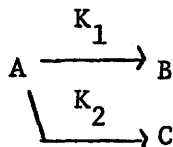
from which

$$B - B_i = A_i - A \quad A1.3$$

Substitution of equation A1.3 in A1.1 and subsequent integration over the reactor length gives an expression for the outlet concentration of B:

$$B = (A_i + B_i) \frac{K_1}{K_1 + K_2} + \frac{K_2 B_i - K_1 A_i}{K_1 + K_2} e^{-\psi\theta(K_1 + K_2)} \quad \text{A1.4}$$

For the parallel reaction



first order in both paths, material balances on A and B, assuming plug flow and for $\frac{\partial A}{\partial t} \ll \frac{\partial A}{\partial z}$ and $\frac{\partial B}{\partial t} \ll \frac{\partial B}{\partial z}$, can be written as

$$\dot{B} = \psi K_1 A \quad \text{A1.5}$$

$$\dot{A} = -\psi(K_1 + K_2)A \quad \text{A1.6}$$

Dividing A1.5 by A1.6 gives

$$\frac{\dot{B}}{\dot{A}} = -\frac{K_1}{K_1 + K_2}$$

from which

$$B - B_i = \frac{K_1}{K_1 + K_2} (A_i - A) \quad \text{A1.7}$$

The material balance for the reversible reaction (A1.3)

can be rewritten as

$$B - B_i = \frac{K_1}{K_1 + K_2} (A_i - \frac{K_2}{K_1} B_i) - \frac{K_1}{K_1 + K_2} \left[\left(1 + \frac{K_2}{K_1}\right) A - \frac{K_2}{K_1} (A_i + B_i) \right] \quad \text{A1.8}$$

Recalling that the equilibrium concentration of A is given by

$$A_{\text{eq}} = \frac{K_2}{K_1 + K_2} (A_i + B_i)$$

then comparison of equations A1.8 and A1.7 leads to the following analogy between first-order reversible reactions and first-order parallel reactions:

REVERSIBLE

PARALLEL

$$A - A_{\text{eq}}$$

$$\frac{K_1}{K_1 + K_2} A$$

B

B

A_i

$$A_i + \frac{K_2}{K_1} B_i$$

B_i

B_i

APPENDIX A2BEHAVIOUR OF THE HAMILTONIAN WITH TIME ALONG
AN OPTIMAL POLICY

From Equations (2.3), (3.1.8) and (3.2.1) the time derivative of H along any optimal path is

$$\frac{dH}{dt} = \frac{\partial H}{\partial \psi} \frac{d\psi}{dt} + \frac{\partial H}{\partial \lambda} \frac{d\lambda}{dt} + \frac{\partial H}{\partial k} \frac{dk}{dt} + \frac{\partial H}{\partial A_i} \frac{dA_i}{dt} \quad \text{A2.1}$$

The third term is always zero since on a stationary policy $\frac{\partial H}{\partial k} = 0$, and on a constrained policy $\frac{dk}{dt} = 0$. Furthermore, from Equations (2.3), (3.2.2) and (3.2.1) it can be shown that

$$\frac{d\psi}{dt} = \frac{\partial H}{\partial \lambda}$$

and

$$\frac{d\lambda}{dt} = - \frac{\partial H}{\partial \psi}$$

Equation A2.1 then reduces to

$$\frac{dH}{dt} = \frac{\partial H}{\partial A_i} \frac{dA_i}{dt} \quad \text{A2.2}$$

For constant inlet concentration of A, $\frac{dA_i}{dt} = 0$ and Equation A2.2 implies that the Hamiltonian is constant along any optimal path.

APPENDIX A3PROOF THAT THE ADJOINT IS POSITIVE FOR $t < \tau$

It is shown in section 3.3 that, except for the case when $\frac{\beta K_1}{K_1 + K_2} - \alpha$ is negative for all admissible temperatures, $H \geq 0$ on an optimal policy.

For $\lambda = 0$, Equation (3.2.1) then implies that

$$\frac{\beta K_1}{K_1 + K_2} - \alpha \geq 0.$$

Suppose $\lambda(t) = 0$ at $t < \tau$ then from Equation (3.2.2)

$$\frac{d\lambda}{dt} = \left[\frac{\beta K_1}{K_1 + K_2} - \alpha \right] \frac{\partial \Delta}{\partial \psi} \leq 0.$$

Suppose $\frac{\beta K_1}{K_1 + K_2} - \alpha = 0$ at any time when $\lambda = 0$, H can then be increased by changing k . By the Maximum principle this is not permissible for a point on the optimal policy. $\therefore \lambda = 0$ implies $\dot{\lambda} < 0$, unless $\psi = 0$ (for $g(\psi) = \psi$ this is possible only if $kt = \infty$).

Since λ is continuous, $\dot{\lambda} < 0$ at $\lambda = 0$ implies that λ crosses zero once and only once. Furthermore since $\lambda(\tau) = 0$ then

$$\lambda > 0 \quad \forall t < \tau.$$

Also from Equation (3.2.1)

$$\frac{\beta K_1}{K_1 + K_2} - \alpha \neq 0 \quad \text{since} \quad \lambda \neq 0.$$

APPENDIX BOPTIMAL POLICY FOR A PARALLEL REACTION FIRST ORDER IN
BOTH PATHS (FORTRAN LISTING)

NOTATION

TI INITIAL REACTOR TEMPERATURE DEG. K
 TU UPPER TEMPERATURE CONSTRAINT DEG. K
 TL LOWER TEMPERATURE CONSTRAINT DEG. K
 EC CATALYST DECAY TEMPERATURE COEFFICIENT DEG. K
 P1 E1/EC
 P2 E2/EC
 AI INLET CONCENTRATION OF REACTANT
 BI INLET CONCENTRATION OF DESIRED PRODUCT
 ALPHA VALUE COEFFICIENT FOR A
 BETA VALUE COEFFICIENT FOR B

```

    DIMENSION X(6),Y(6),PM(6)
    COMMON/BLK1/DIR,PSI,PSIT,P1,P2,A1,A2,BI,AI,BETA,ALPHA,
    1AKK1,AKK2,DTIME,HAM,AC
    READ(5,1) P1,P2           ,AI,BI
    READ(5,1) EC,TI,TU,TL,ALPHA,BETA
    1 FORMAT(7F10.0)
    WRITE(6,40) ALPHA,BETA
    40 FORMAT(15X,*ALPHA = *,F4.3,15X,*BETA = *,F4.2)
    WRITE(6,102)
    102 FORMAT(//,15X,*RATIO OF REACTOR LENGTH TO LINEAR *,
    1*VELOCITY = 1.00 SEC.*)
    WRITE(6,41)
    41 FORMAT(//30X,*TEMPERATURE CONSTRAINTS (K.)*//)
    WRITE(6,42) TL,TU
    42 FORMAT(15X,*LOWER = *,F5.0,5X,*UPPER = *,F5.0//)
    WRITE(6,103) TI
    103 FORMAT(10X,*INITIAL TEMPERATURE =*,F5.0//)
    WRITE(6,43)
    43 FORMAT(20X,*FREQUENCY FACTORS*//)
    AC=100.

C
C   SET FREQUENCY FACTORS SUCH THAT MAXIMUM CONVERSION OF A
C IS 90 PERC AND THE MAXIMUM CONVERSION TO B IS 45 PERCENT.
    A1=1.151296/EXP(-P1*EC/TU)
    A2=1.151296/EXP(-P2*EC/TU)

C
    WRITE(6,44) A1
    44 FORMAT(20X,*A TO B = *,F15.0)
    WRITE(6,45) A2
    45 FORMAT(20X,*A TO C = *,F15.0)
  
```

```

WRITE(6,46)AC
46 FORMAT(12X,*CATALYST DECAY = *,F15.0//)
WRITE(6,47)
47 FORMAT(15X,*ARRHENIUS ACTIVATION ENERGIES*/)
WRITE(6,48)EC
48 FORMAT(20X,*CATALYST DECAY(EC/R)*,F7.0)
WRITE(6,49) P1
49 FORMAT(20X,*RATIO B TO CATALYST *,F4.2)
WRITE(6,50)P2
50 FORMAT(20X,*RATIO C TO CATALYST *,F4.2///)
WRITE(6,52)
52 FORMAT(1X,*TIME(HR)*,1X,* TEMP.*,5X,*HAMILTONIAN*,5X,
1*D2H/DK2*,5X,*PSI*,4X,* A *,4X,* B *,7X,*ADJOINT*,5X,
2* K*,10X,*K1*,9X,*K2*,3X,* PFM INDEX*//)

```

C
C
C

INITIALIZATION SECTION

C
C
C
C
C
C
C

AK=AC*EXP(-EC/TI)

DIR=AK

INITIAL TIME INCREMENT.

DTIME=1000.

INITIAL INCREMENT FOR K.

DELTAK=.000000002

TOLERANCE FOR CONSTANT HAMILTONIAN.

EPS=.00001

INITIAL CATALYST ACTIVITY

PSI=1.00

PSIT=1.00

P=0.0

TIME=0.0

L=-1

AKK1=AK**P1*A1/AC**P1

AKK2=AK**P2*A2/AC**P2

SUMK=AKK1+AKK2

B = BI+AKK1*1I*(1.-EXP(-PSI*SUMK))/SUMK

A=AI*EXP(-PSI*SUMK)

C

CALCULATE VALUE OF STATIONARY HAMILTONIAN

HH2=-BETA*AKK1*AKK2*(P1-P2)*(AI-A)/(SUMK*SUMK)

HH1=(BETA*AKK1/SUMK-ALPHA)*(AI-A)

HAMS=HH1+HH2-(BETA*AKK1/SUMK-ALPHA)*PSI *(P1*AKK1+P2*AKK2)*A

HAM=HAMS

C

TEST FOR VALID INITIAL TEMPERATURE

IF(HAMS) 9,2,2

9 WRITE(6,10) TI,HAMS,B,A

10 FORMAT(5X,*INITIAL TEMPERATURE OUT OF RANGE FOR A *,

1*STATIONARY POLICY TEMP.=*,F5.0,* HAMILTONIAN =*,

2F11.7,* B =*,F8.7,* A=*,F8.7)

STOP

2 TEST=BETA*(B-BI)+ALPHA*(A-AI)

IF(HAMS.GT.TEST) GO TO 9

C

```

C     BEGIN REPETITIVE SECTION
C
C     3 T=EC/ALOG(AC/AK)
C
C     CHECK THAT TEMPERATURE IS BELOW UPPER CONSTRAINT
C
C     IF(T.GE.TU) GO TO 106
C
C     B=BI+AKK1*AI*(1.-EXP(-PSIT*SUMK))/SUMK
C     A=AI*EXP(-PSIT*SUMK)
C     P=(BETA*AKK1/(AKK1+AKK2)-ALPHA)*(AI-A)*DTIME+P
C     TT=EC/ALOG(AC/DIR)
C     ADJUST TIME INCREMENT SUCH THAT TEMPERATURE GAIN EACH
C     STEP IS .2 TO .5 DEGREES
C     IF(ABS(T-TT).LT.0.2) GO TO 100
C     IF(ABS(T-TT).LT.0.5) GO TO 101
C     DTIME=DTIME/2.
C     GO TO 101
100  DTIME=DTIME*2.
101  PSI=PSIT
C     TIME=TIME+DTIME
C     L=L+1
C     IF(L.LT.10) GO TO 14
C     L=0
C     T=EC/ALOG(AC/AK)
C     PTIME=(TIME-DTIME)/3600.
C     WRITE(6,51) PTIME,T ,HAM, DHK2,PSI,A,B ,ADJ,AK,AKK1,AKK2,P
51  FORMAT(1X,F7.2,2X,F6.1,2X,E13.6,3X,E13.6,1X,F5.4,F7.5,
C     1F7.5,3X,E10.3,1X,E10.3,1X,E10.3,1X,E10.3,1X,E12.5)
14  CALL PROCESS(AK)
C     LL=0
C     MN=0
C     NM=0
C     N=1
C     M=1
C     DIR = AK
C     IF(ABS(HAM-HAMS)-EPS) 4,4,5
C
C     FIND TEMPERATURE SUCH THAT THE HAMILTONIAN IS KEPT CONSTANT
C
C     5 X(1)=HAM-HAMS
C     Y(1)=AK
C     AK=AK+DELTAK
25  CALL PROCESS(AK)
C     X(2)=HAM-HAMS
C     Y(2)=AK
C     IF(X(1)) 20, 4,21
21  IF(X(2)-X(1)) 22,23,24
23  DELTAK = 2.*DELTAK
C     AK=AK+DELTAK
C     GO TO 25

```

```
24 IF(NM.GT.5) GO TO 55
    NM=NM+1
    AK=AK-2.*DELTAK
    M=2
    GO TO 25
22 IF(X(2)) 26,27,28
27 AK=Y(2)
    GO TO 4
28 X(1)=X(2)
    Y(1)=Y(2)
    GO TO (55,56) M
56 AK=AK-DELTAK
    GO TO 25
55 AK=AK+DELTAK
    GO TO 25
20 IF(X(1)-X(2)) 32,33,34
33 DELTAK = DELTAK*2.
    AK = AK+DELTAK
    GO TO 25
34 IF(MN.GT.5) GO TO 53
    MN=MN+1
    AK=AK-2.*DELTAK
    N=2
    GO TO 25
32 IF(X(2)) 36,37,26
37 AK=Y(2)
    GO TO 4
36 X(1)=X(2)
    Y(1)=Y(2)
    GO TO (53,54) N
54 AK=AK-DELTAK
    GO TO 25
53 AK = AK+ DELTAK
    GO TO 25
26 IF(X(1).LT.X(2)) GO TO 57
    X1=X(1)
    Y1=Y(1)
    X(1)=X(2)
    Y(1)=Y(2)
    Y(2)=Y1
    X(2)=X1
57 DELT=(Y(2)-Y(1))/100.
    AK=Y(2)-DELT
    CALL PROCESS (AK)
    Y(4)=AK
    X(4)=HAM-HAMS
    Y(5)=Y(2)
    X(5)=X(2)
    IF(X(4).LT.X(5)) GO TO 81
    XX=10.
```

```

WRITE(6,82)
82 FORMAT(/2X,*DELTHAM NOT MONOTONIC,REGION WILL BE REDUCED*/)
DO 83 J=1,20
Y(4)=Y(4)-DELT*XX
CALL PROCESS(Y(4))
X(4)=HAM-HAMS
IF(X(4).GT.X(5)) GO TO 83
IF(X(4).GE.0.0) GO TO 89
Y(4)=Y(4)+DELT*XX
XX=XX/10.
83 CONTINUE
WRITE(6,85) X(4),X(5)
85 FORMAT(/2X,*DELTHAM STILL NOT MONOTONIC*,E15.8,E15.8)
STOP
89 X(5)=X(4)
Y(5)=Y(4)
X(2)=X(5)
Y(2)=Y(5)
GO TO 57
81 AK=Y(1)+DELT
CALL PROCESS (AK)
Y(2)=AK
X(2)=HAM-HAMS
IF(X(1).LT.X(2)) GO TO 86
XX=10.
WRITE(6,82)
DO 87 J=1,20
Y(2)=Y(2)+DELT*XX
CALL PROCESS(Y(2))
X(2)=HAM-HAMS
IF(X(2).LT.X(1)) GO TO 87
IF(X(2).LE.0.0) GO TO 88
Y(2)=Y(2)-DELT*XX
XX=XX/10.
87 CONTINUE
WRITE(6,85) X(1),X(2)
88 X(1)=X(2)
Y(1)=Y(2)
X(2)=X(5)
Y(2)=Y(5)
GO TO 57
86 AK=(Y(1)+Y(5))/2.
CALL PROCESS (AK)
Y(3)=AK
X(3)=HAM-HAMS
SLOPE1=(Y(2)-Y(1))/(X(2)-X(1))
SLOPE5=(Y(5)-Y(4))/(X(5)-X(4))
CALL SPLINE(5,X,Y,PM,SLOPE1,SLOPE5)
CALL INTER(5,X,Y,PM,0.0,YR,0,SLOPE)
CALL PROCESS (YR)
AK=YR

```

```

      IF (ABS (HAM-HAMS)-EPS) 4,4,30
30  LL=LL+1
      X6=HAM-HAMS
      IF (LL.GT.10) GO TO 72
      IF (X6.GT.0.0) GO TO 80
      X(1)=X6
      Y(1)=AK
      X(2)=X(5)
      Y(2)=Y(5)
      GO TO 57
80  X(2)=X6
      Y(2)=AK
      GO TO 57
72  WRITE(6,31) X6
31  FORMAT(/ /5X,*INTERPOLATION FAILED    FINAL DEVIATION =*
      1,E15.8)
      STOP
C
C   CHECK SECOND DERIVATIVE FOR .LE.0.
C
4  SUMK=AKK1+AKK2
   PSI=PSIT
   H1=EXP(-PSI*SUMK)
   H2=BETA*AKK1/SUMK-ALPHA
   H3=AI*PSI/(AK*AK)
   H4=AI*AKK1*AKK2*BETA/(SUMK**2*AK**2)*(P1-P2)
   G1=H4*(1.-H1)*(AKK1*(P2-1.-P1)+AKK2*(P1-1.-P2))/SUMK
   G2=2.*H4*PSI*(P1*AKK1+P2*AKK2)*H1
   G3=H3*H1*(P1*AKK1*(P1-1.)+P2*AKK2*(P2-1.))*H2
   G4=-H2*H1*H3*(P1*AKK1+P2*AKK2)**2
   DHK2=G1+G2+G3+G4
   IF (DHK2) 7,7,6
6  WRITE(6,8) TIME,DHK2
8  FORMAT (5X,*STATIONARY POLICY IS NOT OPTIMAL  TIME =*,
      1F6.2,* D2H/DK2 =*,F6.3)
      STOP
C
C   TEST FOR STOPPING CONDITION
C
7  A=AI*EXP(-PSI*SUMK)
   B=BI+AKK1*AI*(1.-EXP(-PSI *SUMK))/SUMK
   ADJ=(-HAMS+(BETA*AKK1/SUMK-ALPHA)*(AI-A))/(PSI*AK)
   IF (ADJ) 11,12,3
12 T=EC/ALOG(AC/AK)
   PTIME=(TIME-DTIME)/3600.
   P=(BETA*AKK1/(AKK1+AKK2)-ALPHA)*(AI-A)*DTIME+P
   WRITE(6,51) PTIME,T ,HAM,DHK2,PSI,A,B ,ADJ,AK,AKK1,AKK2,P
   WRITE(6,13)
13 FORMAT(5X,*END OF OPTIMAL POLICY*)
      STOP
11 IF (DTIME-10. ) 12,12,15

```



```

15 DTIME=DTIME/2.
   TIME = TIME- DTIME
   PSI=PSI*EXP(-(AK+DIR)/2.*DTIME)
   GO TO 14

C
C
C
106 SUMK=AKK1+AKK2
   PSIF=-ALOG(1.0-HAMS*SUMK/(AKK1*AI*BETA-SUMK*ALPHA*AI))/SUMK
   TF=ALOG(PSIT/PSIF)/AK
   PTF=TF/3600.
   PTIME=TIME/3600.
   WRITE(6,105) PTF,PSIF,T,PTIME
105 FORMAT(/2 X,*POLICY HAS REACHED UPPER CONSTRAINT. *,
1 TIME ON CONSTRAINT =*,F8.2,5X,*FINAL ACTIVITY =*,F7.6
2,5X,*TEMP. =*,F6.1,2X,*TIME =*,F7.2//)
   DT=TF/100.
   TFF=TF+TIME
   D1=(SUMK*ALPHA-BETA*AKK1)/AK
   C4=AKK1/SUMK
   C1=(BETA*C4-ALPHA)
   C2=BETA*C4*AKK2*(P1-P2)/(AK*SUMK)
   C3=(P1*AKK1+P2*AKK2)/AK
   NI=1
109 DECAY=EXP(-AK*DT)
104 PSI=PSIT*DECAY
   IF((PSIT-PSI).GT..0005) GO TO 111
   A=AI*EXP(-PSI*SUMK)
   AD=-A*D1+(ADJ+A*D1)*EXP(DT*AK)
   HAM=C1*(AI-A)-AD*PSI*AK
   IF(ABS(HAM-HAMS)-EPS*10.) 110,110,111
111 DT=DT/2.
   IF(DT.LT.1.0) STOP
   GO TO 109
110 PSIT=PSI
   TIME=TIME+DT
   ADJ=AD
   P=C1*(AI-A)*DT+P
   IF(TIME.GE.T6F) GO TO 152
   NI=NI+1
   IF(NI.GE.10) GO TO 152
   GO TO 104
152 DHDK=C2*(AI-A)+C1*C3*PSIT*A-ADJ*PSIT
   B=BI+C4*(AI-A)
   PTIME=TIME/3600.
   WRITE(6,151) PTIME,HAM,DHDK,PSI,A,B,ADJ,P
151 FORMAT(1X,F8.2,9X,E13.6,3X,E13.6,1X,F5.4,F7.5,F7.5,3X,
1E10.3,34X,E12.5)
   NI=0
   IF((TIME+DT).GE.TFF) STOP
   GO TO 104
END

```

```

SUBROUTINE PROCESS (AK)
C   PROCESS CALCULATES THE HAMILTONIAN FOR A GIVEN TEMP.(AK)
COMMON/BLK1/DIR,PSI,PSIT,P1,P2,A1,A2,BI,AI,BETA,ALPHA,
1AKK1,AKK2,DTIME,HAM,AC
PSIT=PSI*EXP(-(AK+DIR)/2.*DTIME)
AKK1=AK**P1*11/AC**P1
AKK2=AK**P2*A2/AC**P2
SUMK=AKK1+AKK2
A=AI*EXP(-PSIT*SUMK)
HH2=-BETA*AKK1*AKK2*(P1-P2)*(AI-A)/(SUMK*SUMK)
HH1=(BETA*AKK1/SUMK-ALPHA)*(AI-A)
HAM =HH1+HH2-(BETA*AKK1/SUMK-ALPHA)*PSIT*(P1*AKK1+P2*AKK2)*A
RETURN
END

```

```

C
C   SUBROUTINES SPLINE AND INTER ARE USED TO FIND THE TEMP.
C   WHICH WILL KEEP H CONSTANT
C

```

```

SUBROUTINE SPLINE (NP,X,Y,PM,SLOPE1,SLOPEN)
DIMENSION Q(51),U(51)
DIMENSION X(6),Y(6),PM(6)
N=NP-1
DO 1 I=1,N
AA=X(I+1)-X(I)
IF(AA.LE.10.E-20) GO TO 7
1 CONTINUE
H1=X(2)-X(1)
D1=3./H1*((Y(2)-Y(1))/H1-SLOPE1)
H1=X(NP)-X(N)
DNP=6./H1*(SLOPEN-(Y(NP)-Y(N))/H1)
Q(1)=-0.5
U(1)=D1
DO 4 I=2,N
AA=(X(I+1)-X(I))/(X(I+1)-X(I-1))
D=(6./(X(I+1)-X(I-1)))*((Y(I+1)-Y(I))/(X(I+1)-X(I))
* -(Y(I)-Y(I-1))/(X(I)-X(I-1)))
P=(1.-AA)*Q(I-1)+2.
Q(I)=-AA/P
4 U(I)=(D-(1.-AA)*U(I-1))/P
*
*   CALCULATION OF THE N MOMENTS BY BACK SUBSTITUTION.
*
PNP=Q(N)+2.
PM(NP)=(DNP-U(N))/PNP
DO 6 I=1,N

```

```

J=NP-I
6 PM(J)=Q(J)*PM(J+1)+U(J)
RETURN
7 WRITE(6,8) I,X(I),I,X(I+1)
8 FORMAT(10X,*+++ ERROR IN SUBROUTINE SPLINE +++*//
*1CX,*THE VALUES X(*,I2,*) = *,E12.5,* AND X(*,I2,
**+1) = *,E12.5,*ARE IN THE WRONG ORDER.)
STOP
END

```

```

SUBROUTINE INTER (NP,X,Y,PM,XR,YR,KSLOPE,SLOPE)
DIMENSION X(6),Y(6),PM(6)

```

```

*
*
*

```

```

LOCALIZATION OF THE INTERPOLATION SEGMENT.

```

```

IF(XR.LT.X(1).OR.XR.GT.X(NP)) GO TO 1
DO 1 I=1,NP
IF(X(I).GE.XR) GO TO 2
1 CONTINUE
WRITE(6,5) XR,X(1),X(NP)
STOP
2 J=I-1
IF(X(I).EQ.XR) GO TO 3

```

```

*
*
*

```

```

CALCULATION OF THE CORRESPONDING YR VALUE.

```

```

H=X(J+1)-X(J)
YR=(PM(J)/(6.*H))*(X(J+1)-XR)*(X(J+1)-XR)*(X(J+1)-XR)
* +(PM(J+1)/(6.*H))*(XR-X(J))*(XR-X(J))*(XR-X(J))
* +(Y(J)-PM(J)*H*H/6.)*(X(J+1)-XR)/H
* +(Y(J+1)-PM(J+1)*H*H/6.)*(XR-X(J))/H
GO TO 4
3 YR=Y(I)
IF(I.EQ.1) J=1
H=X(J+1)-X(J)
4 IF(KSLOPE.EQ.0) RETURN
SLOPE=-((PM(J)/(2.*H))*(X(J+1)-XR)*(X(J+1)-XR)+(PM(J+1)
1/(2.*H))*(XR-X(J))*(XR-X(J))+(Y(J+1)-Y(J))/H-(PM(J+1)
2-PM(J))*(H/6.))
RETURN
5 FORMAT(10X,*+++ ERROR IN SUBROUTINE INTER +++*//
110X,*THE VALUE OF XR = *,E12.5/10X,*IS OUT OF THE *,
3*INTERPOLATION RANGE X(1) =*,E12.5,* TO X(NP) = *,E12.
45)
END

```