OPTIMIZATION OF A
FIRST ORDER CONSECUTIVE REACTION
IN A TUBULAR REACTOR
WITH CATALYST DECAY

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BY

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TITLE : Optimization of a First Order Consecutive Reaction in a Tubular Reactor with Catalyst Decay.

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SCOPE AND CONTENTS :

Optimal temperature policies with time are derived using Pontryagin's Maximum Principle, maximizing the intermediate in a first order consecutive reaction in the presence of decaying catalyst. A fixed time problem is considered, with uniform temperature and activity along the tubular reactor bed at any instant.

Theoretical developments and numerical solutions are obtained for three cases of first order consecutive reaction, depending on the relative activation energies.

A flowrate control policy is also discussed.

CHAPTER I

INTRODUCTION

The methods for solving an optimization problem, as for any engineering problem, involve the acceptance of certain assumptions about the physical process, that are chosen to simplify the algebra. Accurate numerical results from the method are only meaningful if the original assumptions apply accurately to the process. The same results are most useful only when they can be simulated accurately in practice.

The knowledge of the optimization of the products of a chemical reaction by the use of the calculus of variations has been greatly increased since the early works of Professor F. Horn[1]. The problem of maximising a controllable chemical yield over a fixed period of time (the objective function) requires the optimum choice of the control variable to be made at each instant of time. The control variables may be, for example, temperature, flowrate, the magnitude of a sinusoidal input, or a combination of these. The state variables are the concentrations of the species involved, and, for a reaction subject to catalyst decay, the activity of the catalyst.

Catalyst decay may be caused by surface poisoning from contaminants introduced over the period of operation, or by sintering and other structural damage due to the reaction temperature. Investigations into catalyst decay by Szepe[2] have led to a useful general equation relating catalyst activity to temperature and activity only, based on experimental knowledge, and which is used in the following treatment. The optimal temperature at each instant of time must be chosen to minimize the adverse effect of temperature on catalyst decay over the time of operation.

The Maximum Principle of Pontryagin provides a theory which can relate the separate time behaviour of the state variables on perturbation of the control variables, while maximizing an integral objective function. The analytical solutions for the resulting control policies are generally insoluble, and numerical methods are used to obtain and verify optimal control policies. Using this method, Jackson[3] has examined the optimization of a first-order consecutive reaction without catalyst decay, and recently Drouin[4] has solved the reversible reaction with catalyst decay. Jackson[5] has also investigated the mathematical formulation of time-dependent optimization problems, with particular reference to the numerical solution of a first-order reversible exothermic reaction with catalyst decay. Professor C.M. Crowe[6,7] has examined the optimization of irreversible reactions in single and multiple bed tubular reactors, with catalyst decay.

CHAPTER II

STATEMENT OF THE PROBLEM

The intermediate B in the reaction

$$A \rightarrow B \rightarrow C$$

is to be maximized by conversion in a single isothermal tubular reactor in the presence of a decaying catalyst, over a fixed period of operating time τ.

Certain assumptions are made about the relative rates of reaction and catalyst decay to avoid a distributed-parameter problem.

A general differential mass balance on a plug flow reactor yields the equation (see Appendix A.2)

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

where ψ is the catalyst activity, T is the temperature, B is the concentration of species B, t is the system time, and z is the space time (distance through the bed). The function $f(\psi, T, A, B)$ is the rate of reaction, and may be written as

$$f(\psi, T, A, B) = \psi . f_c(T, A, B) \qquad (2.2)$$

where ψ is defined as

$$\psi = \frac{\text{rate of reaction with decayed catalyst}}{\text{rate of reaction with fresh catalyst}} \qquad (2.3)$$

and $f_c(T, A, B)$ is the chemical rate of reaction. This assumes that the deactivation of both chemical steps is uniform.

The term $\partial B/\partial t$ in (2.1) arises from a change in B following a change in catalyst activity and a compensating change in temperature along the bed. It will be assumed that the rate of catalyst decay is slow compared to the reaction rate along the bed, so that

$$\frac{\partial B}{\partial t} << \frac{\partial B}{\partial z} \tag{2.4}$$

and the catalyst activity is uniform everywhere in the bed. The characteristic equation of the system, (2.1), now becomes

$$\frac{dB}{dz} = \psi . f_c(T, A, B) \tag{2.5}$$

Szepe[2] has shown that many classes of catalyst decay can be generalized as one power equation, in which the rate of decrease of activity depends only on temperature T and activity ψ itself, and not on instantaneous conversion:

$$\frac{d\psi}{dt} = -k(T).\psi^m \tag{2.6}$$

k(T) is the rate constant of decay, and m can be taken as unity for a good representation of the behaviour of many catalysts.

The production of B is to be maximized over the total reaction time τ by choosing the temperature to compensate for decreased catalyst activity at every instant of time. The objective function P is, then, in its simplest form:

$$\max_{T(t)} \; P \text{ with } P = \int_0^\tau B_e(t)dt \tag{2.7}$$

the suffix e denoting the exit value of B from the reactor, after a residence time θ. Since the residence time affects the exit concentration B_e, but not the catalyst activity, it is not considered directly as a control on the decay rate in this problem (see Section 8.2) but can assume any value for the best result. The cases of constant flowrate and variable flowrate will be treated separately, since an optimal flowrate exists for the consecutive reaction (see Section 3.3).

If the inlet concentration of B, B_i, is not zero, but is assumed to be constant with time, it can be subtracted from $B_e(t)$ in (2.7), since it is the increase in B due to the reaction that is required tc be maximized.

Objective functions that are more complicated can be devised, to include, for example, the relative cost of the reactant A, a separation cost factor, or other profit-oriented terms. Whatever the practical considerations, the optimization theory can be applied to the general objective function

$$\max_{T(t)} P \quad \text{with } P = \int_0^{\tau} Q(A, B, \psi, t, T)dt \qquad (2.8)$$

by substituting Q for B. The range of attainable values of $B_e(t)$ will now depend on the complexity of the function $Q(A, B, \psi, t)$.

CHAPTER III

THE KINETICS OF A CONSECUTIVE FIRST-ORDER REACTION IN AN ISOTHERMAL TUBULAR REACTOR WITH DECAYING CATALYST

3.1 Derivation of the exit concentration of B

The problem is to maximize the temperature-controlled yield of B in the reaction

$$A \xrightarrow[1]{K_1} B \xrightarrow[1]{K_2} C \qquad (3.1.1)$$

over a total time τ, in the presence of a catalyst whose rate of decay (from the general equation 2.6) is accelerated by increasing temperature according to the relation

$$\frac{d\psi}{dt} = -k(T).\psi \qquad (3.1.2)$$

The rate constants k, K_1 and K_2 have an Arrhenius relation with temperature:

$$k = A_c \exp(-E_c/RT) \qquad (3.1.3)$$

$$K_1 = A_1 \exp(-E_1/RT) \qquad (3.1.4)$$

$$K_2 = A_2 \exp(-E_2/RT) \qquad (3.1.5)$$

To impress the relatively slow rate of decay of the catalyst, the catalyst Arrhenius frequency factor A_c will have units hr^{-1}, while the chemical frequency factors A_1 and A_2 have units s^{-1}. That is to say, system time t is measured in hours, and the residence time θ in seconds.

The rate of change of B at any point z in the tubular reactor bed is, recalling equation (2.5):

$$\frac{dB}{dz} = \psi . f_c(A,\ B,\ T) = \psi[K_1 A - K_2 B] \qquad (3.1.6)$$

and the rate of change of A is

$$\frac{dA}{dz} = -K_1 A\psi \qquad (3.1.7)$$

The solution required from (3.1.6) and (3.1.7) is the exit concentration of B after a residence time θ. The integration is performed (see Appendix A.3.1) with the previous assumptions of constant activity and constant temperature over a period of time that is large compared to the residence time θ. Hence

$$B_e = \frac{K_1}{K_2 - K_1}[\exp(-K_1\psi\theta) - \exp(-K_2\psi\theta)] \qquad (3.1.8)$$

As the temperature, and hence k, K_1 and K_2, or the activity change with system time t, so B_e will change. The symbol B will be used in the subsequent sections, where

$$B = B_e(t) \qquad (3.1.9)$$

3.2 Behaviour of B with temperature

Since the derivation of an optimal policy depends on the way in which the physical (state) variables change with the control variables, it is useful to obtain a picture of this behaviour before proceeding with an application of the optimization theory.

The variation of B with temperature depends not only on the temperature itself, but also on the activation energy of reaction in the Arrhenius expression. The activation energy behaves as a temperature coefficient. At particular values of E_1 and E_2 in equations (3.1.4) and

(3.1.5), parameters p_1 and p_2 can be defined such that

$$p_1 = E_1/E_c \tag{3.2.1}$$

$$p_2 = E_2/E_c \tag{3.2.2}$$

Hence

$$K_1 = A_1k^{p_1}/A_c^{p_1} = ak^{p_1} \tag{3.2.3}$$

and

$$K_2 = A_2k^{p_2}/A_c^{p_2} = bk^{p_2} \tag{3.2.4}$$

If p_1 and p_2 are of order unity, this means that the temperature coefficients of reaction and of catalyst decay are of comparable magnitude. More information on classes of optimal policies is gained when the temperature sensitivity of both reaction and catalyst decay are similar, and when the greatest exponential curvature of rate constant values occurs within the temperature range of interest.

Turning to the variation of B with temperature, at constant activity, flowrate, and at given values of p_1 and p_2, a maximum in B is observed at a certain temperature given by the solution of the equation

$$\frac{\exp(-K_2\psi\theta) - \exp(-K_1\psi\theta)}{p_2K_2\exp(-K_2\psi\theta) - p_1K_1\exp(-K_1\psi\theta)} = \frac{\psi\theta(K_2 - K_1)}{K_2(p_1 - p_2)} \tag{3.2.5}$$

recalling that T and k are in one-to-one correspondence, from rquation (3.1.3). From an examination of equation (3.1.8) and of the derivative $\partial B/\partial k$ (see Appendix A.3.2), it is found that the shape of the curve of B vs. temperature is always of the form shown in Diagram 3.1, with one maximum and two inflexion points.

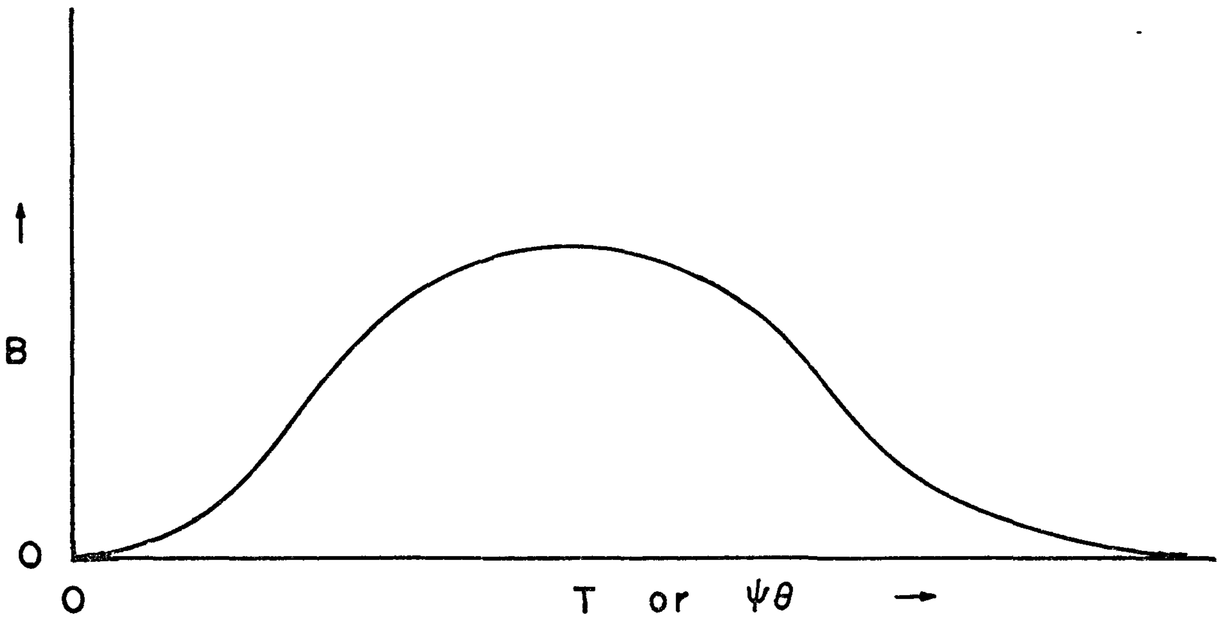


Diagram 3.1

Three cases of the behaviour of B with temperature can be distinguished:

$$p_1 > p_2 \qquad p_1 = p_2 \qquad p_1 < p_2$$

If the ratio of chemical rate constants at one temperature is compared to their ratio at a higher temperature, the following result shows that increasing the temperature favours the reaction in which $p_1 > p_2$.

Let $$R_1 = \frac{K_1(T_\ell)}{K_2(T_\ell)} = \frac{A_1\exp(-p_1E_c/RT_\ell)}{A_2\exp(-p_2E_c/RT_\ell)} = A\exp[-(p_1 - p_2)E_c/RT_\ell]$$

Similarly $$R_2 = A\exp[-(p_1 - p_2)E_c/RT_u]$$

Therefore $$\frac{R_1}{R_2} = \exp[-E_c(p_1 - p_2)\left(\frac{1}{T_\ell} - \frac{1}{T_u}\right)/R] = \exp[D(p_2 - p_1)]$$

where A and D are constants and $T_u > T_\ell$.

Hence $R_1 < R_2$ if $p_2 < p_1$ and $R_1 > R_2$ if $p_2 > p_1$. That is, the production of B from A is favoured at higher temperatures if $p_1 > p_2$. It would be expected, therefore, that an optimal policy for the case $p_1 > p_2$ would yield better results if operating in the higher regions of allowable temperatures.

3.3 Behaviour of B on variation of activity and residence time

The expression for the exit concentration of B, (3.1.8), shows that the effect of varying the catalyst activity ψ is exactly the same as varying the residence time θ; only the magnitude of the change will differ, if ψ and θ have different values [(3.3.1) and (3.3.2)]:

$$\frac{\partial B}{\partial \psi} = \frac{\theta K_1}{K_2 - K_1}[K_2\exp(-K_2\psi\theta) - K_1\exp(-K_1\psi\theta)] \qquad (3.3.1)$$

$$\frac{\partial B}{\partial \theta} = \frac{\psi K_1}{K_2 - K_1}[K_2\exp(-K_2\psi\theta) - K_1\exp(-K_1\psi\theta)] \qquad (3.3.2)$$

It is convenient to treat $\psi\theta$ as a lumped variable, and to term it 'the effective residence time'. Increasing the residence time (or increasing the reactor length) is equivalent to adding catalyst of a higher activity to the reactor, and vice versa. This reciprocal relation is limited for values of ψ in (0,1) but for θ in (θ_ℓ, θ_u), where

$$\theta_\ell \geq 0 \qquad \text{and} \qquad \theta_u \leq \infty$$

Examination of (3.1.8) shows that a maximumin B must occur with respect to $\psi\theta$ (see Appendix A.3.3). This can also be seen by considering the balance of concentrations at any point in the reactor (Diagram 3.2).

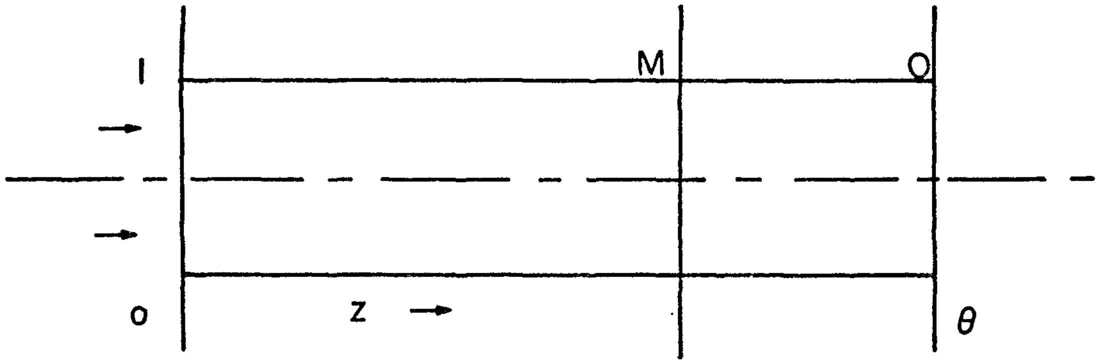


Diagram 3.2 Tubular reactor.

At a particular temperature,

$$\frac{dB}{dz} = \psi(K_1A - K_2B)$$

in the reactor. At I, $B = 0$, so dB/dz is positive. At M, say, $K_1A = K_2B$, and dB/dz is zero. After M and up to O, $A < K_2B/K_1$, so dB/dz is negative as more C is being produced. In fact, the rate of increase of C is a maximum at M.[8] It would be beneficial if either this reactor were shortened to M, or if the residence time were decreased so that M moves to O and species B stops being produced in excess just at the outlet.

The shape of the curve B vs. $\psi\theta$ is similar to the shape of Diagram 3.1. The maximum of B with respect to effective residence time is given analytically by

$$\max_{\psi\theta} B(T,\psi\theta) = \left(\frac{K_1}{K_2}\right)^{\frac{K_2}{K_2 - K_1}} \qquad (3.3.3)$$

and is a function only of temperature, or, more specifically here, increasing with the ratio K_1/K_2.

The corresponding optimum flowrate is given by (see Appendix A.3.4)

$$(\psi\theta)_{opt} = \frac{\ln\left(\frac{K_1}{K_2}\right)}{K_1 - K_2} \qquad (3.3.4)$$

The behaviour of max $B(\psi\theta)$ with respect to relative values of p_1 and p_2 corresponds to that described in Section 3.2. Relation (3.3.4) shows that $(\psi\theta)_{opt}$ decreases with increasing temperature.

3.4 Combined behaviour of B with temperature and $\psi\theta$

Since the optimal temperature policy spans both regions of temperature and effective residence time throughout the time of operation, it is useful to plot the behaviour of B with both of these variables. Such a map is constructed in Figure 7.1.1, showing contours of B. The maxima with respect to both variables follow each other closely in all cases examined to form a three-dimensional sloping ridge, diagonally spanning low residence times (high flows) and high temperatures, to high residence times (low flows) and low temperatures. The maxima with respect to temperature and $\psi\theta$ coincide at all points only for $p_1 = p_2$, when

$$\max_{T} B(T,\psi\theta) = \max_{\psi\theta} B(T,\psi\theta) = \left(\frac{K_1}{K_2}\right)^{\frac{K_2}{K_2 - K_1}} = \left(\frac{A_1}{A_2}\right)^{\frac{A_2}{A_2 - A_1}} = \text{const.} \qquad (3.4.1)$$

For $p_1 \neq p_2$ the common maximum occurs only at one point, when $K_1 = K_2$ (see Appendix A.3.5), and so, from (3.3.3),

$$\max_{(T,\psi\theta)} B = e^{-1} = 0.368 \qquad (3.4.2)$$

This 'common maximum' will not be the highest concentration that can be achieved. It is difficult to ascertain analytically if the maximum in B by choice of $\psi\theta$ at a particular temperature does not occur at the point where $\partial B/\partial k = 0$ coincides with $\partial B/\partial\psi\theta = 0$.

If there were no catalyst decay, it would be an easy method to choose the location giving the highest concentration within the constraints of temperature and residence time for any case.

The optimal policy with catalyst decay will trace a path on such a map as Figure 7.1.1 of contours of B. It will be seen in the following sections that the use of such a map helps to locate and compare different optimal policies. On starting from a given concentration of B, the reaction would proceed to the region of decreasing $\psi\theta$. The region of highest concentration is then found in the direction of higher temperatures. It has been shown to be true for result (3.3.3), but it is difficult to prove analytically that the maximum of B with respect to temperature moves to higher temperatures at lower $\psi\theta$. However, this has been observed from numerical calculations of B for many cases of p_1 and p_2 (for example, Figures 7.1.1, 7.2.1, and 7.3.1). Therefore it will be taken as a hypothesis that this behaviour is generally true. It will further be taken as a hypothesis, at present, that all best (optimal) temperature policies will therefore be rising ones.

CHAPTER IV

APPLICATION OF PONTRYAGIN'S MAXIMUM PRINCIPLE TO A TEMPERATURE CONTROLLED CHEMICAL REACTION WITH CATALYST DECAY - GENERAL CASE

4.1 The Maximum Principle

The following theory will be stated without the proofs which can be found in Pontryagin's work .

Given the system of:

State variables $\underline{x} = (x_1, x_2, \ldots. x_n) \ \varepsilon \ X$

Control variables $\underline{u} = (u_1, u_2, \ldots. u_r) \ \varepsilon \ U$

The control policy is expressed as $\underline{u}(t)$ for $t \ \varepsilon \ [t_o, t_1]$, and is piecewise continuous.

The systems equations are the time derivatives of the state variables:

$$\frac{dx_i}{dt} = f_i(\underline{x}, \underline{u}, t) \qquad i = 1,2, \ldots. n \qquad (4.1.1)$$

where the f_i are continuous in $\underline{x}$, $\underline{u}$, are continuously differentiable with respect to $\underline{x}$, $\underline{u}$, and are piecewise continuous in t.

The problem is to maximize or minimize J with respect to $\underline{u}(t)$, where the integral objective function J is defined as

$$J = \int_{t_o}^{t_1} f_o(\underline{x}, \underline{u}, t)dt \qquad (4.1.2)$$

The adjoint variables λ_i are defined by:

$$\frac{d\lambda_i}{dt} = -\sum_{\alpha=o}^{n} \lambda_\alpha \frac{\partial f_\alpha}{\partial x_i} \qquad (4.1.3)$$

Hence the Hamiltonian H which is to be maximized (minimized) by choice of $\underline{u}(t)$ is formed thus:

$$H = H(\underline{x},\ \underline{u},\ \underline{\lambda},\ t) = \sum_{i=o}^{n} \lambda_i f_i \tag{4.1.4}$$

An optimal policy $\underline{u}^+(t)$ has the property that

$$\underline{\lambda}^+(t) \neq \underline{0} \text{ and } H(\underline{x}^+,\underline{u}^+,\underline{\lambda}^+,t) \geq H(\underline{x}^+,\underline{u},\underline{\lambda}^+,t) \tag{4.1.5}$$

for all $\underline{u} \in U$ at almost every $t \in [t_o,t_1]$.

4.2 Application of the general theory to a reaction subject to catalyst decay

The objective function P was defined in Chapter II:

$$\max_{T(t)} P \text{ with } P = \int_0^\tau B(t)dt \tag{2.7}$$

P is one state variable. The second independent state variable is the catalyst activity, ψ, defined in Section 3.1:

$$\frac{d\psi}{dt} = -k(T).\psi < 0 \tag{3.1.2}$$

This may be regarded as the constraint on the system.

Following from the theory of Section 4.1:

$$x_o = P \qquad f_o = \frac{dP}{dt} = B \tag{4.2.1}$$

$$x_1 = \psi \qquad f_1 = \frac{d\psi}{dt} = -k\psi \tag{4.2.2}$$

Now

$$\frac{d\lambda_i}{dt} = -\sum_{\alpha=o}^{n} \lambda_\alpha \frac{\partial f_\alpha}{\partial x_i} \tag{4.1.3}$$

Therefore

$$\frac{d\lambda_o}{dt} = -\lambda_o\frac{\partial B}{\partial P} - \lambda_1\frac{\partial f_1}{\partial P} \qquad (4.2.3)$$

and

$$\frac{d\lambda_1}{dt} = -\lambda_o\frac{\partial B}{\partial \psi} - \lambda_1\frac{\partial f_1}{\partial \psi} \qquad (4.2.4)$$

Since $\partial B/\partial P = 0$ and $\partial f_1/\partial P = 0$, then $\dot{\lambda}_o = 0$, so λ_o is constant. The Maximum Principle requires that $\lambda_o \geq 0$ for a maximum, and that $\lambda_1(\tau) = 0$. Therefore, using $\lambda = \lambda_1$,

$$\frac{d\lambda}{dt} = -\lambda_o\frac{\partial B}{\partial \psi} + \lambda k \qquad (4.2.5)$$

It can be shown from (4.2.5) that $\lambda_o = 0 \Rightarrow \lambda_1 = 0$ for all t. λ_o is chosen to be unity. Also,

$$\lambda(\tau) = 0 \quad \text{if} \quad \psi(\tau) > 0 \qquad (4.2.5a)$$

$$\lambda(\tau) \geq 0 \quad \text{if} \quad \psi(\tau) = 0 \qquad (4.2.5b)$$

The Hamiltonian was defined as

$$H = H(\underline{x}, \underline{u}, \underline{\lambda}, t) = \sum_{i=o}^{n} \lambda_i f_i \qquad (4.1.4)$$

With $\underline{u} = T$ and $\underline{x} = (P,\psi)'$

$$H = H(P, \psi, T, \lambda, t) = \frac{dP}{dt} - \lambda k\psi \qquad (4.2.6)$$

or, since P is defined explicitly by (4.2.1)

$$H(\psi, T, \lambda, t) = B(\psi, T, B_i(t)) - \lambda k\psi \qquad (4.2.7)$$

This problem will be restricted to cases when $B_i(t)$ is constant and zero, so (4.2.7) may be written as:

$$H(\psi, T, \lambda, t) = B(\psi, T) - \lambda k\psi \qquad (4.2.8)$$

Transformation of T to k

For convenience, the variable $T(t)$ will be transformed to $k(t)$ as the independent variable, since the Arrhenius relation (3.1.3) is one-to-one. The relation between T and the rate constants K_1 and K_2 can be manipulated easily through the fact that

$$\frac{dK_1}{dk} = \frac{p_1 K_1}{k} \qquad \frac{dK_2}{dk} = \frac{p_2 K_2}{k} \qquad (4.2.9)$$

recalling

$$K_1 = ak^{p_1} \qquad K_2 = bk^{p_2} \qquad (3.2.3)\ (3.2.4)$$

so K_1 and K_2 retain their identity.

The Hamiltonian may finally be defined as

$$H(\psi,\ k,\ \lambda,\ t) = B(\psi,\ k) - \lambda k\psi \qquad (4.2.10)$$

Residence time θ

If the residence time is free to be chosen, it is considered as a control variable, so that

$$H(\psi,\ k,\ \theta,\ \lambda,\ t) = B(\psi,\ k,\ \theta) - \lambda k\psi \qquad (4.2.11)$$

This relation is used in deriving an optimal temperature and flowrate policy (Section 8.2). Except in that section, constant flowrate will be assumed for the following theoretical developments.

4.3 Properties of optimal policies

The maximization of P in equation (2.7) is now achieved by finding an optimal policy $k^+(t)$ that satisfies

$$H(\psi^+,\lambda^+,k^+,t) = \max_{k(t)} H(\psi^+,\lambda^+,k,t) \qquad (4.3.1)$$

(applying (4.1.5) to (4.2.10)).

In (4.3.1) ψ^+ and λ^+ are the solutions of (4.2.2) and (4.2.5).

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

(1) Stationary policy S

$$\frac{\partial H}{\partial k}(k^+) = 0 \quad \text{and} \quad \frac{\partial^2 H}{\partial k^2}(k^+) \leq 0 \qquad \text{for} \qquad k_* < k^+ < k^* \qquad (4.3.2)$$

(2) Upper constraint policy C^*

$$\frac{\partial H}{\partial k}(k^+) \geq 0 \qquad \text{if} \qquad k^+ = k^* \qquad (4.3.3)$$

(3) Lower constraint policy C_*

$$\frac{\partial H}{\partial k}(k^+) \leq 0 \qquad \text{if} \qquad k^+ = k_* \qquad (4.3.4)$$

Conditions (2) and (3) refer to upper and lower temperature constraints imposed on the reactor for engineering reasons. Conditions (1), (2), and (3) together with conditions (4.2.5a) and (4.2.5b), applied to the Hamiltonian, the systems and the adjoint equations, enable the optimal policies to be found for the reaction scheme.

Examination of the total derivative of the Hamiltonian with time (Appendix A.4.1) shows that, for constant or zero input of B,

$$\frac{dH}{dt} = 0 \qquad (4.3.5)$$

for both stationary and constrained policies. Therefore, on an optimal policy,

$$H = \text{a constant} \qquad (4.3.6)$$

with time.

In the following sections, the conditions for optimal policies to exist are derived for the consecutive first order reaction scheme.

CHAPTER V

APPLICATION OF THE MAXIMUM PRINCIPLE TO A FIRST-ORDER CONSECUTIVE REACTION WITH CATALYST DECAY - GENERAL CASE

5.1 General equations

On an optimal temperature policy:

$$H = B - \lambda k\psi \tag{4.2.10}$$

$$\frac{d\lambda}{dt} = -\frac{\partial B}{\partial \psi} + \lambda k \tag{4.2.5}$$

$$H = \text{a constant} \tag{4.3.6}$$

$\partial B/\partial\psi$, B and ψ are obtained from the equations

$$B = \frac{K_1}{K_2 - K_1}[\exp(-K_1\psi\theta) - \exp(-K_2\psi\theta)] \tag{3.1.8}$$

$$\frac{d\psi}{dt} = -k\psi < 0 \tag{3.1.2}$$

5.2 Derivation of the stationary policy (constant flowrate)

From necessary condition (4.3.2),

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

Now

$$\frac{\partial H}{\partial k} = \frac{\partial B}{\partial k} - \lambda\psi \tag{5.2.1}$$

Therefore on a stationary curve, S:

$$\lambda\psi = \frac{\partial B}{\partial k} \tag{5.2.2}$$

Substituting in (5.2.1):

$$H_s = B - k\frac{\partial B}{\partial k} \qquad (5.2.3)$$

Also,

$$\frac{\partial^2 H}{\partial k^2} = \frac{\partial^2 B}{\partial k^2} \leq 0 \quad \text{on} \quad S \qquad (5.2.4)$$

It can be seen from these equations that a knowledge of the relation between B and k is already useful, and reference will be made to the observations of Section 3.4 concerning this relation. These equations, together with (4.3.6) and (3.1.2) may be solved for the optimal temperature policy $k^+(t)$. At the final time, $\lambda(\tau) = 0$ since $\psi(\tau) = 0$ only at $\tau = \infty$. Therefore, from (5.2.2)

$$\frac{\partial B}{\partial k}(\tau) = 0 \qquad (5.2.5)$$

This is equivalent to maximizing the instantaneous conversion (conversion $= B/A_i = B$, using units of concentration mole/mole A, and $A_i = 1$, $B_i = 0$ at the inlet i) at the end, for a stationary policy. A simultaneous result is obtained:

$$H = B_{final} \quad \text{in general} \qquad (5.2.6)$$

The stationary curve $k^+(t)$ can be obtained analytically either by solving the above equations (generally impossible), or by examining and solving $dH_s/dt = 0$ (also generally impossible). For example, for the consecutive first-order reaction, solving $dH_s/dt = 0$ gives the following expression for dk^+/dt (see Appendix A.5.1):

$$\frac{dk^+}{dt} = \psi\left(k^+\frac{\partial}{\partial\psi}\left(\frac{\partial B}{\partial k^+}\right) - \frac{\partial B}{\partial\psi}\right)\bigg/\frac{\partial^2 B}{\partial k^{+2}} \qquad (5.2.7)$$

Applying equation (5.2.7) geometrically to the maps of B-contours, (Figures 7.1.1, 7.2.1, 7.3.1) shows that dk^+/dt is always positive for $\partial B/\partial k > 0$, and almost invariably positive for $\partial B/\partial k < 0$. It is difficult to ascertain the sign of dk^+/dt analytically, and the only practical way is to evaluate dk^+/dt at every point in the region being considered, for a particular reaction, by using (5.2.7). An analytical solution was found only for the case $p_1 = p_2$ (see Section 7.1.1).

5.3 Constrained optimal policies

Along a constraint, the policy is isothermal, and dk/dt is zero. The Hamiltonian must be constant along this policy (see Appendix A.4.1), and conditions (4.3.3) and (4.3.4) must be fulfilled. The general equation for the Hamiltonian, (4.2.10), must be used; k is constant, and λ varies according to relations (4.2.10) and (4.2.5) to keep the Hamiltonian constant as the activity ψ decreases exponentially with time. The final time is reached when $\lambda(\tau) = 0$ and the Hamiltonian equals the final concentration.

For the consecutive reaction, it is expected that only an upper constraint policy will be encountered for an initially stationary policy, since a rising temperature policy in all cases is concluded from the observations of Section 3.4, although theoretically a falling temperature policy can be envisaged for a very narrow temperature range in certain cases (see Section 7.2.3).

A policy may have both stationary and constrained segments; for example, it may begin on the stationary curve and end on a constraint, or vice versa.

5.4 Examination of initial temperature limits for stationary policies

An initial temperature limit is defined here as the boundary temperature between the initial stationary and non-stationary policies. Thus a lower and an upper limit, different from the practical constraints, can be found for the initial temperature by examining the systems equations in their initial forms.

(I) Limits on the initial temperature arise from a consideration of the limits imposed on the Hamiltonian. Equation (4.2.10) shows that the Hamiltonian equals the concentration of B at the final time, when $\lambda(\tau) = 0$. Therefore, the initial temperature must be chosen such that the Hamiltonian is neither negative nor greater than the greatest attainable concentration in the region $\psi\theta < \theta$, and $k \leq k^*$. For the stationary policy these limits can be shown geometrically on the graph of B vs. k (Diagram 5.1). For a stationary policy, the Hamiltonian is given by

$$H_s = B - k\frac{\partial B}{\partial k} \qquad (5.2.3)$$

From the construction in Diagram 5.1 the stationary Hamiltonian equals the value of B at the intersection of the tangent at B_{init} and k_{init} and the ordinate axis. Therefore k_ℓ represents the lower limit on initial temperature, at which the Hamiltonian constructed in Diagram 5.1 is zero, and k_u represents the upper temperature limit when the Hamiltonian equals the maximum attainable concentration. It may be noted here that for $p_1 > p_2$ the maximum in B with respect to k increases with decreasing $\psi\theta$ (see Figure 7.2.1 and Section 7.2.1), but not for $p_1 < p_2$.

If the initial temperature is chosen such that $\partial B/\partial k$ is zero,

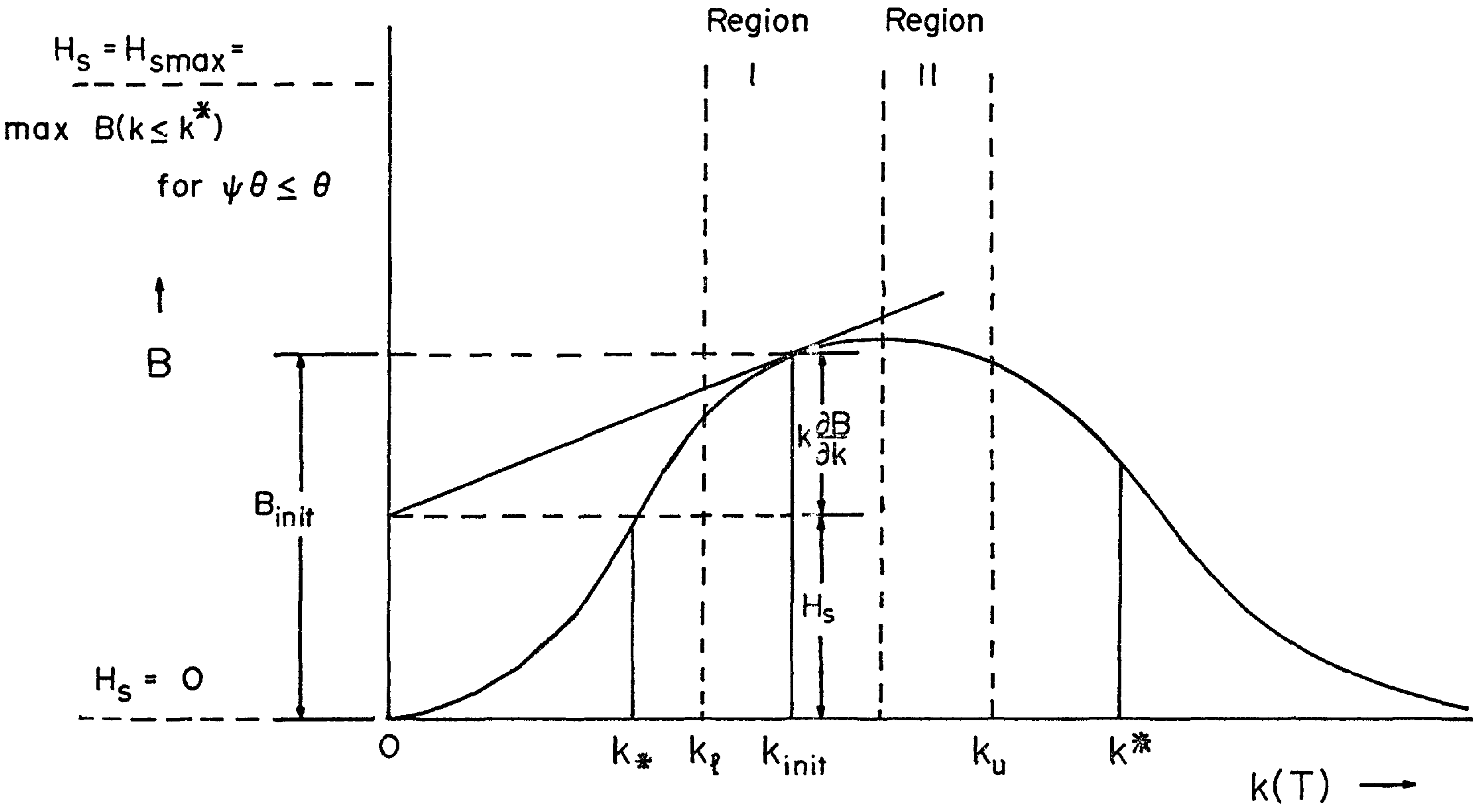


Diagram 5.1 Initial form of B vs. k(T)

then $H_s = B$ and $\lambda = 0$, so that the reactor operates for an infinitesimal time, since the final conditions are fulfilled at the initial time. This temperature will be regarded as the boundary between two classes of policies - one confined to the region where $\partial B/\partial k$ is positive (Region I), the other confined to the region where $\partial B/\partial k$ is negative (Region II).

(2) A stationary policy must also obey the condition

$$\frac{\partial^2 H}{\partial k^2} = \frac{\partial^2 B}{\partial k^2} \leq 0 \qquad (5.2.4)$$

The condition $\partial^2 B/\partial k^2 = 0$ corresponds to the two inflexion points in Diagram 5.1. It is therefore not possible to operate a stationary policy below the lower or above the upper inflexion point, where $\partial^2 B/\partial k^2 > 0$. The lower limit k_ℓ (at which $H_s = 0$) is always above the lower inflexion point by geometry. The upper limit k_u is, however, subject to being below, or at, the upper inflexion point, for those cases where Region II is feasible.

5.5 Restrictions on constrained policies

5.5.1 Ending on the upper constraint: S-C*

On the upper constraint,

$$\frac{\partial H}{\partial k} \geq 0 \qquad \frac{\partial^2 H}{\partial k^2} \text{ may have any value} \qquad (4.3.3)$$

A rising temperature policy will end on the upper constraint if the initial Hamiltonian is feasible but corresponds to a final concentration which is unattainable as a point where $\partial B/\partial k = 0$, so that the policy cannot be stationary at the end. Further, the final concentration on a constrained policy must be attainable along the constraint, if the policy is to be optimal. Now

$$\frac{\partial H}{\partial k} = \frac{\partial B}{\partial k} - \lambda\psi \qquad (5.2.1)$$

Therefore $\lambda\psi \leq \partial B/\partial k$ for the policy to be on the upper constraint. The constraint may be at a temperature where $\partial B/\partial k$ is positive or negative, provided that the condition (4.3.3) is respected.

5.5.2 Totally constrained policy at k^*: C^*

Condition (4.3.3) must hold along this policy. C^* may be feasible at any temperature, for the following reason. Whatever the sign of $\partial B/\partial k$ in (5.2.1), the initial value of the adjoint λ can be chosen to be positive or negative (hence a different total operating time τ, a different final concentration, and a different Hamiltonian) to suit (4.3.3), provided that $d\lambda/dt$ is of the opposite sign (see Section 5.6). This is possible if $\partial B/\partial\psi$ is of favourable sign (see equation 4.2.5). It cannot be predicted if all policies on C^* are optimal even if the Hamiltonian is feasible, but it appears likely that most temperatures can be selected.

5.5.3 Lower constraint policies: $S\text{-}C_*$, C_*, $C_*\text{-}S$

Sections 5.5.1 and 5.5.2 apply to lower constraint policies if the inequality signs are reversed. Initially stationary policies followed by lower constraint policies are not predicted, for the reasons given in Sections 3.4 and 5.3. Lower constraint policies C_*, $C_*\text{-}S$ are possible.

5.6 A discussion of the initial value of the adjoint variable λ

In this section, the different trajectories of λ with time are discussed.

The time behaviour of λ is given by the adjoint equation

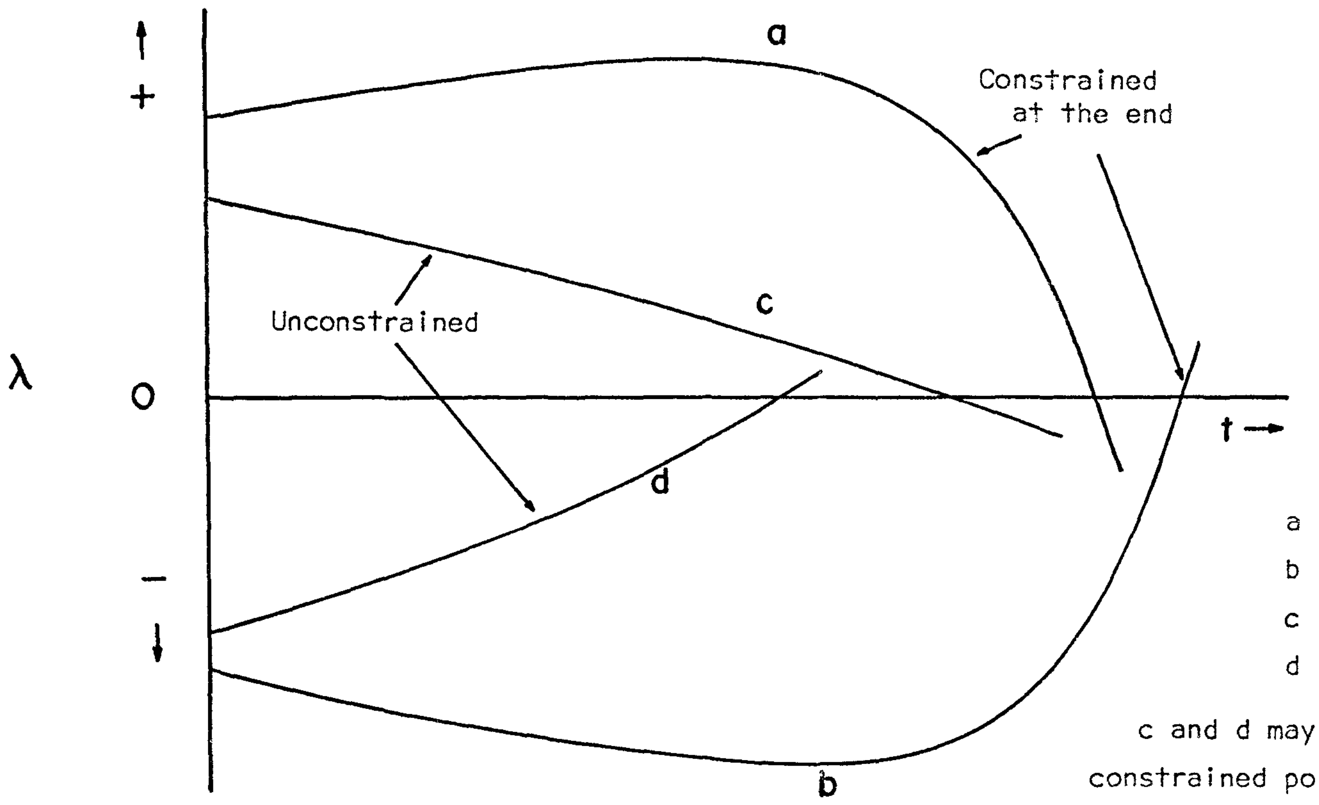
$$\frac{d\lambda}{dt} = -\frac{\partial B}{\partial \psi} + \lambda k \qquad (4.2.5)$$

For initially stationary policies, λ takes on the sign of $\partial B/\partial k$; it will be recalled that $\partial B/\partial k$ may initially be of either sign for an optimal policy, provided that the conditions on the Hamiltonian are respected.

Since, for the consecutive reaction, it has been shown that B has a maximum with respect to the effective residence time $\psi\theta$ (see Section 3), then $\partial B/\partial \psi$ may be positive or negative. It has also been shown theoretically in Section 3 that, except for $p_1 = p_2$, the maxima of B with respect to temperature and $\psi\theta$ coincide at only one point in three-dimensional B-T-$\psi\theta$ space. In general, although it has not been possible to show it theoretically, it has been observed from the numerical computation of B at various $\psi\theta$ and T, and also of the derivatives $\partial B/\partial \psi\theta$ and $\partial B/\partial k$, that by virtue of the separation of the extrema $\partial B/\partial \psi\theta = 0$ and $\partial B/\partial k = 0$, the derivative $\partial B/\partial \psi$ may be of either sign when $\partial B/\partial k$ is of either sign. It follows from equation (4.2.5) above that $d\lambda/dt$ can be initially positive or negative for either sign of λ, depending on the balancing of the terms in the adjoint equation equation, giving four possible variations of λ with time; these are shown in Diagram 5.2. However, the adjoint λ must, at the final time, decrease from the positive, or increase from the negative, to reach zero. Therefore two of the trajectories of λ have turning points when, for λ positive, $d^2\lambda/dt^2$ is negative, and vice versa. Although it has not been proven theoretically, numerical work on the consecutive reaction has shown that, if the initial Hamiltonian is feasible, these two cases (a and b in Diagram 5.2) correspond to policies which end on the upper constraint, when it is impossible to end at $\partial B/\partial k = 0$. Cases c and d correspond to unconstrained stationary policies ending in a finite time at $\partial B/\partial k = 0$.

It will be shown from numerical results in Chapter VII that the four variations in λ are related to the identifiable regions of feasible policies described in Section 5.4, depending on the initial sign of $\partial B/\partial k$ (and hence λ), and $d\lambda/dt$, for $p_1 \neq p_2$. It has not been predicted that there is an exact correspondence here, and an example can be found which shows that other trajectories of λ with time can exist (see Section 7.2.3). This implies that, provided that the restrictions on the Hamiltonian and on the initial temperature are respected, the values of the adjoint are automatically feasible at all times. The results emphasize the duality of state and adjoint variables.

This section has shown that there are no theoretical restrictions on the initial signs of λ and $d\lambda/dt$, but that at the final time the sign of $d\lambda/dt$ must be opposite to that of λ in $(0,\tau)$, and to that of $\partial B/\partial\psi$ at τ. Different optimal policies can be characterised by the time behaviour of the adjoint λ.



Initially:

a	λ+	dλ/dt +
b	λ-	dλ/dt -
c	λ+	dλ/dt -
d	λ-	dλ/dt +

c and d may correspond to constrained policies in certain cases (Section 7.3.3)

Diagram 5.2 Trajectories of λ

CHAPTER VI

METHODS OF OBTAINING NUMERICAL SOLUTIONS TO OPTIMAL POLICIES

6.1 Calculation methods

6.1.1 Stationary policies

At the chosen feasible temperature, the stationary Hamiltonian is calculated. The system time is incremented to allow for a small amount of catalyst decay (approximately .1%) according to equation (3.1.2). The new optimal temperature at the new activity is guessed by binary search, keeping the Hamiltonian constant. The procedure is repeated until the final time is reached, when the Hamiltonian equals the final concentration.

6.1.2 Constrained policies

The general Hamiltonian equation (4.2.10) is used. If the policy is initially stationary, the value of the Hamiltonian is known and equal to the stationary value. As before, the system time is incremented to find the new activity, and the adjoint variable is adjusted to keep the Hamiltonian constant in (4.2.10), at constant temperature.

If the policy begins and ends on the constraint, the final concentration (which is the value of the Hamiltonian) is chosen, and so the initial value of the adjoint at that temperature and at the initial activity can be calculated. The methods of the last paragraph are carried out until the final time is reached, when the concentration of B equals the value of the Hamiltonian.

6.2 Classification of the results: numerical values

Numerical values are chosen such that the policies can range between upper and lower temperature constraints of $900^{\circ}K$ and $700^{\circ}K$ respectively. Three types of consecutive reaction have been identified by the relative chemical activation energies of the two steps (see Section 3.2). These types correspond to:

$$p_1 = p_2 \qquad p_1 > p_2 \qquad p_1 < p_2$$

where $p_1 = E_1/E_c$, $p_2 = E_2/E_c$ and E_1, E_2, E_c are the activation energies of the first and second reaction steps, and of the catalyst decay, respectively.

In order to compare the three types, the following criterion for reaction conditions was used. At an effective residence time of .25 s, and at a temperature of $875^{\circ}K$, the maximum concentration of B with respect to effective residence time (given by equation (3.3.3)) is set at .75. This means that each reaction type will end in approximately the same field of concentrations on a rising temperature policy. The residence time in the constant flowrate cases is set at 1 s, so that the activity in the criterion above is .25; that is, at a point near the end of the policy. Arrhenius frequency factors A_1 and A_2 are obtained from a solution of equations (3.3.3) and (3.3.4), for each pair of p_1, p_2 values, at the point chosen for the criterion. This is equivalent to fitting a given reaction type to a base set of conditions.

Data for the calculations were:

Upper constraint: $T^* = 900^\circ K$

Lower constraint: $T_* = 700^\circ K$

Catalyst decay temperature coefficient: $E_c/R = 15000^\circ K$

Catalyst decay frequency factor: $A_c = 2000000 \text{ hr}^{-1}$

Residence time (constant flowrate cases): 1 s

Initial activity: 1.0

6.3 Results

In the following sections, the theory is applied to the three particular cases of consecutive reaction, to predict types of temperature policies. Numerical results are presented as graphs. In Chapter VII the numerical work examines the effect of initial temperature on final time and on the types of policy for constrained and unconstrained cases. In Chapter VIII special cases are considered; these include comparisons, the use of a performance criterion, and a discussion of the variable flowrate case.

Figure 6.1 shows the Arrhenius relation between the catalyst decay rate constant and the temperature.

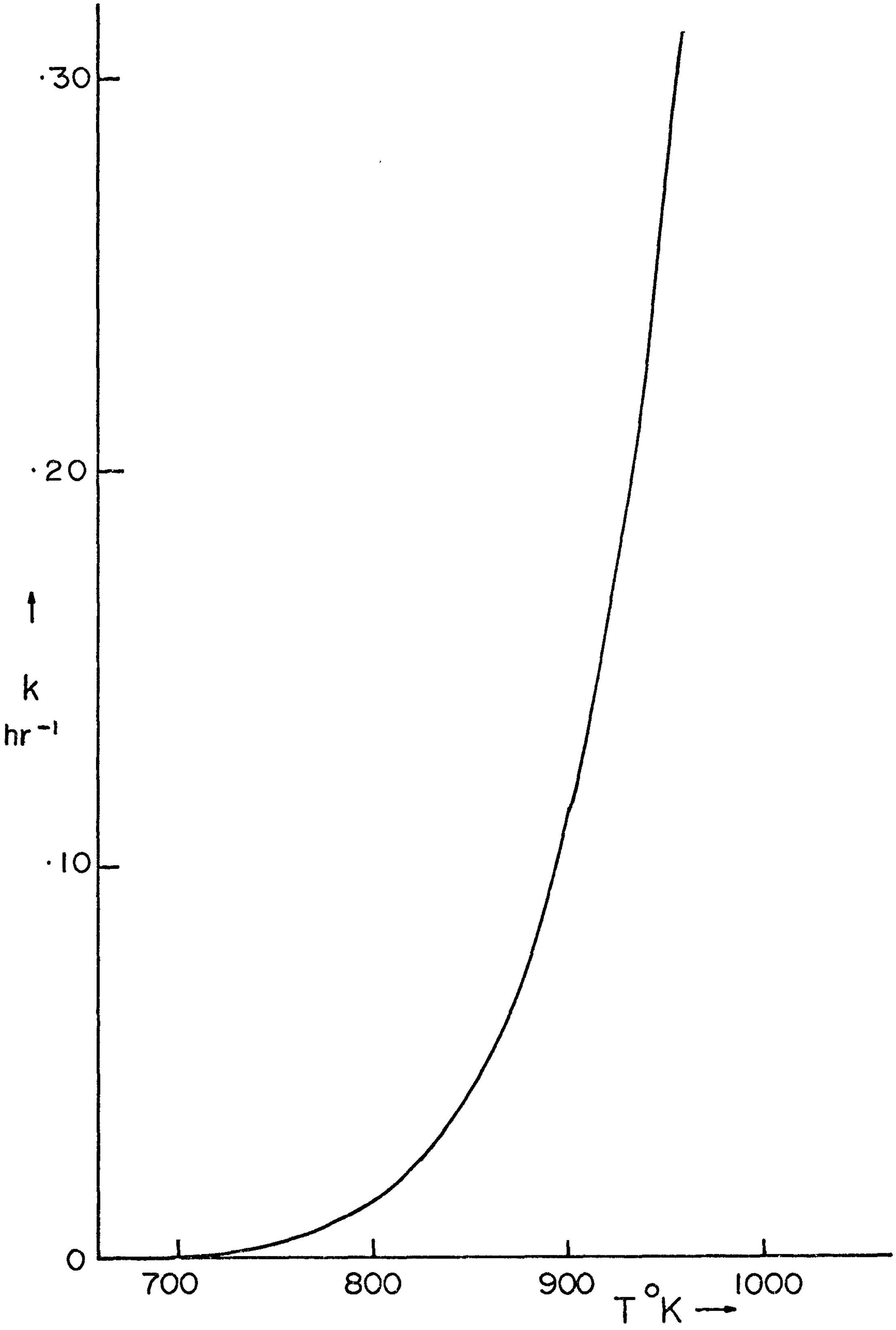


Figure 6.1 Catalyst decay rate constant k vs. temperature

CHAPTER VII

APPLICATION OF THE MAXIMUM PRINCIPLE TO A FIRST-ORDER CONSECUTIVE REACTION WITH CATALYST DECAY - PARTICULAR CASES AND NUMERICAL RESULTS

7.1 Case I. $p_1 = p_2 = p$

7.1.1 A study of the kinetics

In order to help define the conditions under which an optimal policy may exist, the behaviour of B with temperature and effective residence time is examined. Figure 7.1.1 shows contours of B at various T and $\psi\theta$. It was shown in Section 3.4 that the maxima with respect to temperature and effective residence time coincide at a constant value depending only on the ratio of the Arrhenius frequency factors:

$$\max_{(T,\psi\theta)} B = \left(\frac{A_1}{A_2}\right)^{\frac{A_2}{A_2 - A_1}} = \text{const.} \qquad (3.4.1)$$

The position of the optimum effective flow (and hence optimum temperature) is related to the temperature by:

$$(\psi\theta)_{opt} = \frac{\ln\left(\frac{A_1}{A_2}\right)}{(A_1 - A_2)\exp(-pE_c/RT)} = \text{const}_1.\exp(pE_c/RT) \qquad \text{from } (3.3.4)$$

That is,

$$\ln(\psi\theta)_{opt} = \text{const}_2 + \text{const}_3/T \qquad (7.1.1)$$

for $p_1 = p_2$. Also, for constant B, $\psi\theta k^p$ = a constant, therefore the curves in Figure 7.1.1 on a semi-log scale are hyperbolae.

The optimization theory has shown that the bounds of optimal

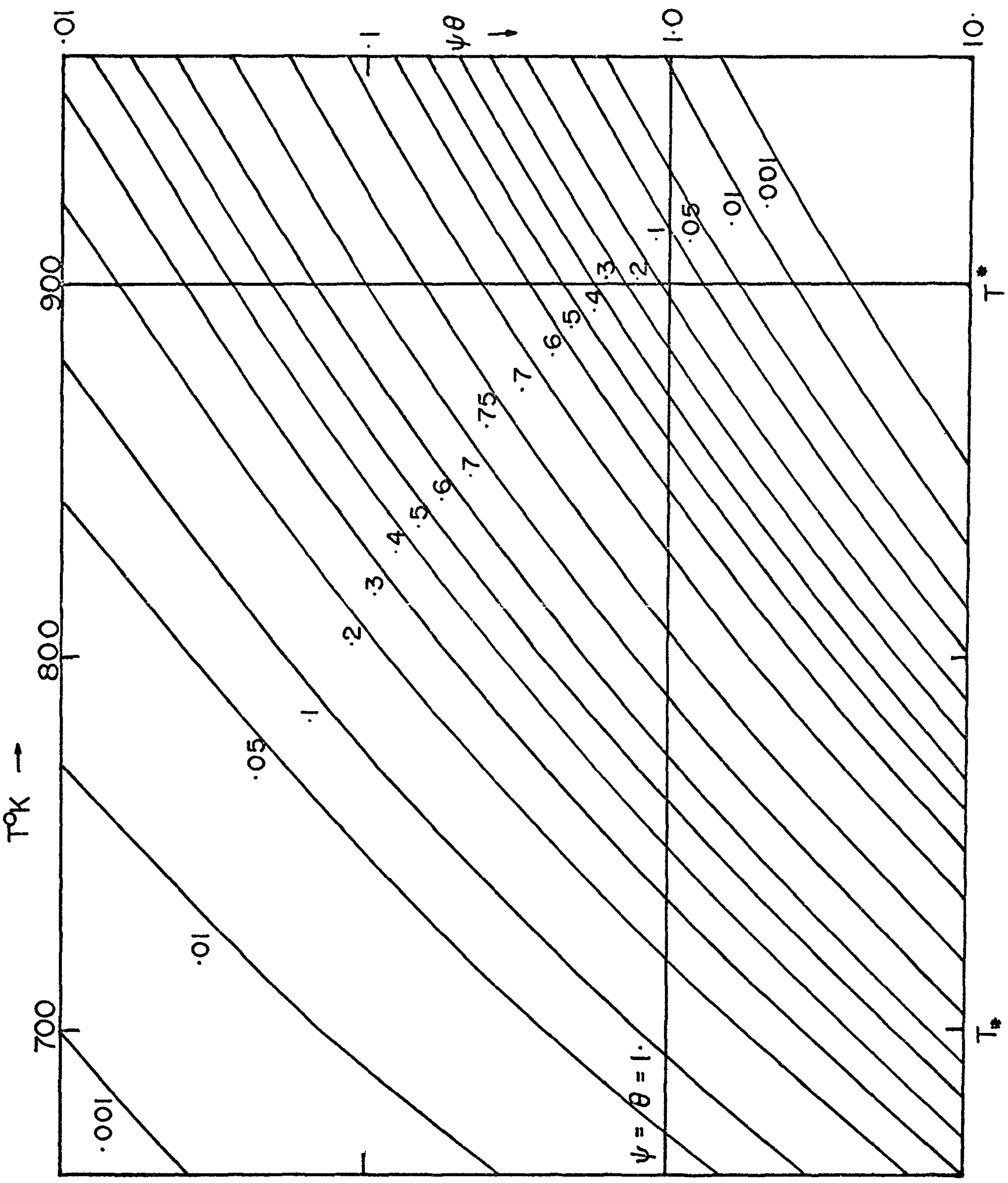


Figure 7.1.1 Concentrations of B at different temperatures T and effective residence times ψθ. Case 1. $p_1 = p_2 = p = 1.0$. Arrhenius frequency factors are $A_1 = 269207670.s^{-1}$ $A_2 = 32048532.s^{-1}$

policies are determined by the signs and magnitudes of the derivatives and variables involved. For this purpose, Figure 7.1.2 shows the sign of $\partial B/\partial k$, for the same field of T and $\psi\theta$ as Figure 7.1.1. For the case $p_1 = p_2$, the sign of $\partial B/\partial\psi\theta$ is the same as that of $\partial B/\partial k$.

7.1.2 Application of the Maximum Principle

The conditions for stationary and constrained policies were discussed in Chapter V. The initial Hamiltonian for the stationary policy is calculated from

$$H_s = B - k\frac{\partial B}{\partial k} \qquad (5.2.3)$$

and a map of values of H_s defines the regions of allowable Hamiltonian values, in accordance with the conditions in Section 5.4. Figure 7.1.3 gives only the sign of H_s (although a table of values of H_s was used in the numerical work) and is therefore useful for finding the lower limit $H_s = 0$. For stationary policies only, the sign and value of the adjoint variable λ at the initial time is equal to that of $\partial B/\partial k$, and so is given by Figure 7.1.2. The discussion of Section 5.6 pointed out the use of the sign of $d\lambda/dt$ in characterizing optimal policies, and this derivative can be evaluated from equation (4.2.5) at the initial time using the initial value of λ. The result is shown in Figure 7.1.4 for p = 1. The final sign of $d\lambda/dt$ is the opposite of $\partial B/\partial\psi\theta$, and so is obtained from Figure 7.1.2.

The representation of all the available information for the system enables a thorough examination of possible optimal policies to be carried out. The selection of initial conditions is done in this way for all cases. The results of the possible stationary (best optimal) temperature

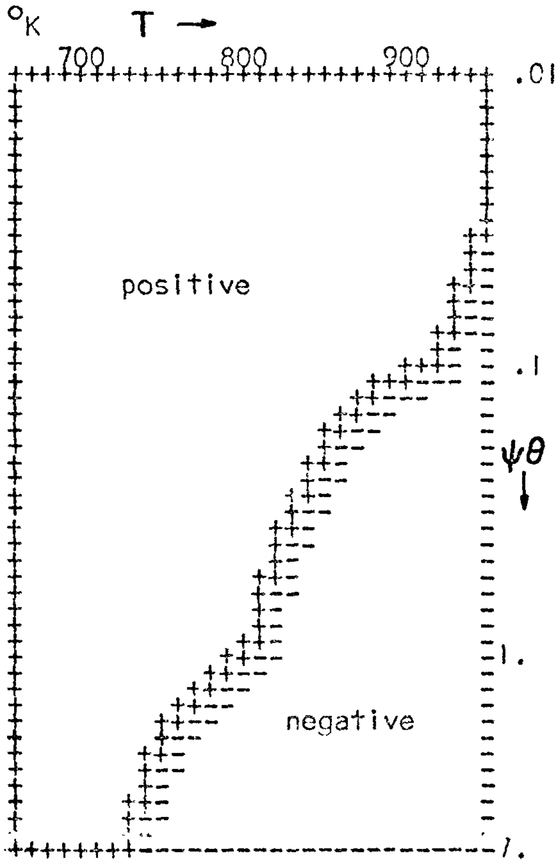


Figure 7.1.2 Sign of ∂B/∂k

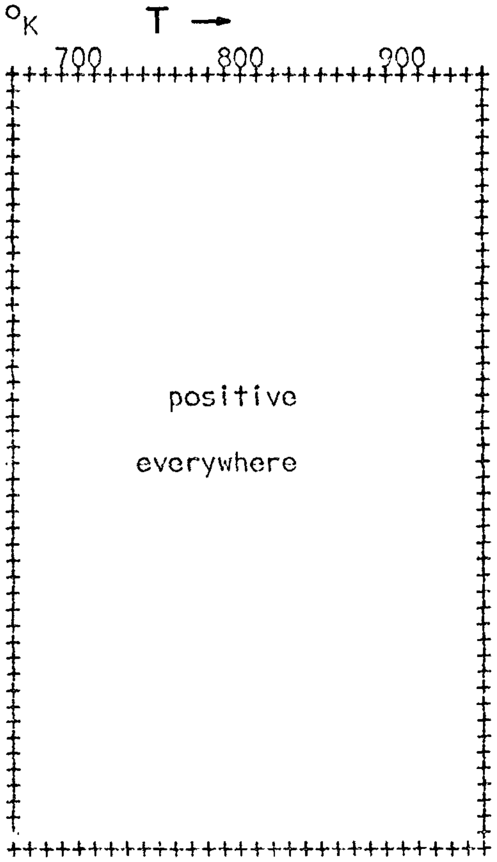
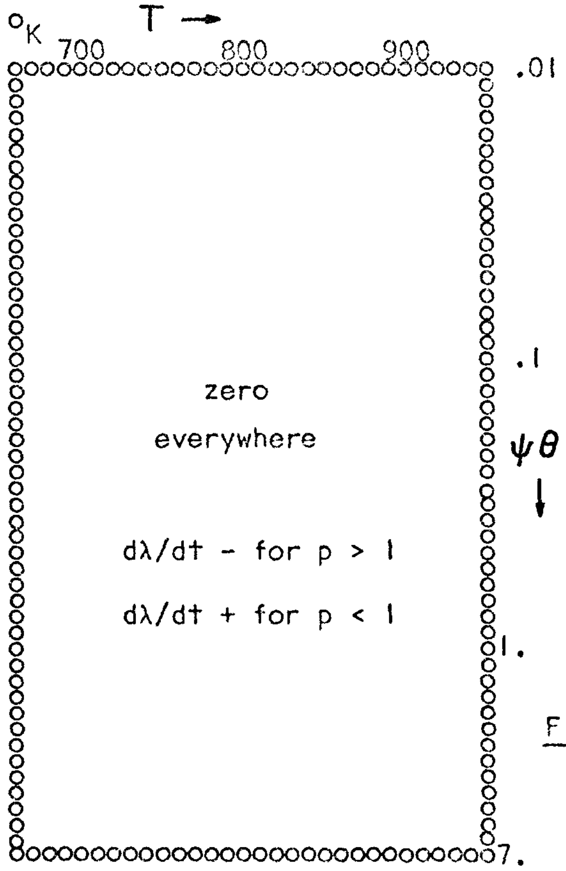


Figure 7.1.3 Sign of H_S



Case 1 $p_1 = p_2 = p$

$p = 1$ in this example

Figure 7.1.4 Sign of dλ/dt

policies are based on the division of the initial feasible temperatures into the two regions I and II, defined in Section 5.4.

Analysis for $p \neq 1$

Since the equations simplify greatly for $p_1 = p_2$, this case can be examined thoroughly. The Hamiltonian along a stationary policy, for $p_1 = p_2 = p$, is given by (Appendix A7.1)

$$H_s = \text{const}_1[\exp(-\text{const}_2 k^p \psi) - \exp(-\text{const}_3 k^p \psi)] - \text{const}_4 k^p \psi [A_2 \exp(-\text{const}_3 k^p \psi) - A_1 \exp(-\text{const}_2 k^p \psi)] = B(\tau) \tag{7.1.2}$$

Therefore, to keep H_s constant,

$$k^p \psi = \text{a constant} \tag{7.1.3}$$

Hence

$$B = \text{a constant} \tag{7.1.4}$$

Therefore the stationary policy is to remain on the contour B = a constant, as the temperature rises according to (7.1.3).

If B is not at its constant maximum value, given by the equation (3.4.1) above, the policy can never end as a stationary one (because the contour B can never cross a point where $\partial B/\partial k$ is zero) but always on the upper constraint.

If B is at its maximum value (that is, at the top of the ridge in Figure 7.1.1) the policy is to continue at this value until the upper constraint, and hence the final optimal time, is reached. Along the ridge $B = B_{max}$,

$$\frac{\partial B}{\partial \psi} = \frac{\partial B}{\partial k} = \lambda = \frac{d\lambda}{dt} = 0 \tag{7.1.5}$$

At the upper constraint, $d\lambda/dt$ becomes negative instantaneously, and hence λ decreases as ψ decreases.

The optimal temperature policy may be obtained analytically from

$$k^p\psi = \text{a constant} \tag{7.1.3}$$

and

$$\frac{d\psi}{dt} = -k\psi \tag{3.1.2}$$

It is the hyperbola (see Appendix A.7.1)

$$\frac{1}{k} = \frac{1}{k_o} - \frac{t}{p} \tag{7.1.6}$$

Alternatively, (7.1.6) can be obtained from the expression for dH_s/dt (see Appendix A.7.2).

Analysis for $p = 1$

The condition for the Hamiltonian to be constant is now

$$k\psi = \text{a constant} \tag{7.1.7}$$

Conditions (7.1.4) and (7.1.5) still hold. Also, $d\lambda/dt = 0$ and λ = a positive constant (see Appendix A.7.3).

The temperature policy is obtained analytically as simply

$$\frac{1}{k} = \frac{1}{k_o} - t \tag{7.1.8}$$

The best optimal policy for $p_1 = p_2$ is to start at the temperature giving a maximum of B.

7.1.3 Numerical results. S-C* policies

The case $p_1 = p_2 = 1$ is taken as an example. All policies end on the upper constraint for $p_1 = p_2$.

Region I Figure 7.1.3 shows that there is no lower limit on initial temperatures above the lower constraint of 700°K, at $\theta = 1$ (and $\psi = 1$). Figure 7.1.1 shows that the upper limit for this region is 808°K (at the concentration datum B = .75). The derivative $d\lambda/dt$ at $\lambda = 0$ is always negative, and $\lambda(0) \geq 0$, for this region.

Figure 7.1.6 shows the effect of initial temperature on total time for optimal policies in Region I. As the initial temperature increases, the total operating time decreases, due to increased catalyst decay rate. The time on the upper constraint also decreases. All curves have an exponential form, which becomes steeper with increasing initial temperature.

Figure 7.1.7 shows the theoretical result B = a constant (7.1.4), and the variation of the activity and of the adjoint λ for one initial temperature. The optimal policy is for the activity to decrease in proportion to the operating time, since $k\psi$ = a constant for p = 1, and after substitution into (3.1.2). The adjoint is constant until the upper constraint is reached, then falls to zero.

Region II No feasible point is possible in this region for a stationary policy, since the Hamiltonian is always greater than the maximum attainable concentration B = .75 (from the geometric construction of equation (5.2.3)).

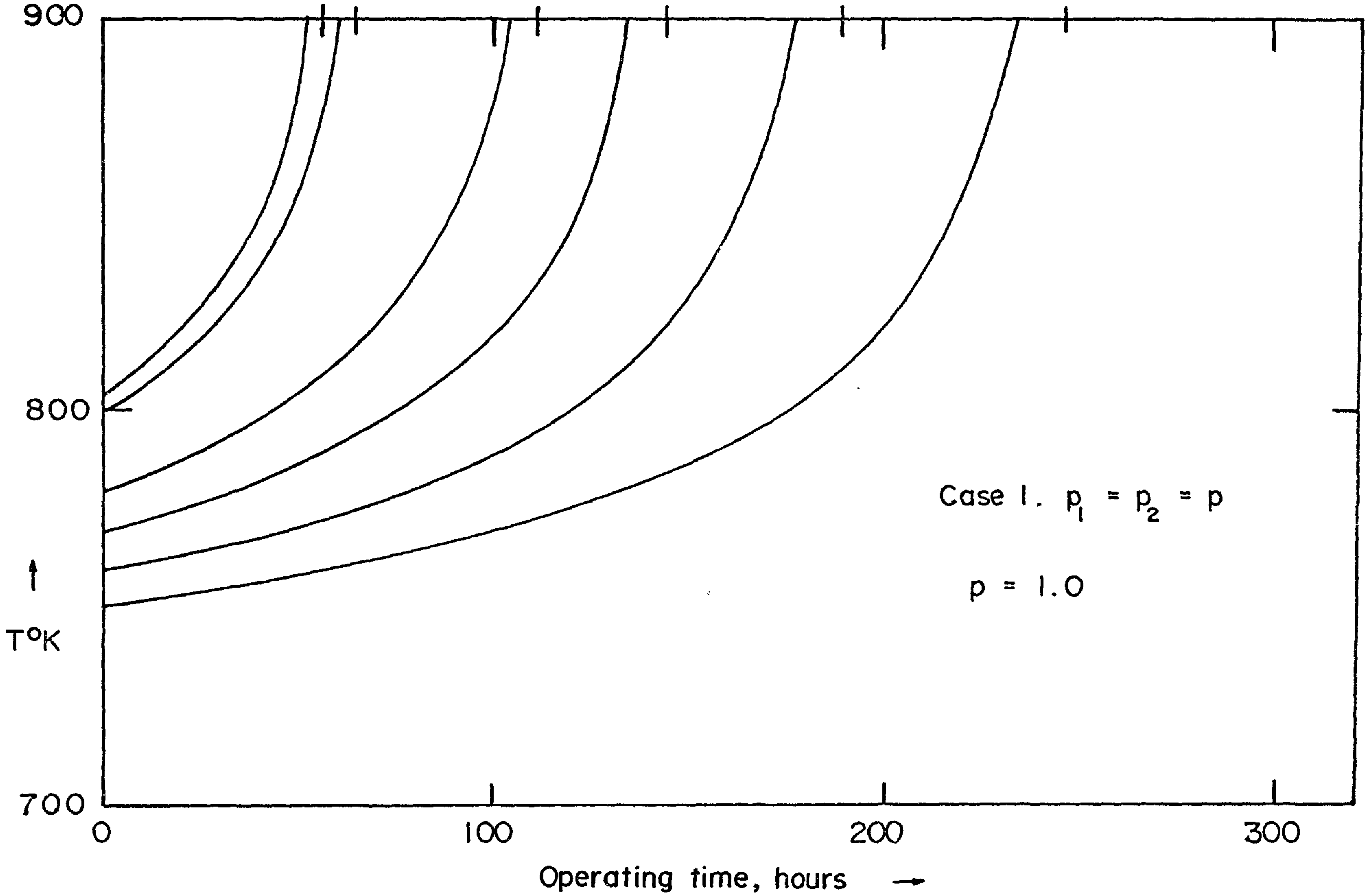


Figure 7.1.5 Effect of initial temperature on total time τ. S-C* policies.

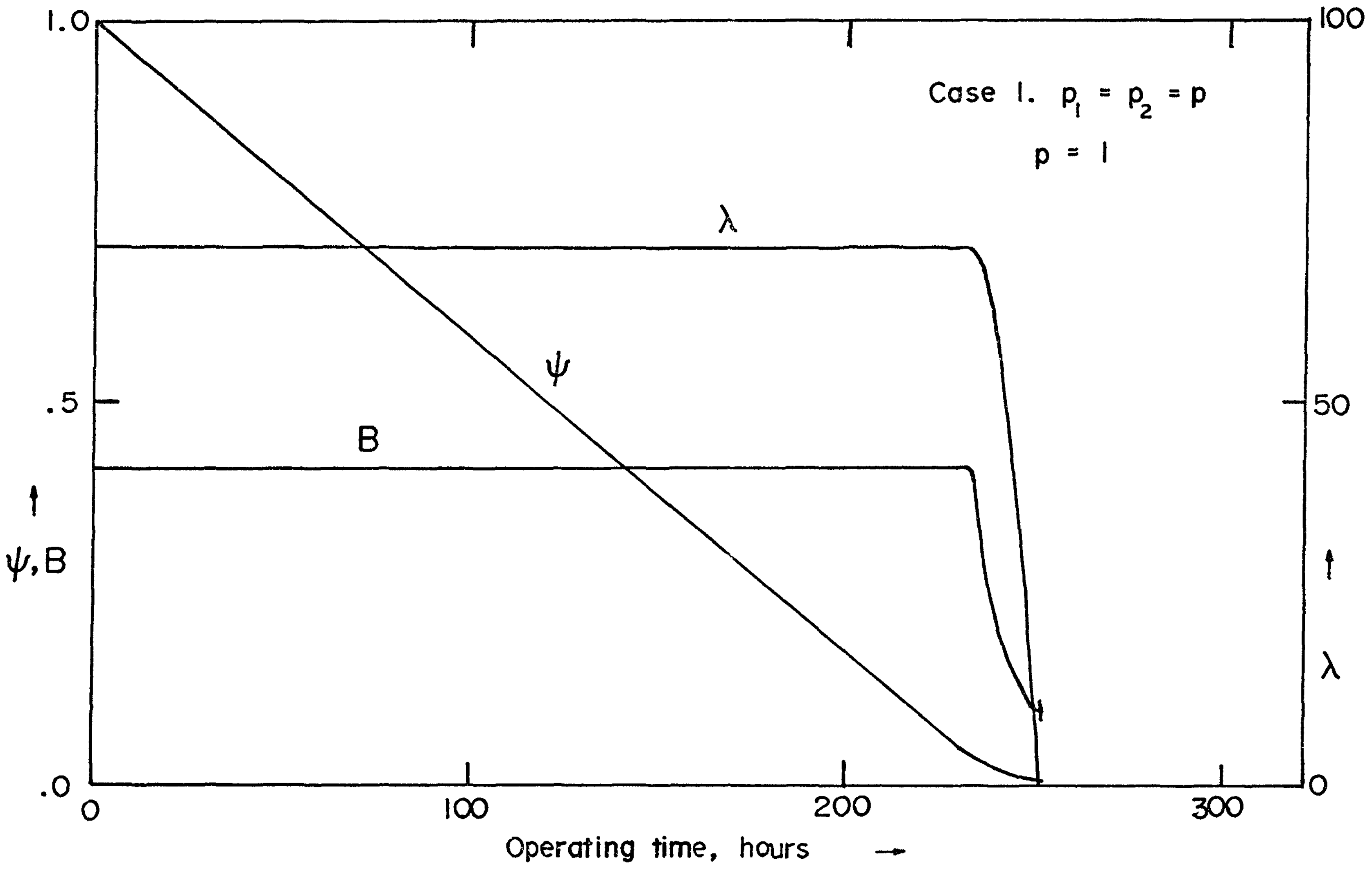


Figure 7.1.6 Plots of the adjoint λ, activity ψ, and concentration B for an initial temperature of 750 K.

7.2 Case 2. $p_1 > p_2$

7.2.1 A study of the kinetics

As discussed in Section 3.4 for $p_1 \neq p_2$, the maxima of B with respect to temperature and effective residence time coincide at one point only, when $K_1 = K_2$. Since the ratio K_1/K_2 increases with temperature, the maxima of B increase in magnitude with decreasing $\psi\theta$ and increasing T, towards the top right hand corner of Figure 7.2.1, for the case $p_1 = 1.2$, $p_2 = .8$. The signs of $\partial B/\partial k$ and $\partial B/\partial\psi\theta$ are shown for this case in Figures 7.2.2 and 7.2.3. The sign of $\partial^2 B/\partial k^2$ is shown for this case in Figure 7.2.4, since this second derivative is important for locating the upper bound in Region II.

7.2.2 Application of the Maximum Principle

As before, the allowable values of the Hamiltonian H_s are chosen from a plot for the particular case; Figure 7.2.5 shows the sign of the Hamiltonian. The sign of $\partial^2 H/\partial k^2 = \partial^2 B/\partial k^2$ is shown in Figure 7.2.4. The initial sign of λ is given by Figure 7.2.2, and of $d\lambda/dt$ (stationary policies) by Figure 7.2.6 for $p_1 = 1.2$, $p_2 = .8$. The final sign of $d\lambda/dt$ is the opposite of $\partial B/\partial\psi\theta$, from (4.2.5), and so is obtained from Figure 7.2.3.

7.2.3 Numerical results. S and S-C* policies

All results were rising temperature policies.

Region I Examination of Figure 7.2.1 shows that there can be no optimal policy S, but always S-C*. This is because all the possible ending concentrations of B for stationary policies, for which $\partial B/\partial k = 0$, are

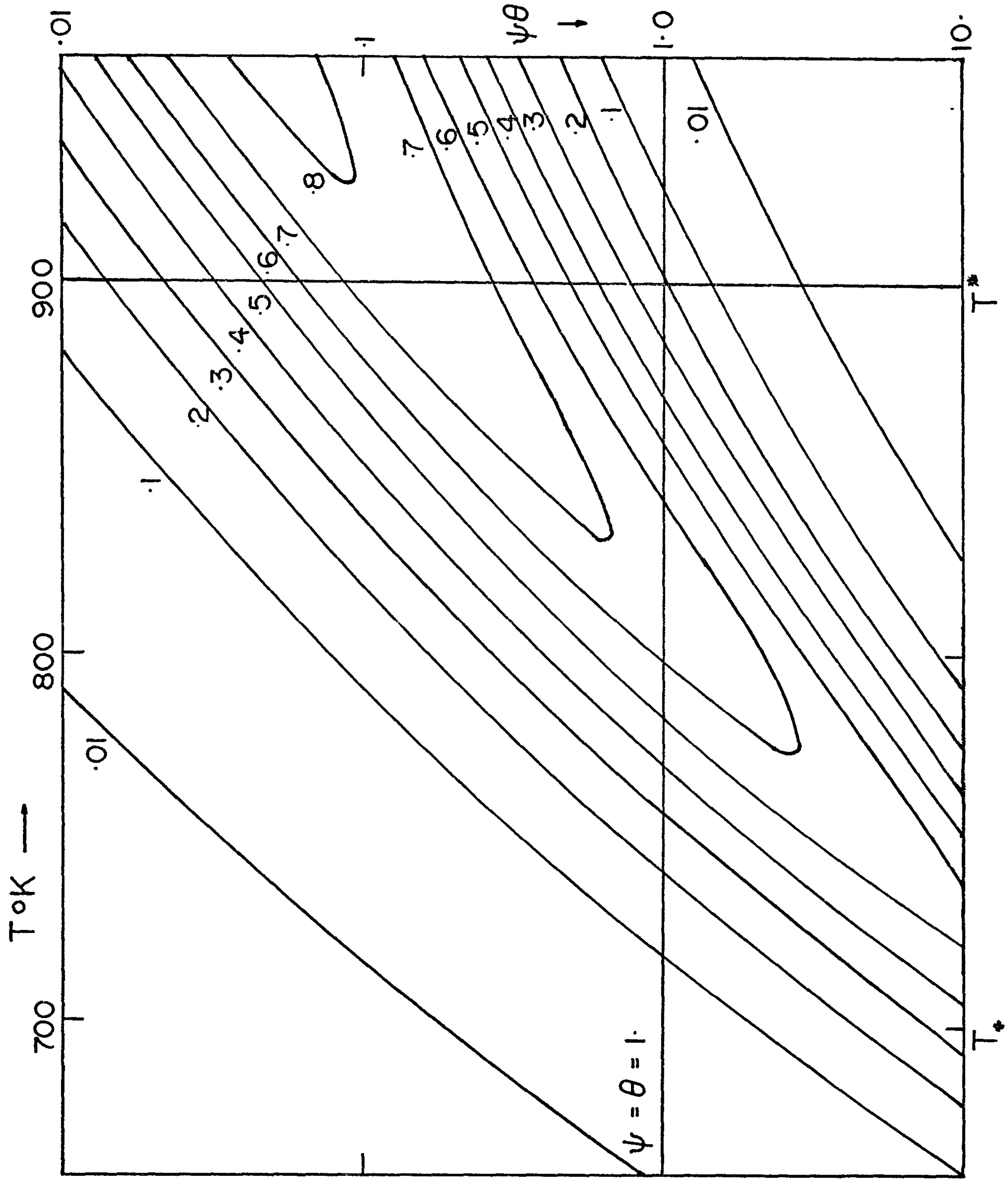


Figure 7.2.1 Concentrations of B at various T, ψθ. Case 2. $p_1 > p_2$. $p_1 = 1.2$ $p_2 = .8$. Frequency factors are $A_1 = 8300600082.4$ s-1.
$A_2 = 1039408.1$ s-1.

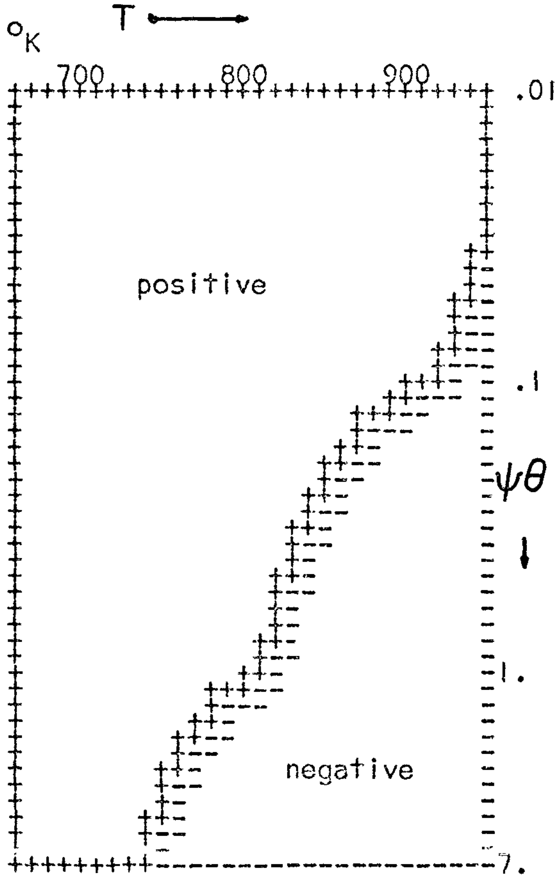


Figure 7.2.2 Sign of ∂B/∂k

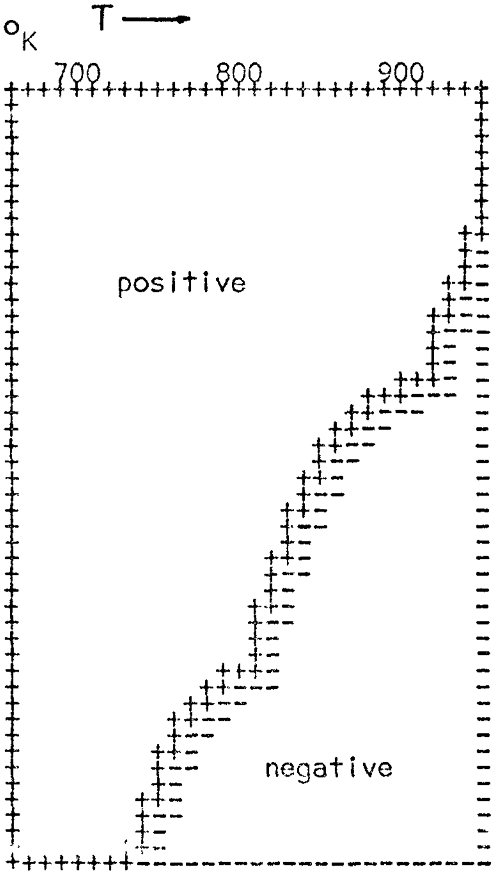
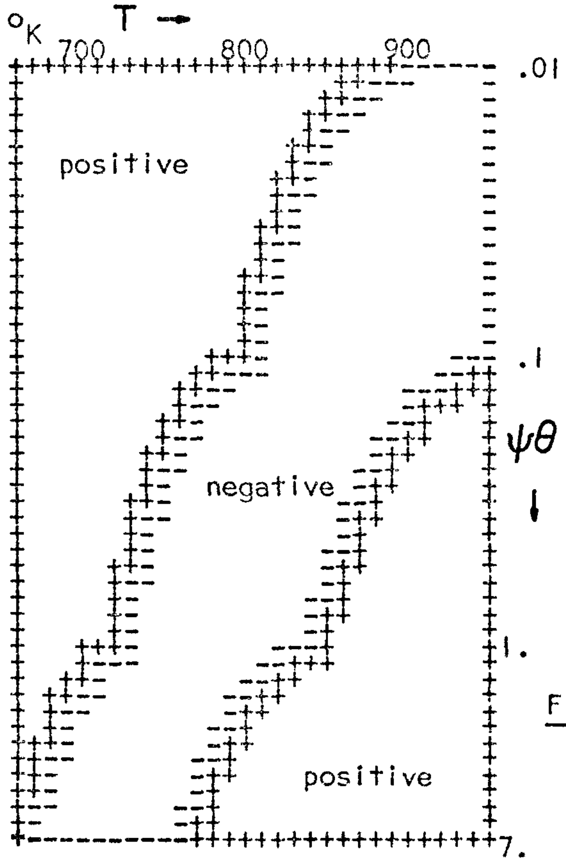


Figure 7.2.3 Sign of ∂B/∂ψθ



Case 2 $p_1 > p_2$

$p_1 = 1.2$ $p_2 = .8$ in this example

Figure 7.2.4 Sign of $\partial^2 H/\partial k^2$

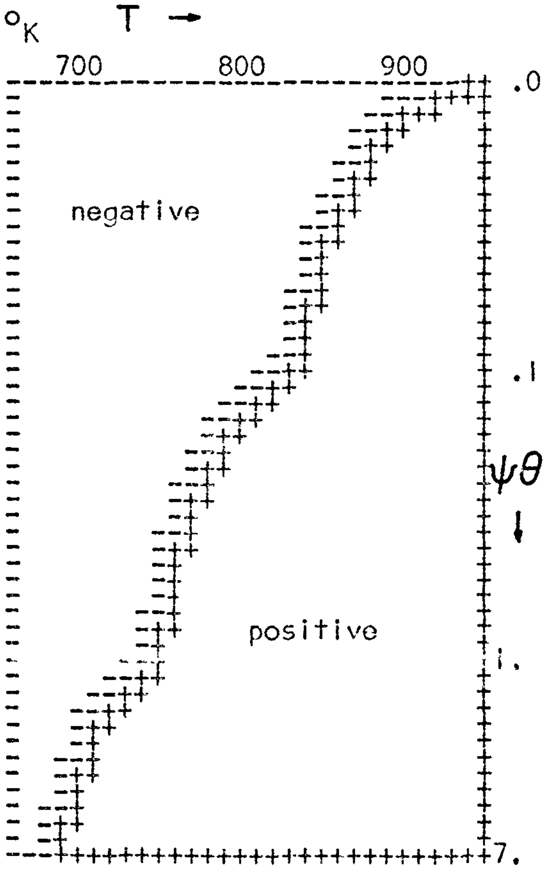


Figure 7.2.5 Sign of H_s

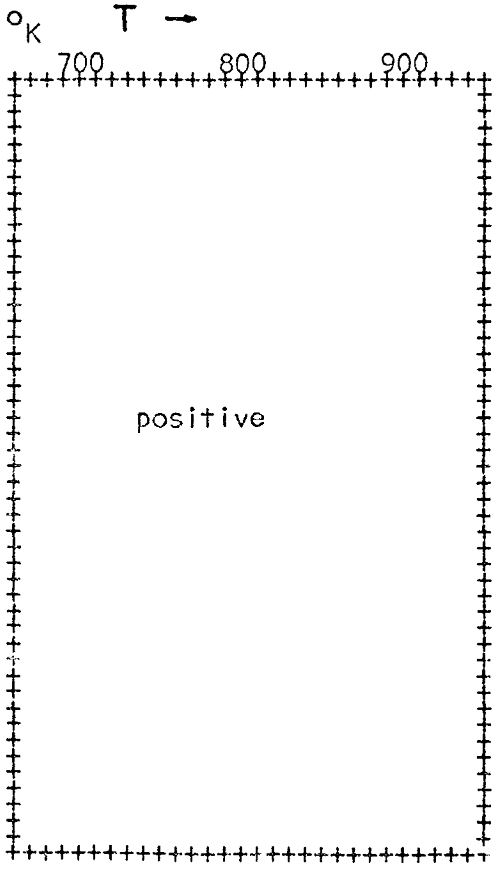


Figure 7.2.6 Sign of dλ/dt

Case 2 $p_1 > p_2$

$p_1 = 1.2$ $p_2 = .8$ in this example

higher than the initial maximum in B at $\psi\theta = 1$, which in turn is higher than all possible values of H_s in Region I.

The sign of $d\lambda/dt$ at $\lambda = 0$ is the opposite to that of $\lambda(0)$ (that is, negative) everywhere except for a very small region near the intersection of the upper constraint and $\partial B/\partial k = 0$, where $\partial B/\partial\psi\theta$ is negative, and so $d\lambda/dt$ may be positive at $t = \tau$ ($\lambda = 0$) here. This region is rejected as non-feasible.

Figure 7.2.7 shows the effect of initial temperature on the total time of operation. The curves have a similar shape to those of Case I ($p_1 = p_2$). However, more time is spent on the upper constraint, and the overall operating time is greater, for a given initial temperature.

Figure 7.2.8 plots the concentration, activity, and adjoint λ for one initial temperature in this region. The profile of the activity now curves slightly upwards from its straight line of descent (a tendency towards more conservation of activity). The concentration increases slightly until the upper constraint is reached. The adjoint has a characteristic trajectory, increasing exponentially near the upper constraint, then reaching a turning point ($d\lambda/dt = 0$) and falling to zero.

Upper and lower initial temperature limits are obtained in the same way as for Case I.

Special cases arise for $p_1 \neq p_2$, when the maxima of B in T and $\psi\theta$ do not occur at the same point. It is now possible, for example, for the derivative $\partial B/\partial\psi$ to be of either sign in Region I alone. This means that $d\lambda/dt$ (which was discussed in Section 5.6 as a means of transforming the behaviour of all state variables) can be of either sign in this region, and will define differently-behaved sub-classes of policies, according to

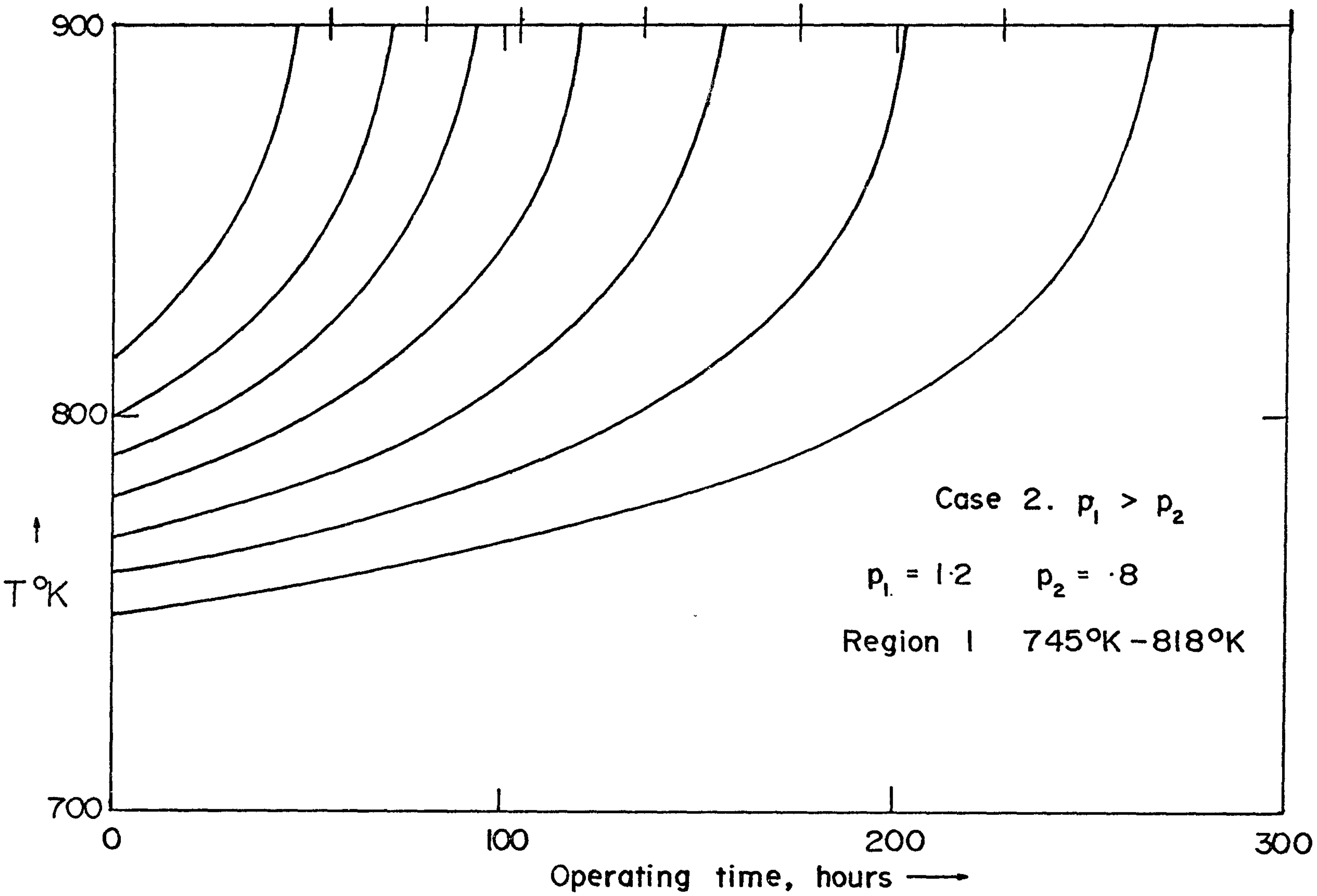


Figure 7.2.7 Effect of initial temperature on total time τ. S-C* policies.

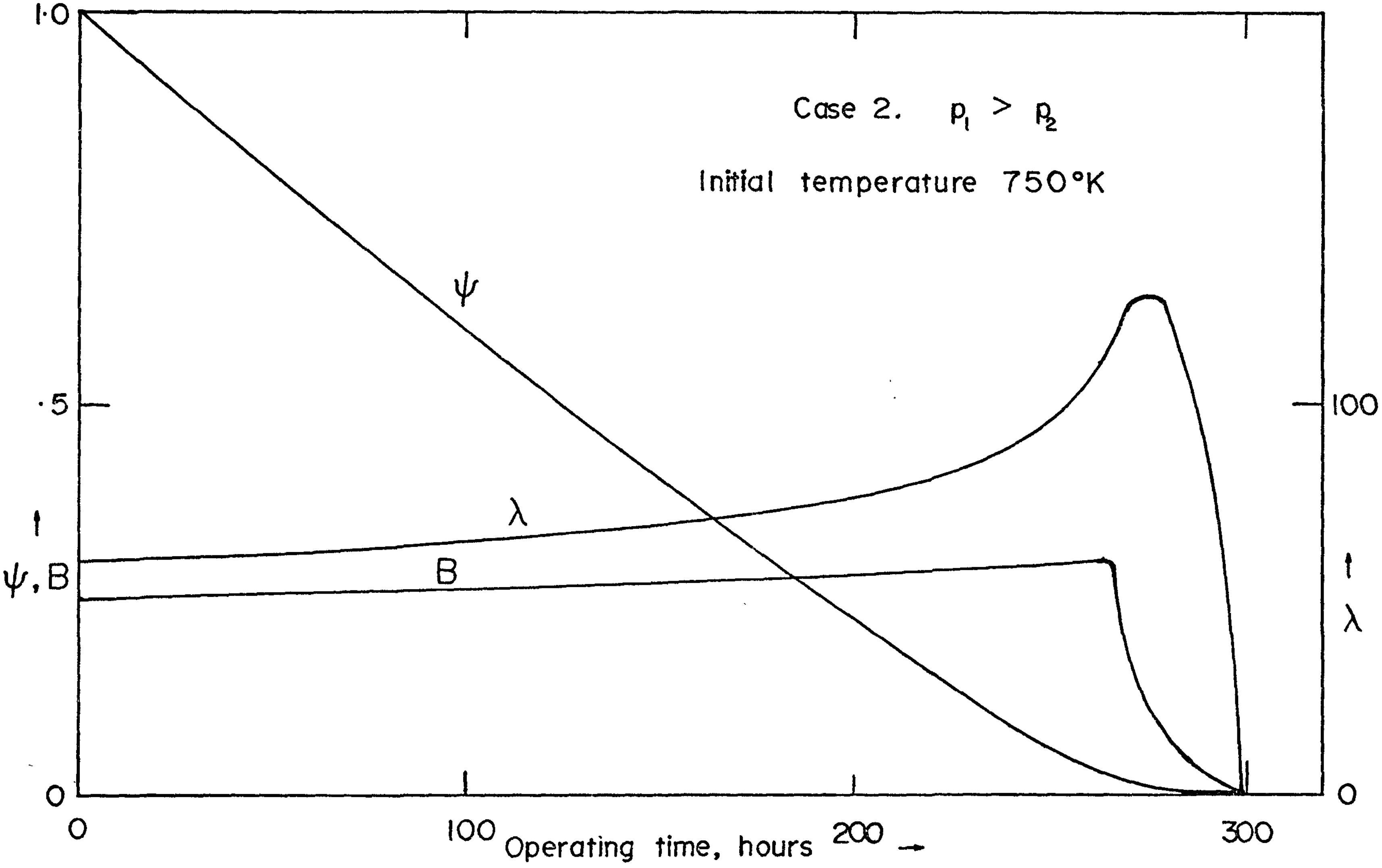


Figure 7.2.8 Variation of the adjoint λ, activity ψ, and concentration B with operating time.

the form of the trajectory of λ with time, and to the resulting fluctuations in total operating time.

Region II In this region, the stationary Hamiltonian H_s is greater in value than the initial concentration of B, from the geometrical construction of equation (5.2.3). Since the final concentration corresponding to H_s is now attainable as a maximum $\partial B/\partial k = 0$ (provided that $H_s < 1.$), then by virtue of the behaviour of B for this case, shown in Figure 7.2.1, it is possible to operate a wholly stationary policy S. The upper limit on the Hamiltonian is given by the maximum concentration attainable in the field $\psi\theta < \theta$, and for $T = T^*$ for constrained optimal policies. The corresponding temperature is the upper limit for any optimal policy in this region, and so policy $S\text{-}C^*$ is rejected for Region II. This upper temperature limit is subject to being lower than the upper inflexion point for B vs. k, above which $\partial^2 H/\partial k^2$ is positive.

Figure 7.2.9 shows the effect of initial temperature on total time for this region. The operating time increases with increasing initial temperature, from zero at the lower bound (818°K) to less than 37 hours at the upper bound (825°K). From a comparison of Figures 7.2.7 and 7.2.9 it would seem that the same total operating time could be achieved with two different initial temperatures. This possibility has not been rejected, but no such example was found for this case. The asymptotic behaviour of the operating time in Figure 7.2.9 indicates that it may be possible to reject this phenomenon on theoretical grounds.

Figure 7.2.10 plots the concentration, activity, and adjoint variable λ against operating time. The behaviour of B and ψ here is similar to that of the stationary portion of the curves of B and ψ in Region I.

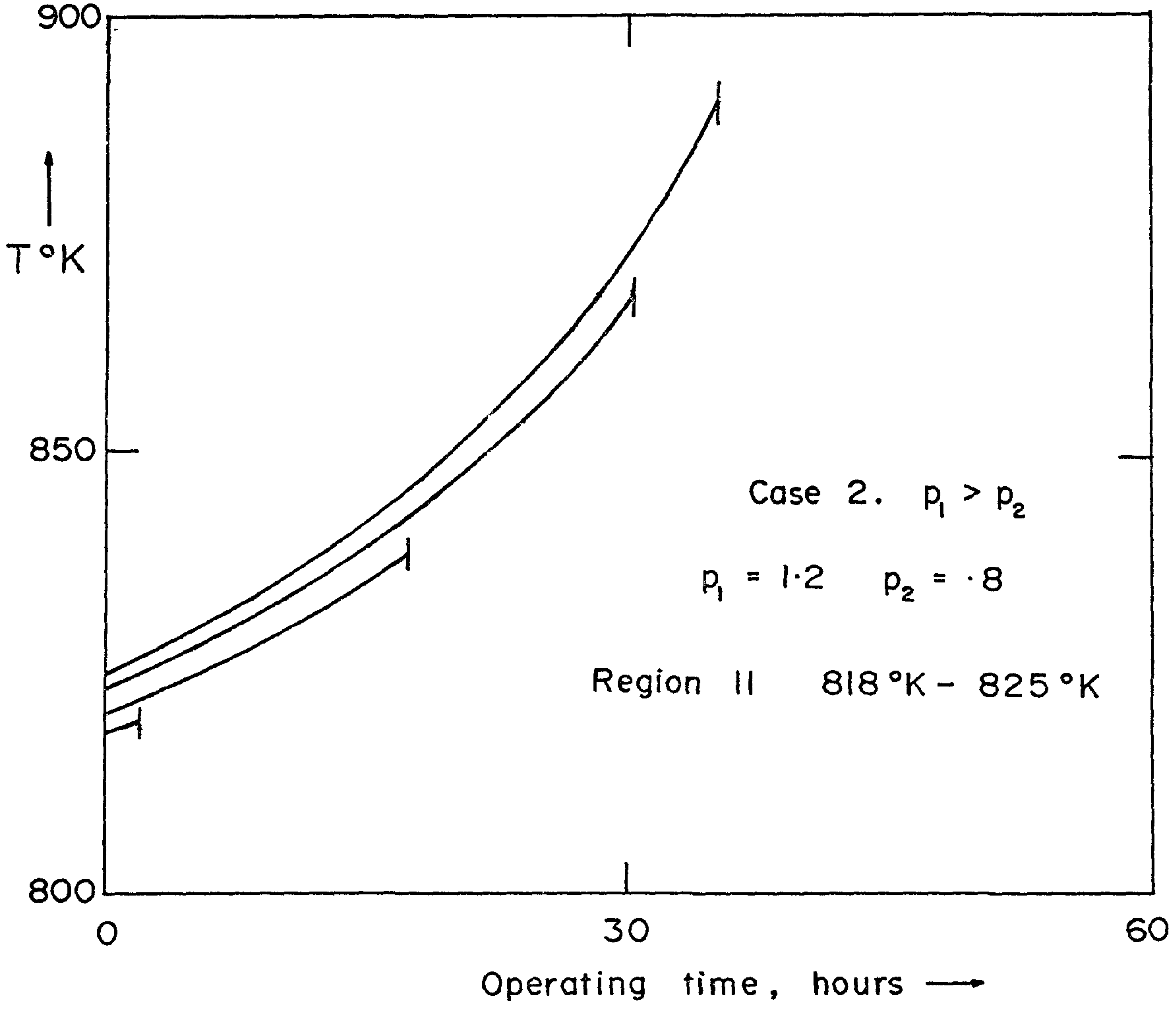


Figure 7.2.9 Effect of initial temperature on total time τ.

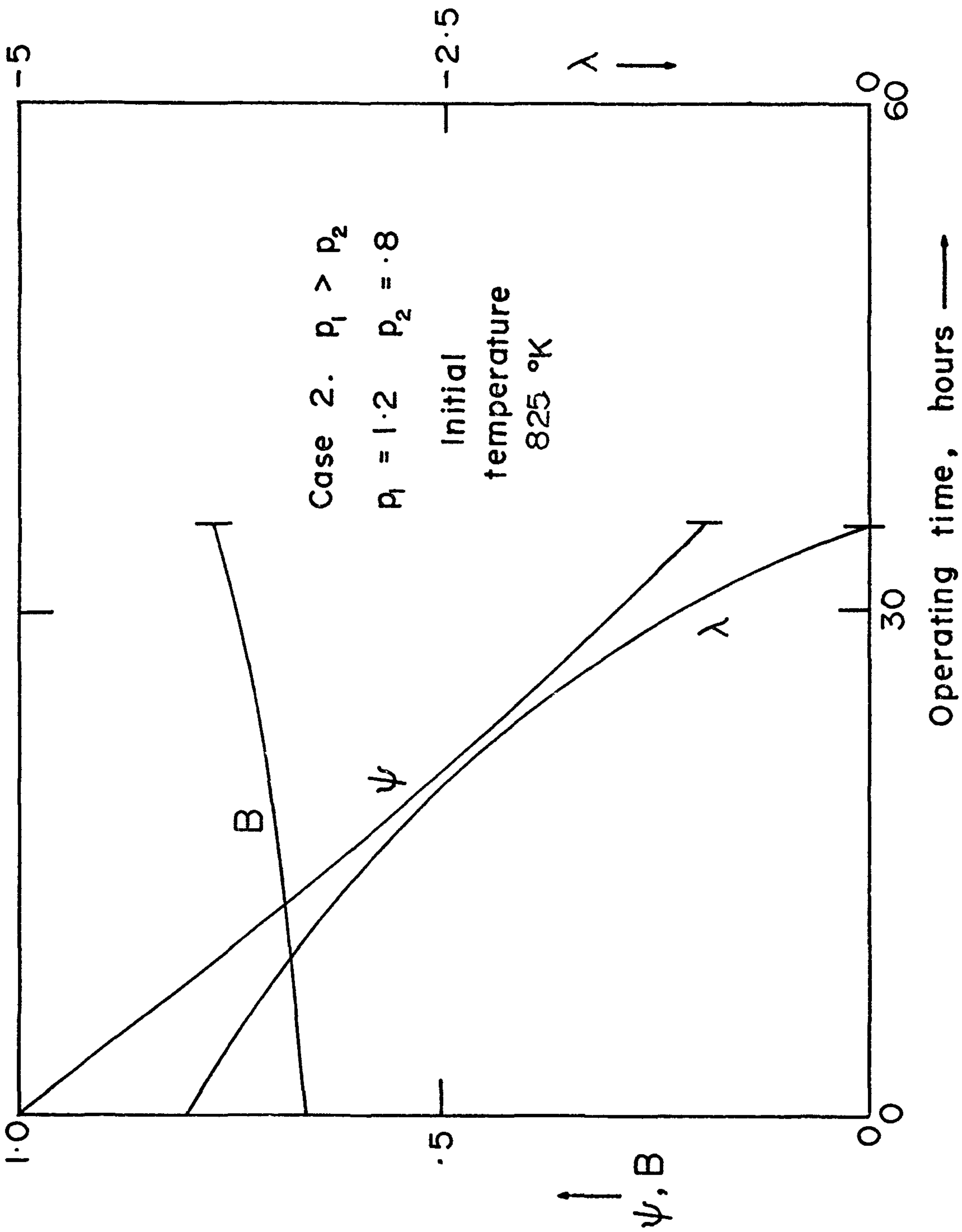


Figure 7.2.10 Variation of the adjoint λ, activity ψ, and concentration B with operating time.

The adjoint λ is characteristically different, increasing sharply from the negative to reach zero at the final time.

It follows that all final concentrations for these stationary policies should lie to the right and above the initial concentration in Figure 7.2.1, on the ridge of maximum concentrations. It should be theoretically possible, if the geometry of Figure 7.2.1 is examined closely, for the final concentration to lie to the left of the initial concentration (see Diagram 7.2.1) so that a falling temperature profile should be observed.

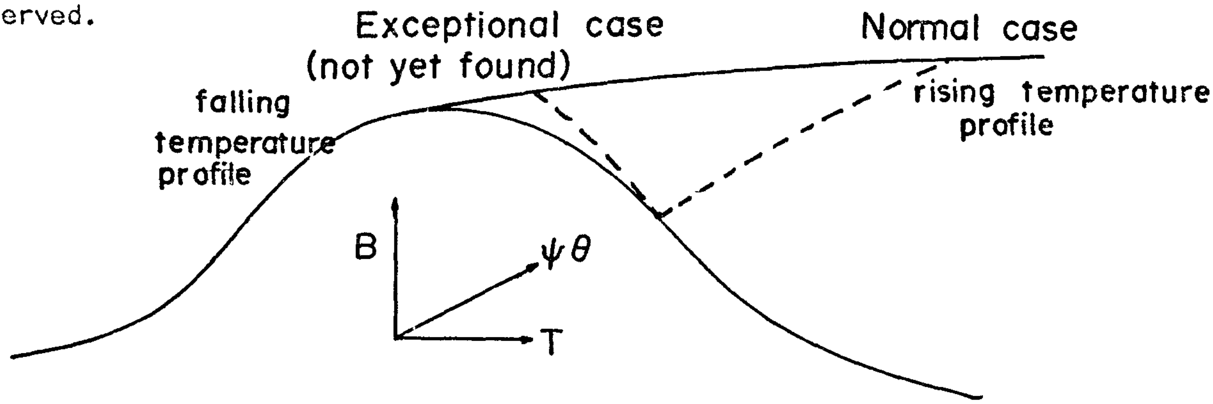


Diagram 7.2.1. Section of Figure 7.2.1

Such a case has not been found for any reasonable temperature range, because, for this example, the concentration of B decreases too quickly with temperature at constant flow, causing the stationary Hamiltonian to rise sharply after the maximum $\partial B/\partial k = 0$. Also, it appears that equation (5.2.7) is probably always positive for this region, by geometry.

7.3 Case 3. $p_1 < p_2$

7.3.1 Study of the kinetics

For this case, lower temperatures of operation, at higher residence times, favour the production of B (see Figure 7.3.1). Figures 7.3.2 and 7.3.3 plot the signs of $\partial B/\partial k$ and $\partial B/\partial\psi\theta$, for the example $p_1 = .8$, $p_2 = 1.2$. It is noted that $\partial B/\partial\psi\theta$ is always positive for $\partial B/\partial k = 0$ in the region under test.

7.3.2 Application of the Maximum Principle

The bounds for stationary policies are found as before from the plots of the Hamiltonian (Figure 7.3.4) and $\partial B/\partial k$ (Figure 7.3.2). The initial sign of λ is given by Figure 7.3.2, and of $d\lambda/dt$ (stationary policies) by Figure 7.3.5 for $p_1 = .8$, $p_2 = 1.2$. The final sign of $d\lambda/dt$ (at $\lambda = 0$) is given by the opposite sign of $\partial B/\partial\psi\theta$ in Figure 7.3.3.

7.3.3 Numerical results. S and S-C* policies

All results were rising temperature policies.

Region I ($\partial B/\partial k > 0$)

Examination of Figure 7.3.1 shows that it is possible to end at any point where $\partial B/\partial k = 0$ in the field $\psi\theta < 1$ ($\theta = 1$ in the constant flowrate examples). Therefore it is possible to operate a stationary policy S starting at any point in Region I for the unconstrained case. There is a limiting temperature (above k_ℓ in Diagram 5.1) for the constrained case, below which the policy is S-C*, since the final concentration is then not attainable as a point where $\partial B/\partial k = 0$; hence a stationary ending is not possible. The final concentration can be reached only along the upper constraint.

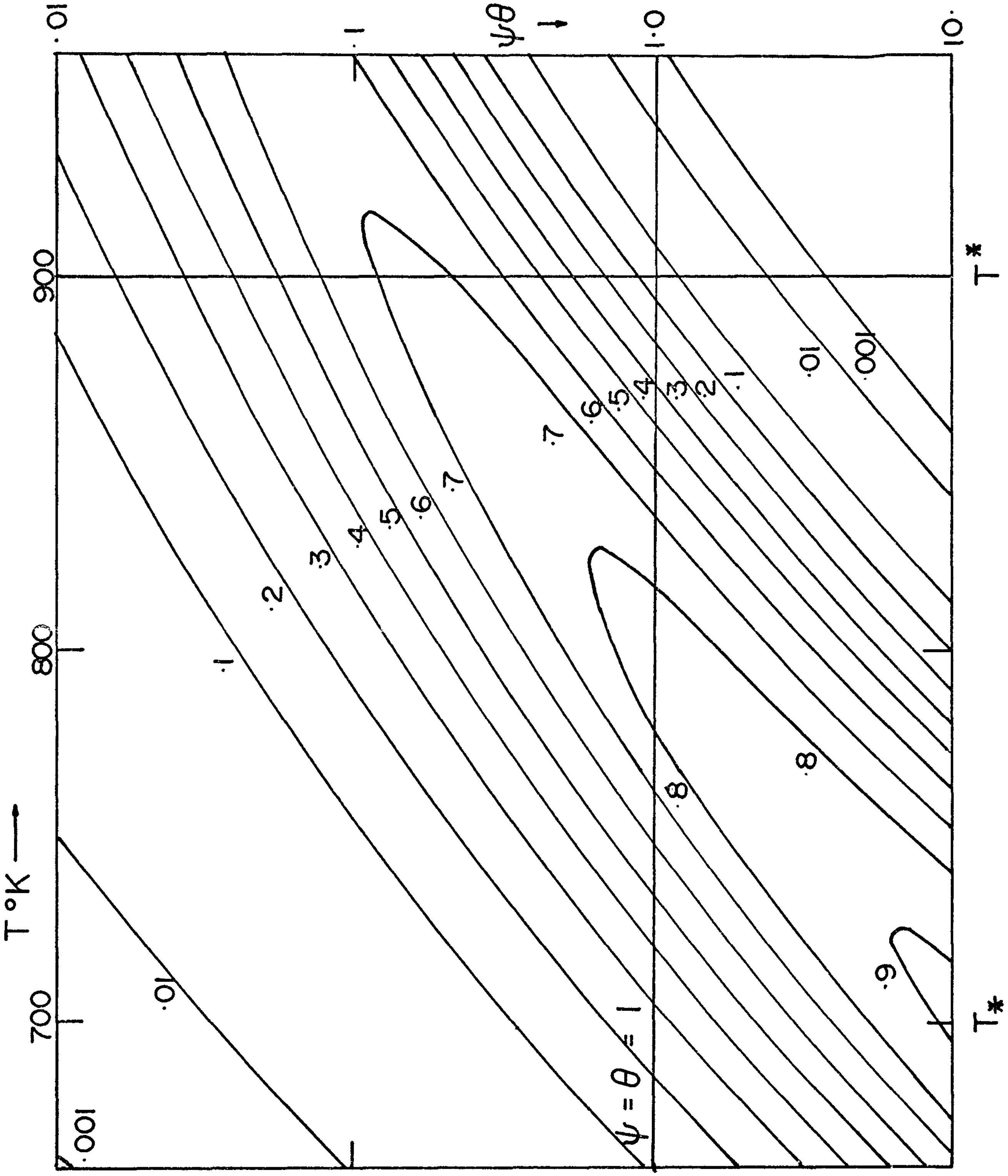


Figure 7.3.1 Concentrations of B at various T and ψθ. Case 3. $p_1 < p_2$. $p_1 = .8$ $p_2 = 1.2$. Arrhenius frequency factors are: $A_1 = 8731027.8$ $A_2 = 988166676.5$ s-1.

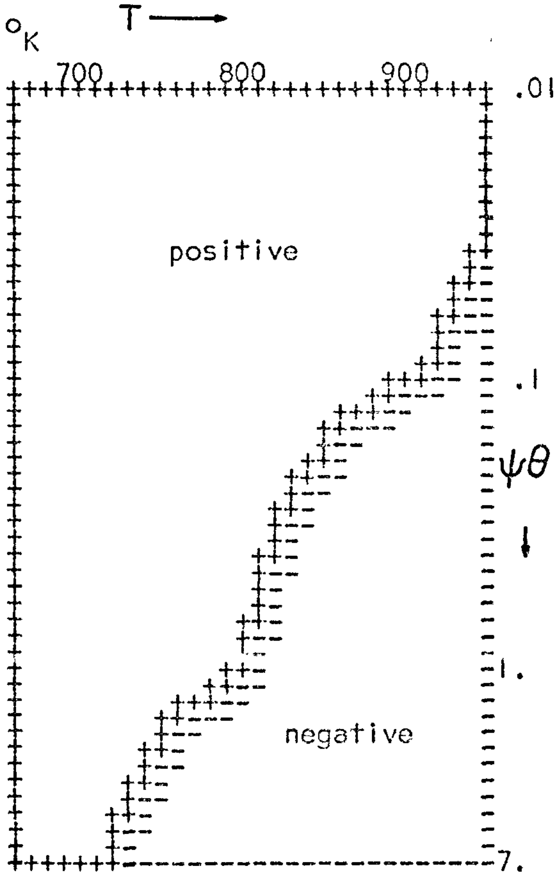


Figure 7.3.2 Sign of ∂B/∂k

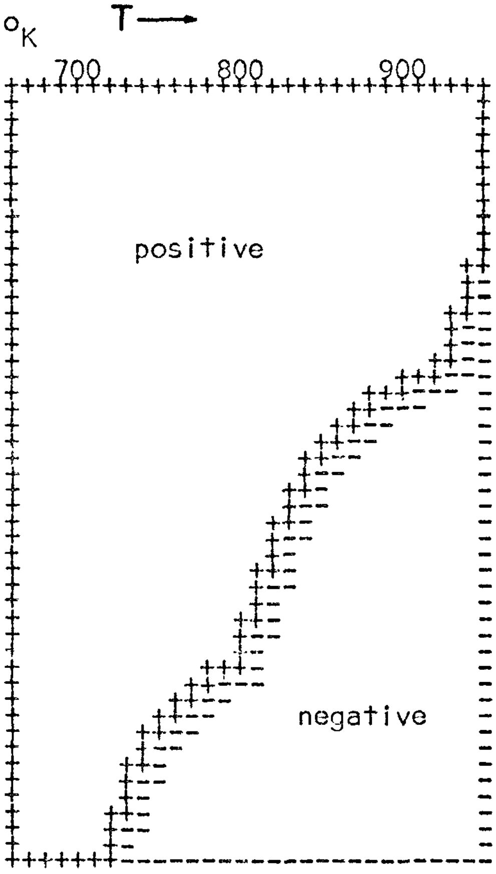


Figure 7.3.3 Sign of ∂B/∂ψθ

Case 3 $p_1 < p_2$

$p_1 = .8 \quad p_2 = 1.2$ in this example

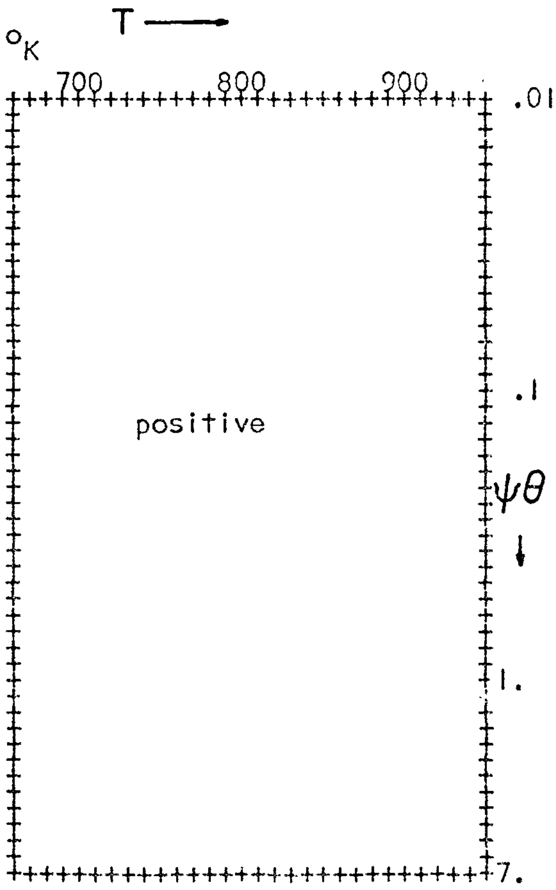


Figure 7.3.4 Sign of H_s

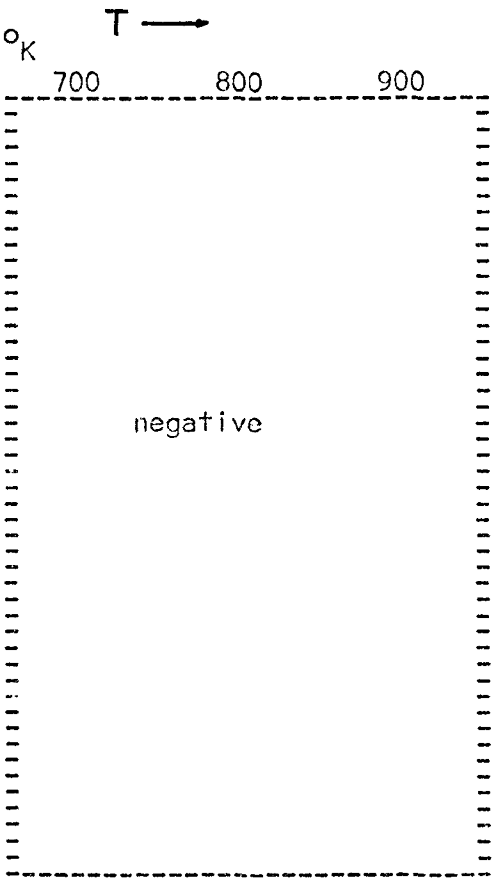


Figure 7.3.5 Sign of dλ/dt

Case 3 $p_1 < p_2$

$p_1 = .8$ $p_2 = 1.2$ in this example

$d\lambda/dt$ is always negative at the final time, since $\partial B/\partial\psi\theta$ is always positive for the regions of optimal policies defined above.

The effect of initial temperature on total time is shown in Figure 7.3.6. The profiles rise exponentially, and the curvature is greater near the end than for the case $p_1 > p_2$. The total operating time, and also the time spent on the upper constraint, increases with decreasing initial temperature. For this case, as little time as possible is spent at higher temperatures, since it is the lower temperatures that benefit the production of B.

The trajectories of the variables λ, ψ and B are shown in Figure 7.3.7. The slightly negative curvature of ψ indicates that activity should be conserved more at lower temperatures (cf. Case 2, where the curvature is slightly positive). B is kept as nearly constant as possible, but the slight decrease with time results from moving to regions of lower concentrations of B (see Figure 7.3.1) (cf. Case 2). The adjoint λ has a characteristically different trajectory.

<u>Region II</u> $(\partial B/\partial k < 0)$

No stationary policy is allowed in this region, since the Hamiltoian corresponds to a concentration which is not attainable in the region $\psi\theta < \theta$.

The results have illustrated the different profiles of the control and the controlled variables, for the three types of activated consecutive first-order reaction. It has been assumed that one example from each type of relative activation energies (p-values) would represent the behaviour of many other pairs of p-values of the same type. This has not been proved,

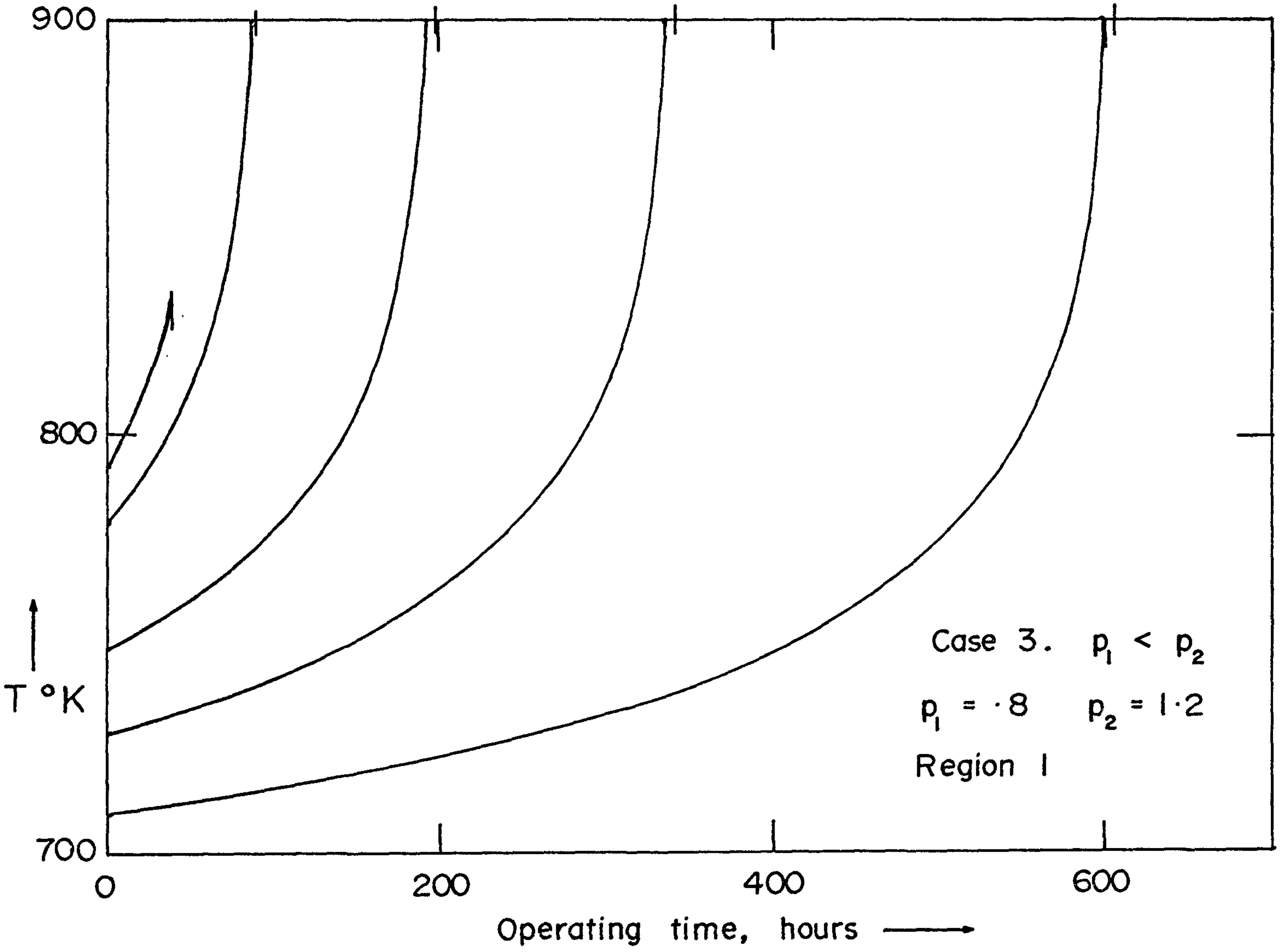


Figure 7.3.6 Effect of initial temperature on total time τ.

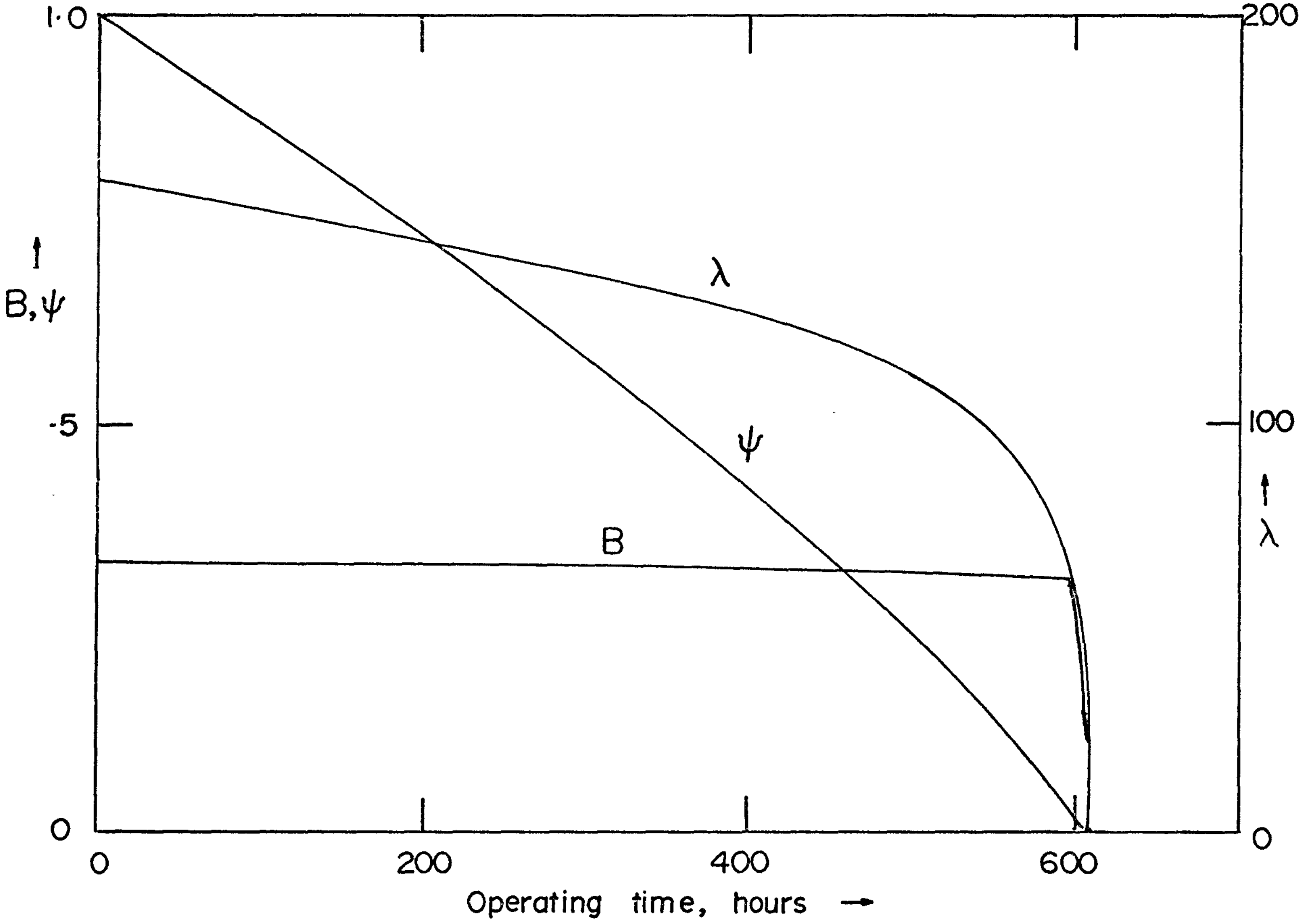


Figure 7.3.7 Variation of the adjoint λ, activity ψ, and concentration B with operating time.

but seems highly probable on physical and mathematical grounds. It would require many more computational experiments to justify this assumption.

The problem of investigating different sub-classes of policies on the basis of the different characteristic trajectories of the adjoint λ (discussed in Section 5.6 as a transformation of all the physical variables into a continuous differential equation) was considered to be beyond the scope of this project. Therefore, only the major differences between the profiles of λ have been emphasized, but the discussions in Sections 5.6 and 7.2.3 could form the starting point of such an investigation.

Chapter VIII gives comparisons between the profiles of more examples of the normal cases described in Chapter VII. The variable flowrate case is discussed, and examples of this are given. A criterion for selecting best optimal policies is established on the basis of practical considerations, and a final comparison of best policies is made.

CHAPTER VIII

COMPARISONS AND SPECIAL CASES

8.1 Comparisons and discussion of the optimal temperature policies

8.1.1 Effect of changing the activation energies of both steps

In Chapter VII, the characteristics of the optimal temperature policies for each case of relative p-values were derived. That is, for each of the cases

Case 1: $p_1 = p_2$ Case 2: $p_1 > p_2$ Case 3: $p_1 < p_2$

one example was chosen and examined for p $O(1)$. A summary of the important results is to be found in the Conclusions. It would be interesting to verify that the behaviour is consistent within each case for p-values greater than and less than those chosen in the previous chapter. For this purpose, the following sets of values have been studied.

	$p_1 = p_2$	$p_1 > p_2$	$p_1 < p_2$
Chapter VII	$p_1=1.$ $p_2=1.$	$p_1=1.2$ $p_2=.8$	$p_1=.8$ $p_2=1.2$
Chapter VIII	$p_1=.95$ $p_2=.95$	$p_1=.8$ $p_2=.5$	$p_1=.5$ $p_2=.8$
	$p_1=1.05$ $p_2=1.05$	$p_1=1.5$ $p_2=1.2$	$p_1=1.2$ $p_2=1.5$

By a study of such diagrams as Figures 7.1.1 - 7.1.3, 7.2.1 - 7.2.6, and 7.3.1 - 7.3.5, it has been verified that the behaviour of B with respect to temperature and effective residence time $\psi\theta$, and also of the derivatives $\partial B/\partial k$ and $\partial B/\partial\psi\theta$, is consistent for all examples chosen within each of the three cases above. Therefore the profile and the type (for example, S, S-C^*)

of optimal temperature policy should be consistent within each type, and this has been found to be true. However, the range of acceptable values of the stationary Hamiltonian H_s (cf. Figure 7.1.3), and also the sign of $d\lambda/dt$, change quite markedly. For this reason, the range of feasible initial temperatures, and the total operating time for a given initial temperature, change in a characteristic way.

Results of comparison tests

The optimal temperature profiles are compared for each case in Figures 8.1.1, 8.1.2, and 8.1.3. As for the cases in Chapter VII, for each set of p-values, the collision factors A_1 and A_2 are chosen such that $B = .75$ at $\psi\theta = .25$ s and $T = 875^{\circ}K$. All examples are for a constant residence time θ of 1 s, as before.

Case 1. $p_1 = p_2 = p$

Figure 8.1.1 shows that for decreasing values of p:

- a given total time of operation requires a lower initial temperature;
- a given initial temperature requires a lower total operating time for finishing on the optimal policy. That is to say, reactions of lower activation energy require lower temperatures for completion of similar temperature policies.

The upper limit on initial temperature decreases with p decreasing.

Case 2. $p_1 > p_2$

Similar results to case 1 were found for Region I; that is, a given total time of operation requires a lower initial temperature for p decreasing, and vice versa for Region II. Figure 8.1.2 shows the effect of changing p_1 and p_2 for initial temperatures in Region I.

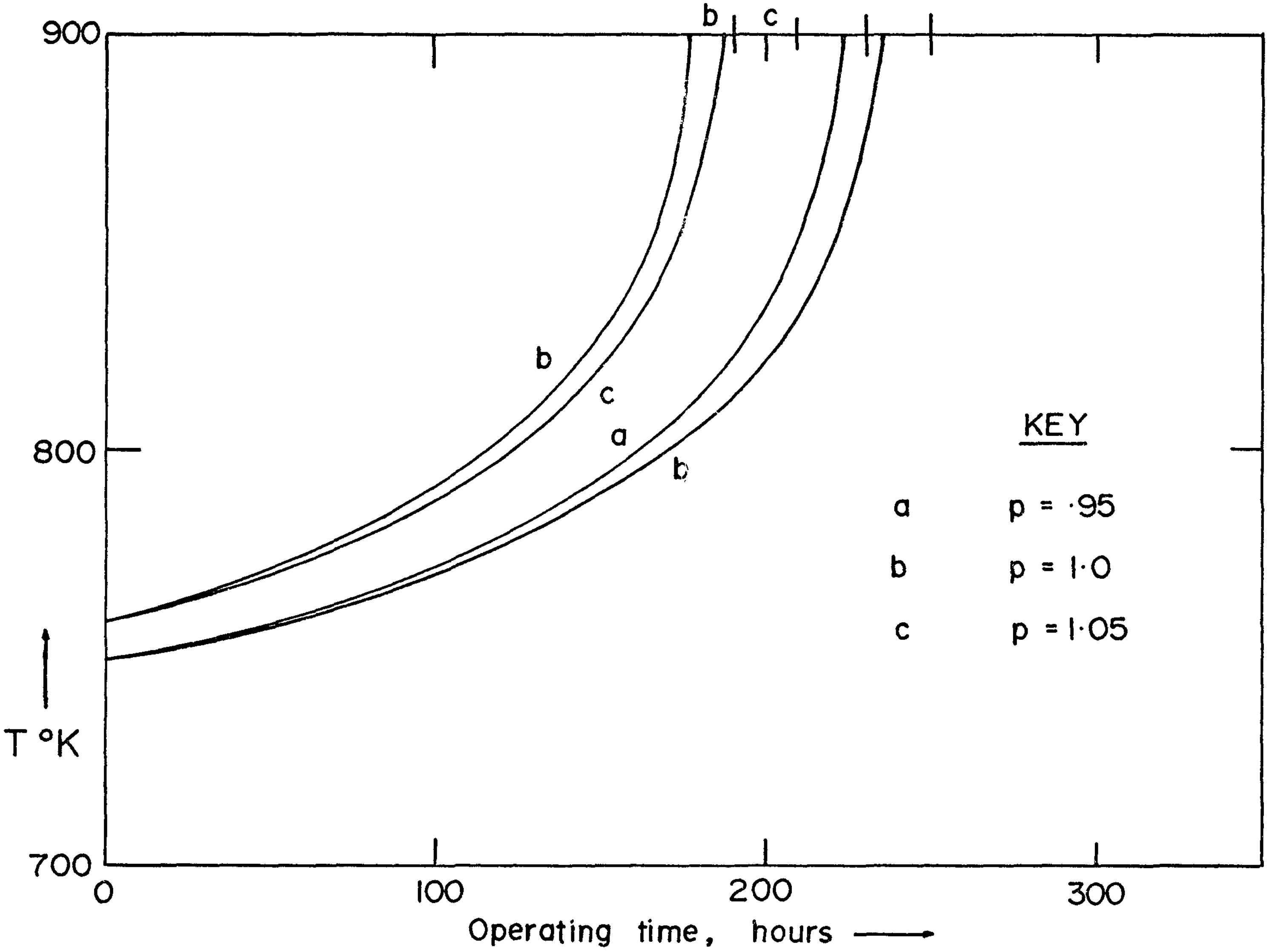


Figure 8.1.1. Effect of different p-values on optimal temperature policies for Case I $p_1 = p_2 = p$.

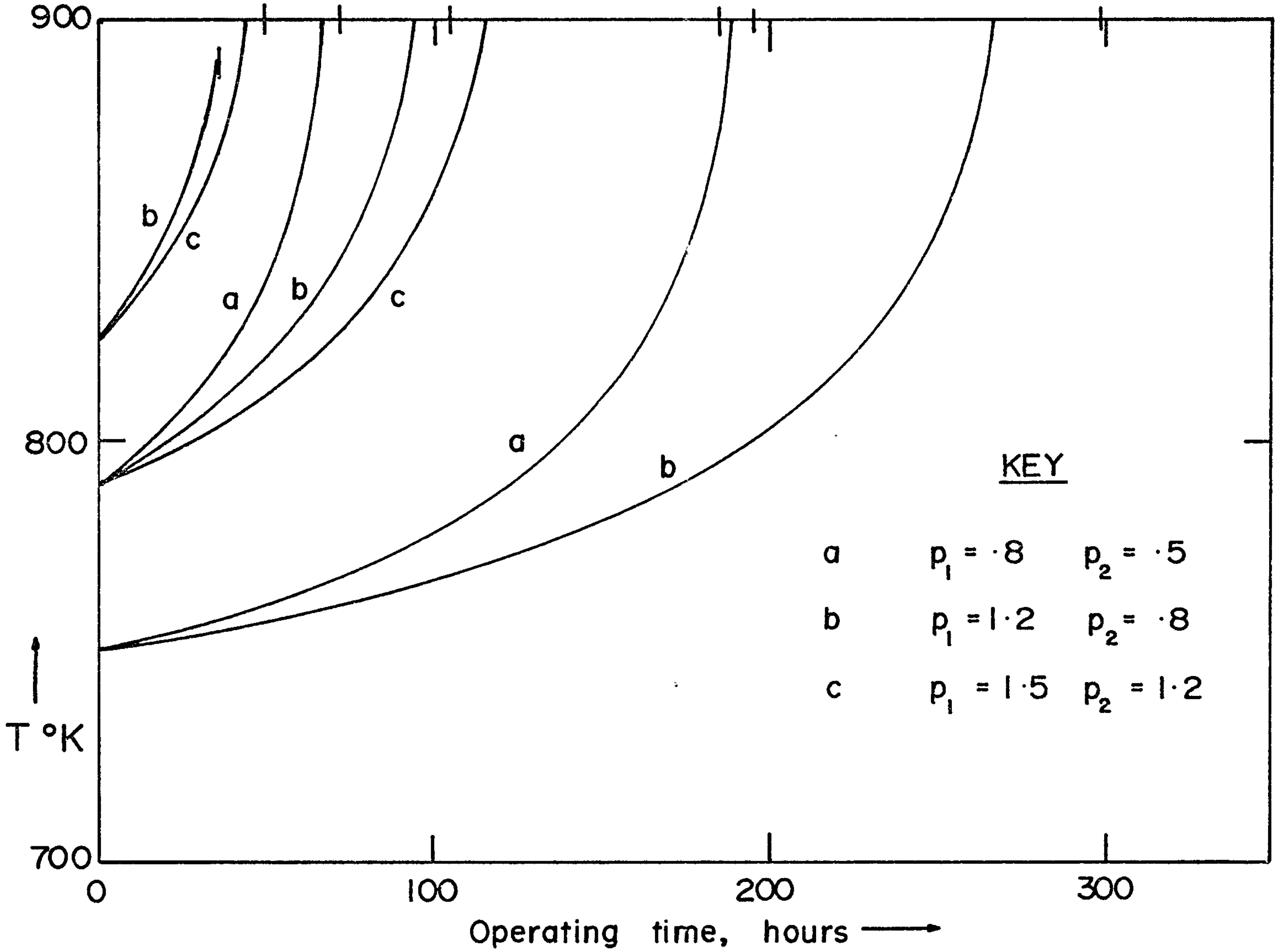


Figure 8.1.2 Effect of different p-values on optimal temperature policies for Case 2 $p_1 > p_2$.

The temperature range for feasible initial temperatures was found to occupy the region of lower temperatures for lower p-values. Thus, no lower limit on initial temperature in the constrained region $700^{\circ}K$-$900^{\circ}K$ was found for Case 2a (see Figure 8.1.2 for the definition of a, b, c). The upper limit was found at $793^{\circ}K$. For Case 2b, the lower and upper limits were $745^{\circ}K$ and $825^{\circ}K$ respectively. The lower limit for Case 2c (highest p-values) was as high as $785^{\circ}K$; the upper limit was at $T_u \approx 835^{\circ}K$.

It was found for Case 2a that below a certain initial temperature in Region I, λ decreased monotonically to zero, instead of passing through a maximum as for Cases 2b and 2c (cf. Figure 7.2.8) (see end of Chapter VII).

Case 3. $p_1 < p_2$

Figure 8.1.3 shows the effect of decreasing or increasing p-values on the optimal temperature policies for this case. Similar results to Cases 1 and 2 are found. That is, a given total time of operation requires a lower initial temperature, for decreasing p-values. The behaviour of the temperature range for feasible initial temperatures is the same as that found for Case 2.

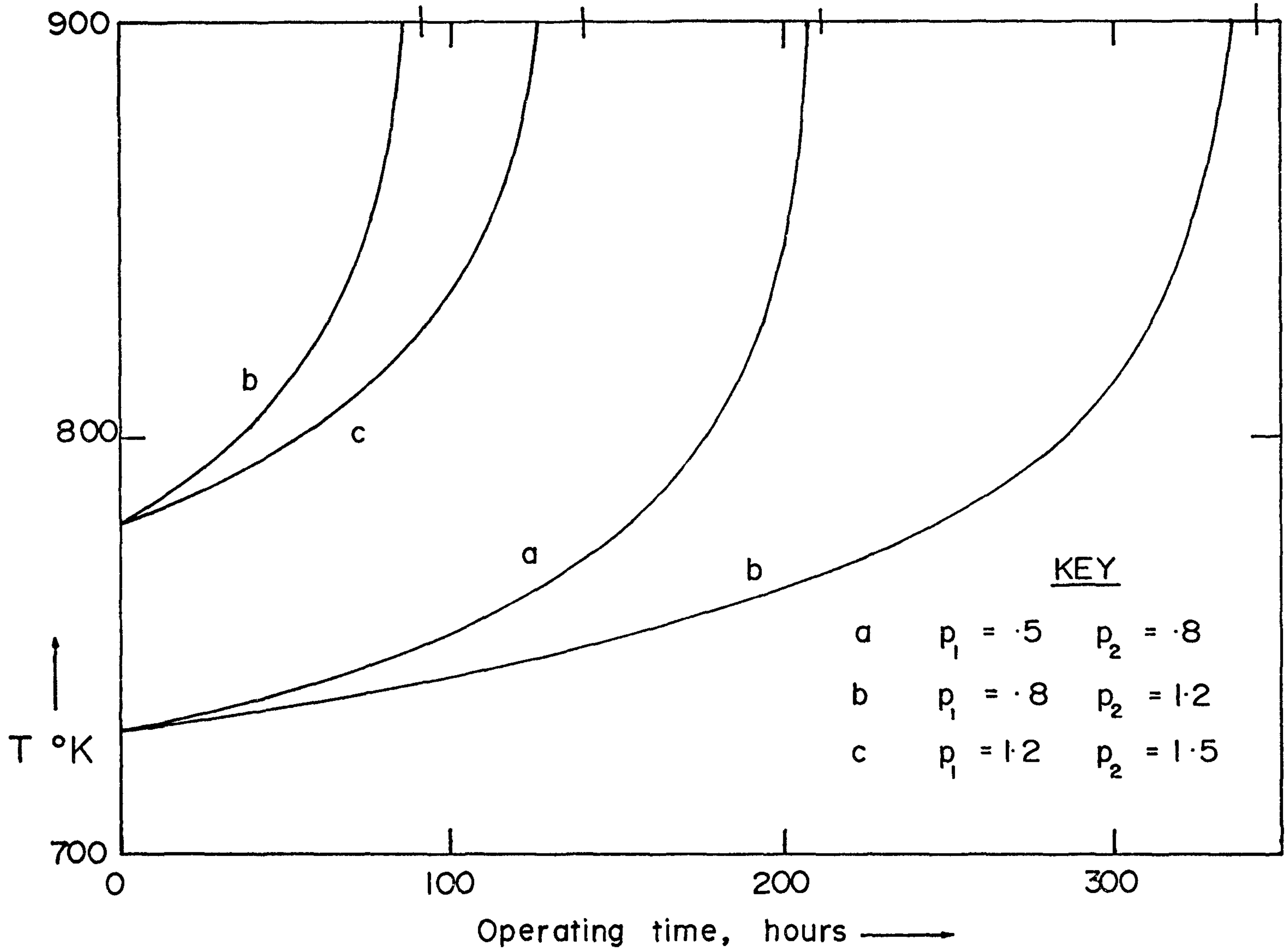


Figure 8.1.3 Effect of different p-values on optimal temperature policies for Case 3 $p_1 < p_2$.

8.1.2 Comparison between the Cases of Chapter VII

The differences in the types of optimal policy for each case arise from the characteristic behaviour of B with temperature and effective residence time. Physical justification can be found for these differences, which could provide an a priori basis for choosing an arbitrary 'best' policy without using the Maximum Principle. Each case will be considered in turn.

Case 1. $p_1 = p_2$

For this case, temperature has no effect on the relative rates of the chemical steps, and this is the reason why the optimal policy is to neither increase nor decrease the initial concentration, but to keep pace with the deactivation of the catalyst.

Case 2. $p_1 > p_2$

In Region I, since higher concentrations are available at higher temperatures, the optimal policy is that the final time should not be reached until full benefit has been obtained from operating at the higher temperatures. This is a justification for not ending on a stationary policy, but to stay away from the 'ridge' until the upper temperature constraint is reached.

The physical justification for operating in Region II, where $\partial B/\partial k$ is negative, is seen by examining Figure 7.2.1. It is equivalent to starting with a reactor that is too long ($\partial B/\partial \psi\theta$ also being negative) and so the activity decreasing (equivalent to shortening the reactor) benefits the production of B. In addition, more is to be gained by raising the temperature, and so moving to regions of higher concentration. A stationary policy is allowed, since ending on the ridge indicates that as much advantage as possible has been obtained from decreased activity.

Case 3. $p_1 < p_2$

Since lower temperatures favour the production of B for this case, the best policy is to remain for as long as possible in the region of lower temperatures. Therefore, the profiles in Region I of Figure 7.3.6 are flat near the beginning of the policy, and rise sharply to the final temperature. A stationary policy is allowed, since less is to be gained by continuing upwards in temperature until an arbitrary upper constraint is reached in the region of lower concentrations.

Operation in Region II is not favoured, for the following reason. Although the policy in this region benefits from shortening the reactor (or decreasing the residence time), it is better for this case to start at as low a temperature as possible, near the region of higher concentrations. These are most accessible in Region I, and along the side of the ridge (in Figure 7.3.1) where $\partial B/\partial k$ is positive.

The justification for expecting rising temperature profiles was provided at the end of Chapter III.

8.2 Variable flowrate case

8.2.1 Application of Pontryagin's Maximum Principle

The facility to vary the flowrate, and hence the residence time θ, may be regarded as a separate control on the system, influencing the exit concentration of B, but not the decay rate of the catalyst. The general Hamiltonian may be written as:

$$H(\lambda,\ k,\ \psi,\ \theta,\ B) = B(k,\ \psi,\ \theta) - \lambda k\psi \qquad (4.2.11)$$

Optimising with respect to temperature requires that

$$\frac{\partial H}{\partial k} = \frac{\partial B}{\partial k} - \lambda\psi = 0 \qquad (5.2.1)$$

Optimising with respect to flowrate (residence time) requires that

$$\frac{\partial H}{\partial \theta} = \frac{\partial B}{\partial \theta} = 0 \qquad (8.2.1)$$

Therefore, optimising with respect to temperature and flowrate requires that on a stationary policy

$$H_s = B - k\frac{\partial B}{\partial k} \qquad (5.2.3)$$

and

$$B = \max_\theta B(k,\psi\theta) \qquad (8.2.2)$$

The second derivatives $\partial^2H/\partial k^2 = \partial^2B/\partial k^2$, and $\partial^2H/\partial\theta^2 = \partial^2B/\partial\theta^2$ must be negative or zero on the stationary policy.

The stationary policy is executed in the following way. At a given initial temperature, for activity $\psi = 1$, the initial residence time θ is chosen such that

$$(\psi\theta)_{opt} = \frac{\ln\left(\frac{K_1}{K_2}\right)}{K_1 - K_2} \qquad (3.3.4)$$

However, since the expression (5.2.3) is a function of k and $\psi\theta$ only, substitution of (3.3.4) causes H_s to be a function of temperature only. Therefore, in order to maintain a constant Hamiltonian, optimising with respect to flow and temperature requires that the temperature be kept constant, and that the residence time θ be increased to compensate for decreased activity, according to the relation:

$$\theta_{opt} = \frac{\text{const.}}{\psi} \tag{8.2.3}$$

where

$$\text{const.} = \frac{\ln\left(\frac{K_1}{K_2}\right)}{K_1 - K_2} \tag{8.2.4}$$

The residence time cannot be increased beyond a certain value θ_u (similarly there is a lower constraint θ_ℓ), at which point the policy is constrained with respect to residence time ($\partial H/\partial\theta \geq 0$). The temperature can be varied, so the policy is still stationary with respect to temperature, unless the policy was initially on a temperature constraint. The policy is free to end on a stationary or a constrained point, as for the constant flowrate cases described in Chapter VII.

8.2.1 Results of variable flowrate policy

Each of the three cases of relative activation energies produce distinctive policies.

Case I. $p_1 = p_2$

The flowrate for which $\partial B/\partial\theta = 0$ coincides with the temperature for which $\partial B/\partial k = 0$ (see Figure 7.1.1). Therefore the optimal flowrate policy follows the same path as the best constant flowrate policy -

that is, along the top of the ridge to the upper temperature constraint (for the best τ). The value of the objective function will be greater, however, because of the initial period at constant temperature, when the flowrate is decreasing.

Case 2. $p_1 > p_2$

The temperatures at which $\partial B/\partial \theta = 0$ lie everywhere in Region I, where $\partial B/\partial k$ is positive, for this case (except at the 'common maximum' temperature, where $K_1 = K_2$; this condition has not been examined). Therefore an optimal flowrate policy can occur in Region I only, and is followed by a temperature policy S-C*.

Examples were taken for the values $p_1 = 1.2$, $p_2 = .8$, and the temperature profiles are plotted in Figure 8.2.1. It must be noted that this is not equivalent to starting on the lower temperature constraint for the constant flowrate case, since $\partial H/\partial k \nless 0$, but $\partial H/\partial k = 0$.

Discussion of the results for Case 2

The time spent on the variable flowrate policy does not monotonically increase or decrease with respect to initial temperature, due to the different rates of isothermal catalyst decay at different initial temperatures. The improvement in yield is illustrated in the next section.

Case 3. $p_1 < p_2$

The temperatures at which $\partial B/\partial \theta = 0$ occur everywhere in Region II, where $\partial B/\partial k$ is negative, and where it is not possible to operate a stationary temperature policy. (A constrained temperature policy could be tried in Region II). Therefore, for a given initial temperature in Region I,

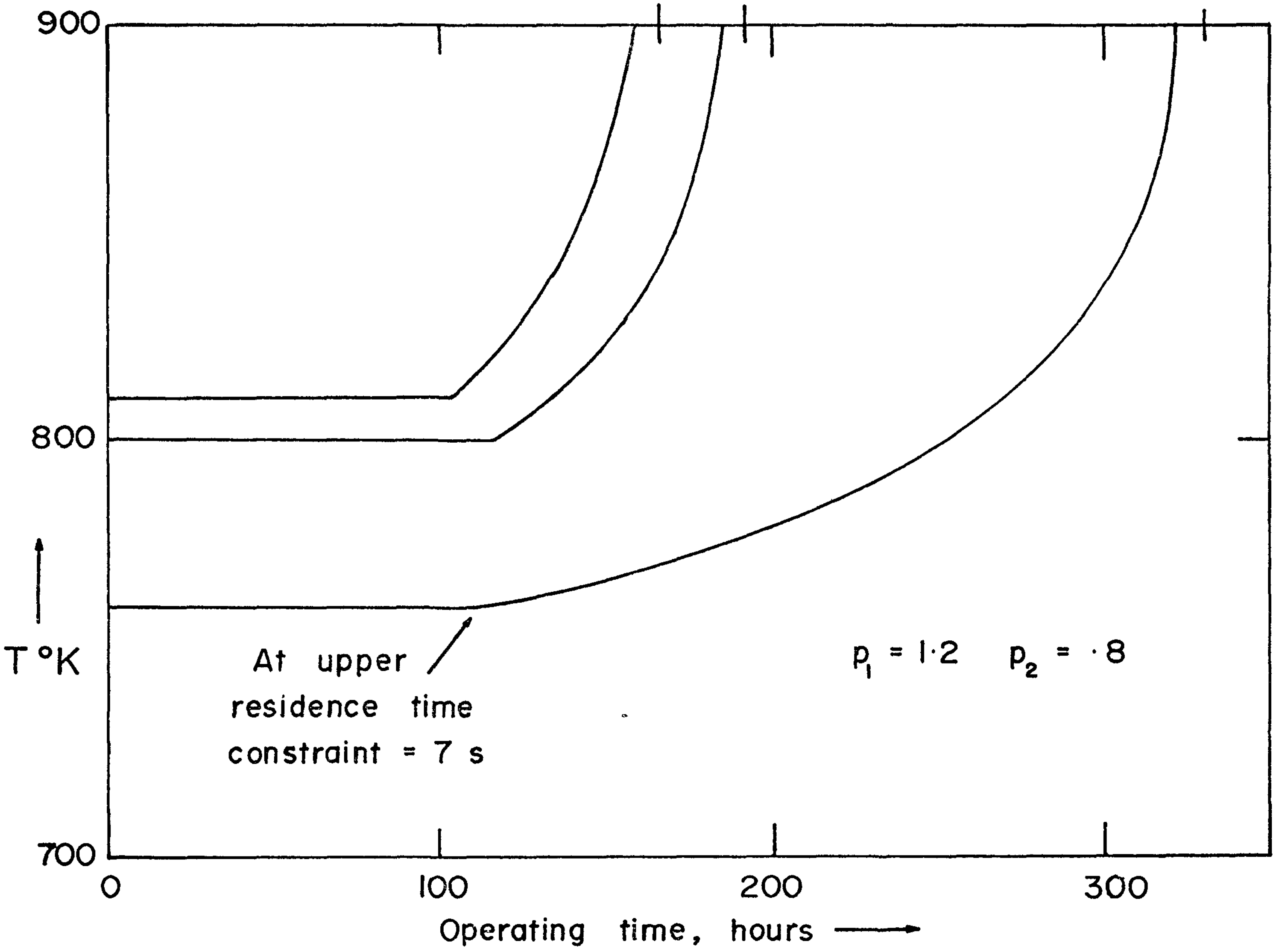


Figure 8.2.1 Variable flowrate and temperature policy for Case 2 $p_1 > p_2$.

where $\partial B/\partial k$ is positive, the best flowrate is chosen to give the maximum value of the objective function, on a temperature policy finishing as either S or $S\text{-}C^*$.

The next section includes a test for comparing the performance of the variable flowrate case with isothermal and constant flowrate temperature policies.

8.3 Performance criterion. A comparison of policies

8.3.1 Definition of a performance criterion

The results of Chapter VII have provided optimal values of the objective function P, where

$$P = \int_0^{\tau} B(k,\psi\theta)dt \qquad (2.7)$$

For practical reasons it is necessary to be able to choose the best optimal policy, and the simplest criterion is the time-averaged concentration

$$\Pi = \frac{P}{\tau + t_r} \qquad (8.3.1)$$

where t_r is the time allowed for removal of the decayed catalyst. A finite value for t_r must be included, since otherwise the best Π would be at $\tau = 0$. The highest value of Π indicates the best optimal policy, and its corresponding initial temperature. The higher is t_r, the higher must be τ for maximum Π. It must be noted that although τ is fixed for solving the optimization problem, for practical reasons the initial temperature is selected to maximize Π on a wholly optimal policy. That is to say, for a fixed total operating time τ, and for fixed t_r, there is one initial temperature that gives a maximum value of Π, and that temperature corresponds to a completed optimal policy, at $t = \tau$, and $\lambda = 0$.

8.3.2 Results using the time-averaged concentration criterion Π

As an example, Case 2 was chosen for obtaining values of Π on policies ending at $t = \tau$ ($\lambda = 0$). The values are presented in Table 8.1 below.

Table 8.1. Values of Π for $p_1 = 1.2$, $p_2 = .8$

Initial temperature, °K	Total operating time, τ hours	Performance criterion $\Pi = P/(\tau + t_r)$. t_r=12hrs.
760	229	.305
765	200	.341
780	135	.448
790	104	.513
800	80	.561
805	71	.575
810	63	.582
812	59	.583
815	55	.582
820	18	.414
823	31	.505
825	35	.527

The maximum in Π occurs at an initial temperature of about 812°K. This corresponds to the best fixed total operating time τ of approximately 60 hours, for $t_r = 12$ hours.

8.3.3 Comparison of optimal policy types using Π

In order to illustrate the improvements in yield by using an optimal temperature policy, the values of Π for various initial temperatures were evaluated for a fixed operating time of 240 hours, and a maintenance time t_r of 12 hours, and plotted for the following three types:

1. Best isothermal (non-optimal) policy.
2. Constant flowrate optimal policy.
3. Variable flowrate optimal policy.

The results are shown in Figure 8.3.1 for Case 2 ($p_1 > p_2$). They show clearly the order of improvement to be expected from operating such optimal policies at the initial temperatures corresponding to the peaks of their respective types in Figure 8.3.1. The improvement is greatest for type 3 and least for type 1. The maximum is more clearly defined for the more complex controlled case V.

The performance of the variable flowrate policy would be more realistically assessed if the exit concentration of B were multiplied by its flowrate F, thus optimizing the amount of B directly. This can be done either a posteriori from these results, or by creating a new objective function M, where

$$M = \int_0^\tau B.F dt = \int_0^\tau B.\frac{\text{const}.V dt}{\theta} \qquad (8.3.2)$$

and where V is the volume of the reactor,and then applying the Maximum Principle again. It would then not be expected that the optimal flow is that which maximizes B.

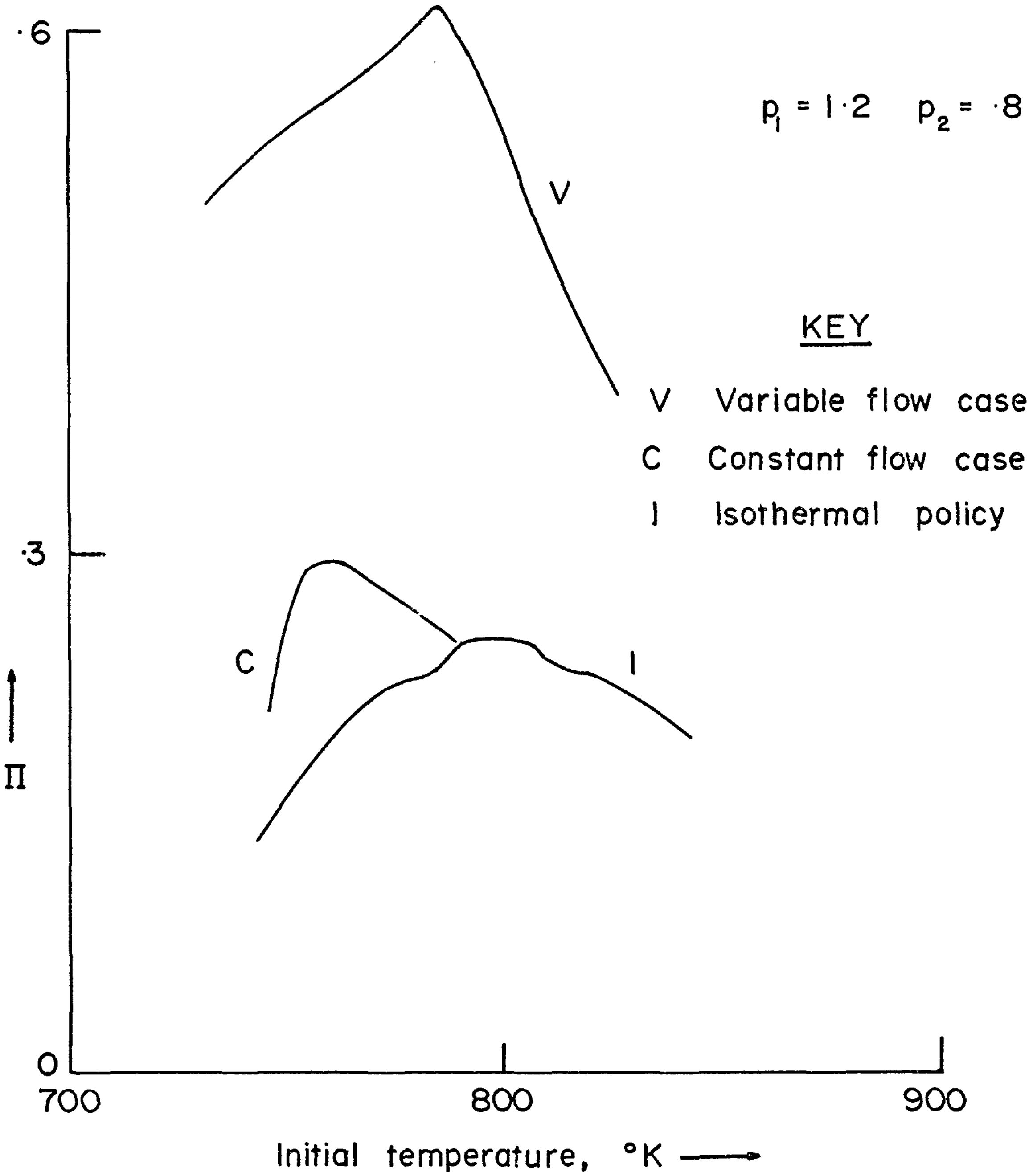


Figure 8.3.1 Comparison of optimal policy types.

CONCLUSIONS

Optimal temperature policies have been found from the application of Pontryagin's Maximum Principle to the consecutive first-order reaction with catalyst decay, for the three cases of relative activation energies:

$$\frac{E_1}{E_2} < 1 \qquad \frac{E_1}{E_2} = 1 \qquad \frac{E_1}{E_2} > 1$$

where subscripts 1 and 2 refer to the first and second chemical steps respectively. The important results are summarised below.

(1) For $p_1 = p_2$, all initially stationary policies end on the upper constraint (S-C^*). The best optimal policy is to maximize B with respect to temperature or to the effective residence time. Changing the temperature has no effect on the relative rates of reaction for this case.

(2) For $p_1 > p_2$, there exists a region of initial temperatures for which stationary policies always end on the upper constraint (S-C^*). There is also a region of higher initial temperatures where all optimal policies are stationary (S).

(3) For $p_1 < p_2$, there is a range of initial temperatures for which subsequent best optimal policies are stationary (S), and also a range for which initially stationary policies end on the upper constraint (S-C^*).

(4) Falling temperature policies were neither predicted nor found.

(5) A means for selecting a best optimal policy is based on the time-averaged value of the objective function.

(6) A variable flowrate optimal policy can be operated for this reaction. The results are better than those of the constant flowrate policies, which are in turn better than the best isothermal policy.

All temperature profiles have an exponential form, and their implementation in practice would not be difficult.

SUMMARY AND FUTURE WORK

Optimal temperature policies have been derived by means of the calculus of variations for the first order consecutive reaction with catalyst decay. The problem has been formulated in the most convenient analytical way, assuming isothermal conditions and constant catalyst activity along a tubular reactor for a residence time that is small compared to the total operating time. For fast-decaying catalysts, reference must be made to the optimization of distributed-parameter systems.

(1) Future work on this reaction scheme could involve an appraisal of the assumptions of identical deactivation rates of both chemical steps, and of the form of the deactivation rate equation.

(2) The region beyond the 'common maximum' of B with respect to temperature and flowrate has not been examined, and it is believed that certain conditions may be reversed there.

(3) A stricter proof or deduction is required for certain analytical results and hypotheses. For example, it must be proved that the maximum of B with respect to temperature moves to lower $\psi\theta$ at higher temperatures for all values of p_1 and p_2; that all optimal policies have rising temperature profiles; and that the characteristic variations of the adjoint λ correspond to sub-classes of optimal policies.

(4) Future work can extend this case to combinations of first- and higher-order reaction steps. A more complex deactivation equation can be tried. The performance criteria should be assessed.

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NOMENCLATURE

A - concentration (mole/mole) of reactant.
A - with subscript 1, 2 or c, Arrhenius frequency factor (s^{-1}).
a - a constant
B - concentration of intermediate B
b - a constant
C - concentration of waste product C
C - with subscript or superscript * : constrained policy
E - Arrhenius activation energy (kcal/mole)
H - Hamiltonian function
K - Arrhenius chemical rate constant (s^{-1})
k - rate constant of catalyst decay (hr^{-1})
P - the objective function
p - ratio of activation energies; $p_1 = E_1/E_c$, $p_2 = E_2/E_c$
S - stationary policy
T - temperature ($^{\circ}K$)
t - system time (hr)
t_r - time for removal of catalyst - reactor shutdown time (hr)
z - space-time in the reactor (s)

Subscripts

c - chemical in f_c; catalyst in A_c, E_c

e - exit

i - inlet

ℓ - lower

s - stationary

u - upper

o - condition at t or z = 0

1 - pertaining to chemical step 1

2 - pertaining to chemical step 2

* - lowest attainable value

Superscripts

m - order of catalyst decay rate

* - highest attainable value

' - transpose

\+ - indicates optimal trajectory

Greek letters

θ - residence time (s) in the reactor

λ - adjoint variable to activity ψ

Π - performance criterion

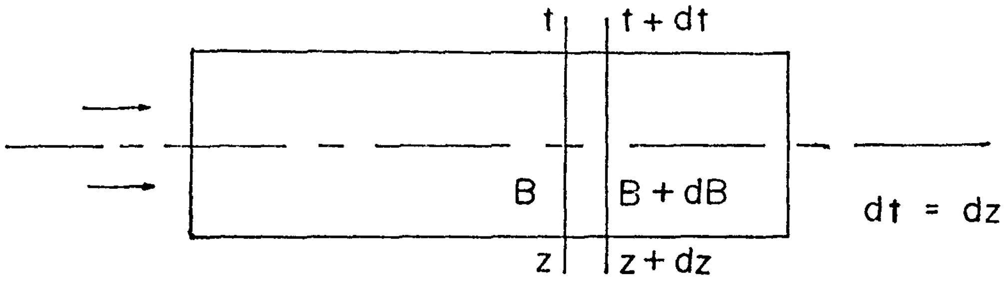
τ - total reaction time (hr)

ψ - catalyst activity

APPENDICES

APPENDIX II

A.2 Derivation of the general rate equation in a tubular reactor



The general mass balance in space time z and system time t is:

Rate of reaction of B = rate of accumulation of B (A.2.1)

The rate of reaction f(ψ, T, A, B) is a function of two sets of variables, defined by: A, B changing in space time, and ψ, T changing with system time. Therefore the rate of accumulation of B is the sum of two terms; the change in B due to a change in space time variables, and the change in B due to a change in system time variables. Hence, from (A.2.1),

$$f(\psi, T, A, B) = \frac{\partial B}{\partial z} + \frac{\partial B}{\partial t} \qquad (A.2.2)$$

Strictly, df/2 should be added to the left hand side, but this is negligible compared to f.

APPENDIX III

A.3.1 Derivation of the exit concentration of B

Equations (3.1.6) and (3.1.7) describe the rate of change of A and B in the tubular reactor bed:

$$\frac{dB}{dz} = \psi[K_1 A - K_2 B] \qquad (3.1.6)$$

$$\frac{dA}{dz} = -K_1 A\psi \qquad (3.1.7)$$

Integrating (3.1.7), with A = 1 at z = 0,

$$A = \exp(-K_1\psi z) \qquad (A.3.1.1)$$

Therefore, on rearranging (3.1.6) above,

$$\frac{dB}{dz} + \psi K_2 B = K_1 \exp(-K_1\psi z).\psi \qquad (A.3.1.2)$$

The general solution of (A.3.1.2) is

$$B = a\exp(-K_2\psi z) + b\exp(-K_1\psi z) \qquad (A.3.1.3)$$

Substitution of (A.3.1.3) into (A.3.1.2) gives

$$b = \frac{K_1}{K_2 - K_1} \qquad (A.3.1.4)$$

The boundary condition B = 0 at z = 0 gives

$$a = \frac{K_1}{K_2 - K_1} \qquad (A.3.1.5)$$

Hence substitution of (A.3.1.4) and (A.3.1.5) into (A.3.1.3) gives the solution:

$$B = \frac{K_1}{K_2 - K_1}[\exp(-K_1\psi\theta) - \exp(-K_2\psi\theta)] \qquad (3.1.8)$$

A.3.2 Defining the shape of the curve of B vs. T

The following steps show that B → 0 as T → 0 and T → ∞.

B is given by

$$B = \frac{K_1}{K_2 - K_1}[\exp(-K_1\psi\theta) - \exp(-K_2\psi\theta)] \qquad (3.1.8)$$

This equation is indeterminate for T → 0.

Now

$$\lim_{T\to 0}\ [\exp(-K_1\psi\theta) - \exp(-K_2\psi\theta)] = 0$$

and

$$\lim_{T\to 0}\ \frac{K_1}{K_2 - K_1} = \lim_{T\to 0}\ \frac{1}{\mathrm{const.}k^{p_2-p_1} - 1} = \begin{array}{ccc} -1 & \text{if} & p_2 > p_1 \\ \text{const.} & \text{if} & p_2 = p_1 \\ 0 & \text{if} & p_2 < p_1 \end{array}$$

Therefore

$$\lim_{T\to 0} = 0 \qquad (A.3.2.1)$$

It can be proved by repeated use of L'Hôpital's Rule that $\partial B/\partial k \to 0$ as T → 0, hence B is asymptotic to zero.

$$\frac{\partial B}{\partial k} = [\exp(-K_1\psi\theta) - \exp(-K_2\psi\theta)]\frac{K_1K_2(p_1 - p_2)}{k(K_2 - K_1)^2}$$
$$+ \frac{K_1\psi\theta}{(K_2 - K_1)k}[p_2K_2\exp(-K_2\psi\theta) - p_1K_1\exp(-K_1\psi\theta)]$$

Similarly, the limits of B (using (3.1.8)) and $\partial B/\partial k$ as T → ∞ are zero.

Therefore the two asymptotes at T = 0 and T = ∞ must include at least one maximum, and hence two inflexion points. Only one maximum is seen to be possible, on physical grounds, by making a similar examination of relative rates as in Section 3.3.

A.3.3 Defining the shape of the curve of B vs. $\psi\theta$

B and $\partial B/\partial\psi\theta$ tend to zero directly as $\psi\theta \to 0$ and as $\psi\theta \to \infty$. The proof that one maximum only occurs is deduced physically from the behaviour of relative rates in Section 3.3. Therefore the shape of the curve is similar to that shown in Diagram 3.1.

A.3.4 Derivation of the optimal flowrate

Now

$$B = \frac{K_1}{K_2 - K_1}\left[\exp(-K_1\psi\theta) - \exp(-K_2\psi\theta)\right] \qquad (3.1.8)$$

Therefore

$$\frac{\partial B}{\partial\psi\theta} = \frac{K_1}{K_2 - K_1}\left[K_2\exp(-K_2\psi\theta) - K_1\exp(-K_1\psi\theta)\right] \qquad (A.3.4.1)$$

At the optimal flowrate, $\partial B/\partial\psi\theta = 0$, so

$$K_2\exp(-K_2\psi\theta) = K_1\exp(-K_1\psi\theta) \qquad (A.3.4.2)$$

Therefore $$(\psi\theta)_{opt} = \frac{\ln\left(\frac{K_1}{K_2}\right)}{K_1 - K_2} \qquad (3.3.4)$$

A.3.5 Derivation of the common maximum of B

The maximum of B with respect to temperature is obtained by solving (3.2.5) for the maximal temperature:

$$\frac{\exp(-K_2\psi\theta) - \exp(-K_1\psi\theta)}{p_2K_2\exp(-K_2\psi\theta) - p_1K_1\exp(-K_1\psi\theta)} = \frac{\psi\theta(K_2 - K_1)}{K_2(p_1 - p_2)} \tag{3.2.5}$$

If this point coincides with the maximum with respect to flowrate, then (3.3.4) must also be satisfied:

$$(\psi\theta)_{opt} = \frac{\ln\left(\frac{K_1}{K_2}\right)}{K_1 - K_2} \tag{3.3.4}$$

Substitution of (3.3.4) into (3.2.5) shows that only the relation

$$K_1 = K_2 \tag{A.3.5.1}$$

satisfies the resulting equation.

APPENDIX IV

A.4.1 Examination of the time derivative of the Hamiltonian

In general,

$$H = H(\psi,\ k,\ \lambda,\ t) = B(\psi,\ k,\ B_o(t)) - \lambda k \psi \qquad (4.2.7)$$

Therefore

$$\frac{dH}{dt} = \frac{\partial H}{\partial \psi}\cdot\frac{d\psi}{dt} + \frac{\partial H}{\partial \lambda}\cdot\frac{d\lambda}{dt} + \frac{\partial H}{\partial k}\cdot\frac{dk}{dt} + \frac{\partial H}{\partial B_o}\cdot\frac{dB_o}{dt} \qquad (A.4.3.1)$$

From (4.2.7)

$$\frac{\partial H}{\partial \psi} = -\lambda k \qquad (A.4.3.2)$$

$$\frac{\partial H}{\partial \lambda} = -k\psi \qquad (A.4.3.3)$$

It can be shown from (A.4.3.1), (A.4.3.2), (4.2.5) and (3.1.2) that

$$\frac{\partial H}{\partial \psi}\cdot\frac{d\psi}{dt} + \frac{\partial H}{\partial \lambda}\cdot\frac{d\lambda}{dt} = 0 \qquad (A.4.3.4)$$

So, for constant or zero input of B,

$$\frac{dH}{dt} = \frac{\partial H}{\partial k}\cdot\frac{dk}{dt} \qquad (A.4.3.5)$$

Therefore dH/dt is zero for either a stationary policy ($\partial H/\partial k = 0$) or a constrained policy ($dk/dt = 0$).

APPENDIX V

A.5.1 Analytical expression for the optimal temperature policy

Now

$$H_s = B - k\frac{\partial B}{\partial k} = H_s(k,\psi) = \text{a constant} \qquad (5.2.3)$$

Therefore

$$\frac{dH_s}{dt} = \frac{\partial H_s}{\partial k}\cdot\frac{dk}{dt} + \frac{\partial H_s}{\partial \psi}\cdot\frac{d\psi}{dt} \qquad (A.5.1.1)$$

So from (5.2.3)

$$\frac{dH_s}{dt} = \frac{dk}{dt}\left(\frac{\partial B}{\partial k} - k\frac{\partial^2 B}{\partial k^2} - \frac{\partial B}{\partial k}\right) + \frac{d\psi}{dt}\left(\frac{\partial B}{\partial \psi} - k\frac{\partial}{\partial \psi}\left(\frac{\partial B}{\partial k}\right)\right) = 0 \qquad (A.5.1.2)$$

Hence the result (5.2.7) on substitution of (3.1.2):

$$\frac{dk}{dt} = \psi\left(k\frac{\partial}{\partial \psi}\left(\frac{\partial B}{\partial k}\right) - \frac{\partial B}{\partial \psi}\right)\Big/\frac{\partial^2 B}{\partial k^2} \qquad (5.2.7)$$

The analytical expression for dk/dt in terms of k and $\psi\theta$ is too complex to solve. However, equation (5.2.7) above can be interpreted in terms of the geometry of plots of B with respect to temperature and effective residence time, and can be evaluated at any point.

APPENDIX VII

A.7.1 Proof that H_s is a function only of $k^p\psi$ for $p_1 = p_2$

Analytical derivation of the optimal temperature policy

The stationary Hamiltonian, H_s, is given by:

$$H_s = B - k\frac{\partial B}{\partial k} \qquad (5.2.3)$$

Therefore

$$H_s = \frac{K_1}{K_2 - K_1}[\exp(-K_1\psi\theta) - \exp(-K_2\psi\theta)][1 - \frac{K_2(p_1 - p_2)}{K_2 - K_1}] - \frac{K_1\psi\theta}{K_2 - K_1}[p_2K_2\exp(-K_2\psi\theta) - p_1K_1\exp(-K_1\psi\theta)] \qquad (A.7.1.1)$$

Setting $p_1 = p_2 = p$ gives

$$H_s = \frac{K_1}{K_2 - K_1}[\exp(-K_1\psi\theta) - \exp(-K_2\psi\theta)] - \frac{K_1\psi\theta p}{K_2 - K_1}[K_2\exp(-K_2\psi\theta) - K_1\exp(-K_1\psi\theta)] \qquad (A.7.1.2)$$

Also $K_1 = \frac{A_1}{A_c^p}k^p$, $K_2 = \frac{A_2}{A_c^p}k^p$ for $p_1 = p_2$.

Hence the result (7.1.2)

****

On a stationary policy, the Hamiltonian is constant with time.

Therefore

$$\frac{dH_s}{dt} = 0 \qquad (A.7.1.3)$$

The result (5.2.7) was obtained from (A.7.1.3):

$$\frac{dk}{dt} = \psi\left(k\frac{\partial}{\partial\psi}\left(\frac{\partial B}{\partial k}\right) - \frac{\partial B}{\partial\psi}\right)/\frac{\partial^2 B}{\partial k^2} \qquad (5.2.7)$$

Setting $p_1 = p_2$ gives directly

$$\frac{dk}{dt} = \frac{k^2}{p} \quad \text{(A.7.1.4)}$$

Hence the result (7.1.6), using the boundary condition $k = k_o$ at $t = 0$.

A.7.2 Analytical derivation of the optimal temperature policy for $p_1 = p_2$, from result (7.1.3)

Now $k^p\psi$ = a constant (7.1.3)

Taking the time derivatives of the variables in (7.1.3):

$$pk^{p-1}.\psi\frac{dk}{dt} - k^{p+1}.\psi = 0 \quad \text{(A.7.3.1)}$$

Therefore, substituting (3.1.2),

$$pk^{p-1}.\psi\frac{dk}{dt} - k^{p+1}.\psi = 0 \quad \text{(A.7.3.2)}$$

Therefore

$$\frac{dk}{dt} = \frac{k^2}{p} \quad \text{(A.7.3.3)}$$

If $k = k_o$ at $t = 0$, the solution of (A.7.3.3) is:

$$\frac{1}{k_o} - \frac{1}{k} = \frac{t}{p} \quad \text{(A.7.3.4)}$$

A.7.3 Examination of $d\lambda/dt$ for $p_1 = p_2$ on a stationary policy

The adjoint equation is

$$\frac{d\lambda}{dt} = -\frac{\partial B}{\partial \psi} + \lambda k \qquad (4.2.5)$$

On a stationary policy, for $p_1 = p_2$, from (4.2.5):

$$\frac{d\lambda}{dt} = \frac{K_1\theta}{K_2 - K_1}[K_1\exp(-K_1\psi\theta) - K_2\exp(-K_2\psi\theta)] +$$

$$\frac{k}{\psi}.\frac{K_1\psi\theta p}{k(K_2 - K_1)}[K_2\exp(-K_2\psi\theta) - K_1\exp(-K_1\psi\theta)] \qquad (A.7.2.1)$$

Therefore

$$\frac{d\lambda}{dt} = (p - 1).\frac{\partial B}{\partial \psi} \qquad (A.7.2.2)$$

Hence the results in Section 7.1.

COMPUTER PROGRAM LISTING

```
HPCC                                                          ALEXANDER P.
RUN(S)
SETINDF.
REDUCE.
LGO.
'        6400 END OF RECORD
      PROGRAM TST (INPUT,OUTPUT,TAPE5=INPUT,TAPE6=OUTPUT)
C
C   THIS PROGRAM COMPUTES OPTIMAL POLICIES FOR CONSTANT AND VARIABLE
C   FLOWRATE CASES, AND ALSO ISOTHERMAL POLICIES
C
C   SYMBOL MEANINGS FOR INPUT
C
*   AA,BB,AC   ARRHENIUS FREQUENCY FACTORS
*   ECR   ARRHENIUS TEMPERATURE COEFFICIENT EC/R
*   P1,P2   ACTIVATION ENERGY RATIOS
*   TCU,TCL   UPPER, LOWER TEMPERATURE CONSTRAINTS
*   DELTS   SYSTEM TIME INTEGRATION STEP LENGTH
*   THETA   RESIDENCE TIME, SECONDS
*   THETAU,THETAL   UPPER, LOWER RESIDENCE TIME CONSTRAINTS
*   IVFL,ISO,ITOT   ARE EXPLAINED BELOW
*   TEMP   INITIAL TEMPERATURE
C
C
      DIMENSION TITLE(13)
      H(PSI)=AK1*(EK1-EK2)*(1.-AK2*PD/AKA)/AKA-AK1*PSTH*(P2*AK2*EK2-P1*
     1AK1*EK1)/AKA
      READ(5,42) TITLE
      WRITE(6,43) TITLE
      READ(5,1) AA,BB
      READ(5,1) AC,ECR
      READ(5,1) P1,P2 $ PD=P1-P2
      READ(5,1) TCU,TCL
      READ(5,1) DELTS
      READ(5,1) THETA
      READ(5,1) THETAU,THETAL
      READ(5,31) IVFL
      READ(5,31) ISO
      READ(5,31) ITOT
      WRITE(6,31) IVFL,ISO ITOT
      IF(ISO.EQ.1)WRITE(6,38)
      IF(ITOT.EQ.1)WRITE(6,48)
      DO 26 N=1,6
      READ(5,1) TEMP
```

```
C
C    SET UP INITIAL VALUES
       MUTEST=0 $ KPRNT=0
       SBDT=SBDTS=0.
       KC=35
       TI=TEMP
       TIME=0. $ PSI=1. $ PSTH=THETA
       DELT=DELTS
C    CATALYST FREQUENCY FACTOR IN UNIT HR.-1
C    REACTION FREQUENCY FACTOR IN UNIT S-1
       WRITE(6,40)
C
C    EVALUATE INITIAL RATE CONSTANTS
       AK=AC*EXP(-ECR/TEMP)
       AK1=AA*EXP(-P1*ECR/TEMP) $ AK2=BB*EXP(-P2*ECR/TEMP) $ AKA=AK2-AK1
C
C    IF IVFL = 1, OPERATE VARIABLE FLOWRATE CASE (UP TO STATEMENT 32)
       IF(IVFL.LT.1) GO TO 32
       WRITE(6,47)
       THETA=ALOG(AK2/AK1)/AKA
       IF(THETA.GT.THETAU)GOTO33
       IF(THETA.LT.THETAL)GOTO35
C    ISOTHERMAL DECAY FOR OPTIMAL VARIABLE FLOW CONTROL
       PSI=THETA/THETAU
       TIME=-ALOG(PSI)/AK
       WRITE(6,37) TIME
       SBDT=TIME*(AK1/AK2)**(AK2/(AK2-AK1))
       THETA=THETAU
       GO TO 32
    33 WRITE(6,34)
       THETA=THETAU
       GO TO 32
    35 WRITE(6,36)
       THETA=THETAL
    32 CONTINUE
       PSTH=PSI*THETA
       EK1=EXP(-AK1*PSTH) $ EK2=EXP(-AK2*PSTH) $ EKA=EK1-EK2
C
C    EVALUATE INITIAL HAMILTONIAN
       HS=H(PSI)
       AMU1=(AK1*EKA/AKA-HS)/AK
       IF(HS.LT.0.)GOTO2
       IF(AMU1.LT.0.)GOTO5
C    TIME UNIT FOR CATALYST DECAY IS HR.
C
    22 CONTINUE
C    ISOTHERMAL POLICY IS EXECUTED IF ISO = 1
       IF(ISO.EQ.1)GOTO24
       TIME=TIME+DELT
       PSIS=PSI
       PSI=PSIS*EXP(-AK*DELT) $ PSTH=PSI*THETA
C
```

```
C   GUESS NEXT TEMPERATURE
      EK1=EXP(-AK1*PSTH) $ EK2=EXP(-AK2*PSTH)
      DELHS=HS-H(PSI)
      STEP=.3
   11 CONTINUE
C   TEST BINARY SEARCH PROCEDURE
      IF(ABS(DELHS).LT..00010)GOTO12
      TEMP=TEMP+STEP
      AK1=AA*EXP(-P1*ECR/TEMP) $ AK2=BB*EXP(-P2*ECR/TEMP)$AKA=AK2-AK1
      EK1=EXP(-AK1*PSTH) $ EK2=EXP(-AK2*PSTH)
      DELHS1=HS-H(PSI)
      IF(ABS(DELHS1).LT.ABS(DELHS))GOTO10
      TEMP=TEMP-STEP
      STEP=-STEP*.3
      GO TO 11
   10 DELHS=DELHS1
      GO TO 11
   12 CONTINUE
      AK=AC*EXP(-ECR/TEMP)
C
C    INTEGRATE B.DT
      SBDTS=SBDT
      EKA=EK1-EK2
      CBE=AK1*EKA/AKA
      ABDT=CBE*DELT+SBDTS
C
C   HAS TEMPERATURE REACHED EITHER CONSTRAINT
      IF(TEMP.GE.TCU)GOTO13
      IF(TEMP.LE.TCL)GOTO14
C
C   HAS POLICY REACHED FINAL TIME YET
      HNEW=HS-DELHS
      AMU=(CBE-HNEW)/(AK*PSI)
      IF(MUTEST.EQ.1)AMU=-AMU
      IF(ITOT.EQ.1)GOTO39
      IF(AMU.LE..0)GOTO15
      GO TO 44
   39 CONTINUE
      IF(TIME.GE.240.)GOTO15
      IF(AMU.LE..0)ISO=1
   44 CONTINUE
      IF(MUTEST.EQ.1)AMU=-AMU
C
C
C    PRINTING CONTROL
      KPRNT=KPRNT+1
      IF(KPRNT.EQ.1)GOTO27
      IF(KPRNT.LE.KC)GOTO9
      KPRNT=0
   27 CONTINUE
C
```

```
C     TEST SECOND DERIVATIVE
      D2HDK2=AK1*PSTH*(2.*AK2*PD-AKA)*(P2*AK2*EK2-P1*AK1*EK1)/(AK*AKA)**
     12+AK1*AK2*PD*((AK2+AK1)*PD-AKA)*EKA/(AK*AK*AKA**3)+AK1*PSTH*(P2*P2
     2*AK2*(1.-AK2*PSTH)*EK2-P1*P1*AK1*(1.-AK1*PSTH)*EK1)/(AK*AK*AKA)
      IF(D2HDK2.GE.0.)GOTO18
      DCBEDK=(CBE-HNEW)/AK
C
C     EVALUATE FIRST DERIVATIVE
      DHDK=DCBEDK-AMU*PSI
      DCBDPSI=AK1*THETA*(AK2*EK2-AK1*EK1)/AKA
      DMUDT=-DCBEDPSI+AMU*AK
      WRITE(6,23)TIME,TEMP,HNEW,AMU,CBE,PSI,D2HDK2,AK,DCBEDK,AK1,AK2,DCB
     1DPSI,DMUDT,DHDK,SBDT
    9 CONTINUE
      IF(ABS((PSI-PSIS)/PSI).GT..010)DELT=DELT/2.
      IF(ABS((PSI-PSIS)/PSI).LT..005)DELT=DELT*2.
      GO TO 22
   13 WRITE(6,20) $ GO TO 16
   14 WRITE(6,21)
   16 CONTINUE
      WRITE(6,29) TIME
C
C     CONSTRAINED POLICY
C
   24 CONTINUE
      HNEW=HS
      TIME=TIME+DELT
      PSIS=PSI
      PSI=PSIS*EXP(-AK*DELT) $ PSTH=PSI*THETA
C
C     INTEGRATE B.DT
      EK1=EXP(-AK1*PSTH) $ EK2=EXP(-AK2*PSTH) $ EKA=EK1-EK2
      CBE=AK1*EKA/AKA
      SBDTS=SBDT
      SBDT=CBE*DELT+SBDTS
      IF(ABS((PSI-PSIS)/PSI).GT..010)DELT=DELT/2.
      IF(ABS((PSI-PSIS)/PSI).LT..005)DELT=DELT*2.
      AMU=(CBE-HNEW)/(AK*PSI)
C
C     IF ITOT = 1, POLICIES ARE RUN TO A FIXED TOTAL TIME OF 240 HR.
      IF(ITOT.EQ.1)GOTO45
      IF(MUTEST.EQ.1)AMU=-AMU
      IF(AMU.LE..0)GOTO15
      IF(CBE.LT..001)GOTO15
      IF(MUTEST.EQ.1)AMU=-AMU
      GO TO 46
   45 IF(TIME.GE.240.)GOTO15
   46 CONTINUE
C
C     PRINTING CONTROL
```

```
      KPRNT=KPRNT+1
      IF(KPRNT.EQ.1)GOTO28
      IF(KPRNT.LE.KC)GOTO8
      KPRNT=0
   28 CONTINUE
      DCBDPSI=AK1*THETA*(AK2*EK2-AK1*EK1)/AKA
      DMUDT=-DCBDPSI+AMU*AK
C
C     IS POLICY STILL ON THE CONSTRAINT
      DHDK=AK1*AK2*PD*EKA/(AK*AKA**2)+AK1*PSTH*(P2*AK2*EK2-P1*AK1*EK1)/
     1(AK*AKA)-AMU*PSI
      DCBEDK=AK1*(EK1*(AK2*PD/AKA-P1*AK1*PSTH)+AK2*EK2*(P2*PSTH-PD/AKA))
     1/(AK*AKA)
      WRITE(6,23)TIME,TEMP,HNEW,AMU,CBE,PSI,D2HDK2,AK,DCBEDK,AK1,AK2,DCB
     1DPSI,DMUDT,DHDK,SBDT
    8 CONTINUE
      GO TO 24
    2 WRITE(6,3)
      GO TO 24
    5 WRITE(6,6)
      MUTEST=1
      GO TO 22
   15 WRITE(6,17)
      GO TO 4
   18 WRITE(6,19)
    4 CONTINUE
      SBDT=SBDT/(TIME+12.)
      WRITE(6,30) TIME,SBDT
      WRITE(6,7) ECR,AC,P1,P2,AA,BB,T1
      WRITE(6,25)
   26 CONTINUE
      STOP
    1 FORMAT(5F15.5)
    3 FORMAT(2X,*INITIAL TEMPERATURE IS BELOW LOWER LIMIT*)
    6 FORMAT(2X,*INITIAL TEMPERATURE IS ABOVE UPPER LIMIT*)
    7 FORMAT(//,5X,*EC/R=*,F10.3,//,5X,*CATALYST FREQUENCY FACTOR=*,
     1F15.3,//,5X,*ACTIVATION ENERGY FACTORS ARE P1=*,F4.1,2X,*P2=*,F4.1
     2//,5X,*REACTANT FREQUENCY FACTORS ARE AA =*,F14.1,3X,*BB=*,F14.1,
     3//,*     INITIAL TEMPERATURE WAS *,F5.1)
   17 FORMAT(2X,*POLICY HAS REACHED FINAL TIME*)
   19 FORMAT(2X,*SECOND DERIVATIVE IS POSITIVE. NO LONGER ON OPTIMAL POL
     1ICY*)
   20 FORMAT(2X,*TEMPERATURE IS AT UPPER CONSTRAINT*)
   21 FORMAT(2X,*TEMPERATURE IS AT LOWER CONSTRAINT*)
   23 FORMAT(1X,F6.2,F6.1,F7.5,E9.2,2F5.3,E1o.2,F6.4,E9.2,2F6.3,4E9.2)
   25 FORMAT(/,2X,*---------- NEXT RUN ----------*)
   29 FORMAT(2X,*TOTAL TIME ON STATIONARY POLICY = *,F7.1,* HR.*)
   30 FORMAT(2X,*TOTAL TIME WAS *,F7.1,/,2X,*AVERAGE CONCENTRATION = *,
     1F6.3)
   31 FORMAT(5I5)
```

```
   34 FORMAT(2X,*OPTIMAL FLOW LESS THAN MINIMUM CONSTRAINT*)
   36 FORMAT(2X,*OPTIMAL FLOW GREATER THAN MAXIMUM CONSTRAINT*)
   37 FORMAT(2X,*TIME ON VARIABLE FLOWRATE POLICY =*,F6.1)
   38 FORMAT(2X,*ISOTHERMAL POLICY*)
   40 FORMAT(2X,* TIME TEMP    HAMN    AMU      CBE  PSI  D2HDK2      AK    D
     1CBEDK    AK1     AK2  DCBDPSI  DMUDT      DHDK       SBDT*,/)
   41 FORMAT(1H1)
   42 FORMAT(13A6)
   43 FORMAT(/,20A6,/)
   47 FORMAT(2X,*VARIABLE FLOWRATE OPTIMAL POLICY*)
   48 FORMAT(2X,*FIXED TOTAL TIME OF 240 HRS.*)
      END
'        6400 END OF RECORD
   CASE B.     P1=1.2     P2=.8
8300600082.4   1039408.1
2000000.       15000.
1.2            .8
900.           700.
.25
1.
7.             .3
0
0
0
780.
790.
812.
820.
823.
825.
'              END OF FILE
```