COMPUTATIONAL STUDY OF THE OPTIMIZATION OF A CATALYTIC REACTOR FOR A REVERSIBLE REACTION WITH CATALYST DECAY

DEDICATION

To my wife, Michelle

COMPUTATIONAL STUDY OF THE OPTIMIZATION OF A CATALYTIC REACTOR FOR A REVERSIBLE REACTION WITH CATALYST DECAY

BY

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MASTER OF ENGINEERING (1969) McMASTER UNIVERSITY
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SCOPE AND CONTENTS

The optimal temperature policy with time is sought which maximizes the total amount of reaction in a fixed time in a tubular reactor with uniform temperature and decaying catalyst for a single reversible reaction.

A numerical procedure together with theoretical developments is used to solve this problem for two kinetic models. The problem is treated in the format of Pontryagin's Maximum Principle.

Computer listings are given in the Appendix for the following cases

A) Optimal policy for irreversible reactions

B) Optimal policy for isothermal irreversible reactions

C) Optimal policy for reversible reactions.

CHAPTER I

INTRODUCTION

Many chemical processes are subject to catalyst decay in chemical reactors, which justifies the study of catalyst decay problems. The decay may be due to poisoning (e.g. a result of impurities contained in the feed), to sintering (e.g. when the surface area of the catalyst is reduced because of physical deterioration of the catalyst from high operating temperature), or to fouling (e.g. when coke is deposited on the catalyst).

Since catalyst activity has a history, the operation of such reactors subject to decaying activity will depend upon the entire previous history of the operating variables, and optimization of these are of prime interest these days. The solution is well known for irreversible reactions and many workers[1,2,3,4] have emphasized different aspects of it. Included in the appendix is the "listing" for the general case of an irreversible reaction, and also the one for finding the best isothermal policy.

Jackson[1,2] has considered the optimal temperature profile in a tubular reactor with a reversible exothermic reaction. The problem is easily formulated, but no analytical solutions are avialable yet.

Ogunye and Ray[5,6] have developed a general numerical method for calculating the optimal control policy using a modified gradient method for a reversible reaction.

In the subsequent pages, the necessary conditions for an optimum policy will be derived theoretically. However, because of the complexity of such systems, a numerical method together with the analytical developments is used to get a complete solution for reversible reactions.

CHAPTER II

STATEMENT OF THE PROBLEM

In this section the objective function, which has to be maximized is defined. Also, all the assumptions related to the system utilized (isothermal tubular reactor) are listed.

For the single tubular reactor with uniform temperature, the following assumptions are required:

(1) There is a single reversible reaction. A material balance for a plug flow reactor is in terms of catalyst activity ψ, temperature T, conversion X.

$$\frac{\partial X}{\partial t} + \frac{\partial X}{\partial Z} = f(\psi, T, X) \qquad (2.1)$$

where $f(\psi, T, X)$ is the rate of reaction, Z is the space-time (distance) through the bed, t is the time on stream and $X = X_o(t)$ at $Z = 0$. The catalyst activity ψ is defined[7,8] as the ratio of the rate of reaction with decayed catalyst to that with fresh catalyst.

(2) The activity of the catalyst ψ is assumed to depend on temperature T and ψ itself, but not on conversion X, as follows:

$$\frac{d\psi}{dt} = -g(\psi)k(T) \qquad \psi = \psi_f \text{ at } t = 0 \text{ for } Z \text{ in } (0,\theta) \qquad (2.2)$$

with $0 \leq g(\psi) \leq 1$. Since the temperature in the reactor is assumed to be uniform at any time, equation (2.2) implies that ψ is uniform over the distance Z.

(3) The change of activity ψ is assumed to be negligible over a time equal to the space time so that ψ is effectively constant for integration over Z and $\frac{\partial X}{\partial t} << \frac{\partial X}{\partial Z}$

(4) K_1 and K_2 are the rate constant of the forward and backward reactions and are assumed to be proportional to k^p and k^{p_1} respectively with $p = E_1/E_c$ and $p_1 = E_2/E_c$, where E_1 is the activation energy of the reaction and E_c is the activation energy for the decay rate.

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

$$\text{Max. } P \text{ with } P = \int_0^\tau X(t)dt \tag{2.3}$$

subject to

$$0 \leqslant k_\infty \leqslant k \leqslant k^* \leqslant k_\infty .$$

Now following this section, rate expressions are introduced for two kinetic models and the general treatment using the maximum principle is derived.

CHAPTER III

THEORETICAL DERIVATIONS

3.1 KINETICS:

In this section, for reversible reactions, two kinetic models are derived for the rate expression.

For the reaction $A \underset{K_2}{\overset{K_1}{\rightleftharpoons}} B$, the rate of reaction is expressed as:

$$\text{Rate} = \psi[K_1(T)\ F_1(X) - K_2(T)\ F_2(X)]$$

where $F_1(X) = C_A^U$

$F_2(X) = C_B^W$.

U and W are the reaction orders of the forward and backward reactions. Reaction orders will now be expressed as order (U - W).

For our first kinetic model of order (1 - 1), at equilibrium the rate is zero, which implies that the equilibrium conversion X_{A_E} is equal to $\frac{K_{EQ}}{(1 + K_{EQ})}$ where $K_{EQ} = K_1/K_2$, and the equilibrium conversion is a function of temperature only.

In another form, for first order reactions in both directions,

$$\text{Rate} = -\frac{dC_A}{dt} = (K_1\ C_A - K_2\ C_B)\psi$$

$$-\frac{dC_A}{dt} = [K_1(C_{A_o} - C_{A_o}\ X_A) - K_2(C_{B_o} + C_{A_o}\ X_A)]\psi$$

Also,

$$-\frac{dC_A}{dt} = C_{A_o}\frac{dX_A}{dt} .$$

The conversion (X) is defined as the fraction of reactant concentration C_{A_o} converted into product. C_{B_o} is taken as zero so that C_{A_o} is the concentration of A achieved by reversing the reaction until $C_{B_o} = 0$. The scale of conversion is from zero to one.

Then, for reaction order (1 - 1),

$$\text{Rate} = (K_1 + K_2)(X_{A_E} - X)\psi$$

$$= K(T)\, F(X, k)\psi \qquad (3.1.1)$$

Now, compared with the irreversible case, the rate of reaction is no longer a product of functions of only one variable. This fact makes the analytical solution much more complex, if not impossible.

Then equation (2.1) with assumption (3) is integrated to give

$$\psi(K_1 + K_2)\theta = \int_{X_o}^{X(\psi,k,X_o)} \frac{dX}{(X_{A_E} - X)} \qquad (3.1.2)$$

where $Z = \theta$ is the end of the reactor.

Now consider our second kinetic model which is a first order reaction forward and a second order backward, $A \underset{2^{nd}}{\overset{1^{st}}{\rightleftarrows}} B$. In this case it is not profitable to express the rate as a function of the equilibrium conversion; therefore the rate is equal to $\psi[K_1(1 - X) - K_2 C_{A_o} X^2]$ and integrating all along the reactor yield

$$\psi\theta = \int_{X_o}^{X(\psi,k,X_o)} \frac{dX}{(K_1(1 - X) - K_2 C_{A_o} X^2)} \qquad (3.1.3)$$

These two equations (3.1.2 and 3.1.3) for different kinetics provide one of the system equations, the other one is obtained from the rate of decay of catalyst.

In this section, the rate expressions for our two kinetic models have been shown and will be used subsequently althrough this work. Notice that these equations contain three variables. Knowing two of them will yield the third one.

The next section applies Pontryagin's Maximum Principle to our system equations, and for the sake of simplicity the rate expressions (3.1.1 and 3.1.3) are substituted by the letter ρ because it is frequently used through this work.

3.2 GENERAL CASE:

In the following pages, the general derivation of the optimal policy is conveniently treated in the format of Pontryagin's Maximum Principle[9,10]. Throughout this paper all the implications related to it are taken as known, and these derivations hold for all kinetic models.

Equation (2.2) can be written

$$\frac{d\psi}{dt} = \phi(\psi, k) = -kg(\psi) \leq 0 \qquad (3.2.1)$$

with $\psi(0) = \psi_i$ and $\psi(\tau) \geq 0$

The system equations are

$$\frac{dP}{dt} = X = f^{\circ}$$

$$\frac{d\psi}{dt} = \phi = f^{1}$$

where P and ψ are the state variables. Now the adjoint variable μ_i is defined as

$$\dot{\mu}_i = - \sum_{\alpha=0}^{n} \mu_\alpha \frac{\partial f^\alpha}{\partial X^i}$$

Then

$$\dot{\mu}_o = -\mu_o \frac{\partial X}{\partial P} - \mu_1 \frac{\partial \phi}{\partial P}$$

and

$$\dot{\mu}_1 = -\mu_o \frac{\partial X}{\partial \psi} - \mu_1 \frac{\partial \phi}{\partial \psi}$$

Since $\frac{\partial X}{\partial P} = 0$ and $\frac{\partial \phi}{\partial P} = 0$,

we have $\dot{\mu}_o = 0$ so that μ_o = constant at any time. From Pontryagin's Maximum Principle, Theorem 7, implies that, for a fixed time problem and variable endpoints μ_o at the final time equals 1 (for a maximum) and all the other adjoints to be zero also at the final time. Therefore, using $\mu = \mu_1$

$$\frac{d\mu}{dt} = - \frac{\partial X}{\partial \psi} - \mu \frac{\partial \phi}{\partial \psi} \qquad (3.2.2)$$

with $\mu(\tau) = 0$ if $\psi(\tau) > 0$

and $\mu(\tau) \geq 0$ if $\psi(\tau) = 0$.

The space time θ is set to unity, so that τ is the number of space times. Equation (3.1.2), linking conversion to the activity and temperature is rewritten then as

$$\psi(K_1 + K_2) = \int_{X_o}^{X} \frac{dX}{F(X, k)} \qquad (3.2.3)$$

where $F(X, k) = (X_{A_E} - X)$,

and for the second kinetic model with equation (3.1.3)

$$\psi = \int_{X_o}^{X} \frac{dX}{[K_1(1 - X) - K_2 C_{A_o} X^2]} \tag{3.2.4}$$

It is assumed that F, g and K are continuous functions of their arguments and are twice differentiable, and that k and X_o are piecewise continuous functions of time t.

The Hamiltonian H is defined by

$$H = \sum_{i=0}^{n} \mu_i f^i$$

or

$$H(\psi,\mu,k,t) = X(\psi,k,X_o(t)) + \mu\phi(\psi,k) \tag{3.2.5}$$

The maximization of P in equation (2.1) is then equivalent, according to Pontryagin's Maximum Principle[9,10], to requiring of an optimal policy $k^+(t)$ that it satisfy

$$H(\psi^+,\mu^+,k^+,t) = \text{Max}_{k(t)} H(\psi^+,\mu^+,k,t) \tag{3.2.6}$$

at almost any t and for all admissible values of k. In equation (3.2.6) ψ^+ and μ^+ are the solutions of equations (3.2.1) and (3.2.2) using $k^+(t)$. If $k^+(t)$ is the optimal policy, then one of the following three conditions is necessary at any time $t \leq \tau$:

(a) $$\frac{\partial H}{\partial k}(k^+) = 0 \quad \text{and} \quad \frac{\partial^2 H}{\partial k^2}(k^+) \leq 0 \qquad k_* < k^+ < k^* \tag{3.2.7}$$

(b) $$\frac{\partial H}{\partial k}(k^+) \geq 0 \qquad \text{if} \quad k^+ = k^* \tag{3.2.8}$$

(c) $$\frac{\partial H}{\partial k}(k^+) \leq 0 \qquad \text{if} \quad k^+ = k_* \tag{3.2.9}$$

From equation (3.2.5) we have

$$\left.\frac{\partial H}{\partial k}\right|_{\psi,\mu,t} = \left.\frac{\partial X}{\partial k}\right|_{\psi,X_o} + \mu\,\frac{\phi}{k} \tag{3.2.10}$$

Now, taking the partial derivative with respect to k on both sides of equation (3.2.3) or (3.2.4) and with ρ = rate and X_s the exit conversion at any instant on the stationary path

$$\left.\frac{\partial X}{\partial k}\right|_{\psi,X_o} = \rho(X_s,k)\int_{X_o}^{X_s}\frac{1}{\rho^2}\left.\frac{\partial \rho}{\partial k}\right|_{X,\psi} dX \tag{3.2.11}$$

Substitution of (3.2.11) in (3.2.10) yields

$$\left.\frac{\partial H}{\partial k}\right|_{\psi,\mu,t} = \rho(X_s,k)\int_{X_o}^{X_s}\frac{1}{\rho^2}\left.\frac{\partial \rho}{\partial k}\right|_{X,\psi} dX + \frac{\mu\phi}{k} \tag{3.2.12}$$

The stationary policy S can be found and implies that

$$\left.\frac{\partial H}{\partial k}\right|_{\psi,\mu,t} = 0$$

or

$$\mu\phi = -k\,\rho(X_s,k)\int_{X_o}^{X_s}\frac{1}{\rho^2}\left.\frac{\partial \rho}{\partial k}\right|_{X,\psi} dX \tag{3.2.13}$$

along S.

Thus, along S the Hamiltonian is

$$H_s = X_s - k\rho(X_s,k)\int_{X_o}^{X_s}\frac{1}{\rho^2}\left.\frac{\partial \rho}{\partial k}\right|_{\psi,X} dX \tag{3.2.14}$$

or, more compactly,

$$H_s = X_s - k\left.\frac{\partial X}{\partial k}\right|_{\psi,X_o} \tag{3.2.15}$$

On any optimal path (in Appendix I) the total derivative of the Hamiltonian with time is

$$\frac{dH}{dt} = \frac{\rho(X,k)}{\rho(X_o,k)} \frac{dX_o}{dt} \qquad (3.2.16)$$

and $\frac{dH}{dt}$ (on S) = $\frac{dH}{dt}$ (general).

3.2.1 First Kinetic Model (Order 1 - 1)

Equation (3.2.14) and (3.2.3) for the rate expression with $K_1 = Ak^p$ and $K_2 = Bk^{p_1}$ is integrated to give

$$H_s = X_s - (p - p_1) X_{A_E}(1 - X_{A_E}) \left[\frac{X_s - X_o}{X_{A_E} - X_o}\right] + (X_{A_E} - X_s) \ln\left(\frac{X_{A_E} - X_s}{X_{A_E} - X_o}\right) \left[X_{A_E}(p - p_1) + p_1\right]$$

-------- (3.2.17)

We see from equation (3.2.17) that the Hamiltonian on the stationary policy is a function of X, X_o, and k.

Solving $\frac{dH}{dt}$ on the stationary policy

$$\frac{dH}{dt} \text{ (on S)} = \frac{\partial H}{\partial X}\frac{dX}{dt} + \frac{\partial H}{\partial X_o}\frac{dX_o}{dt} + \frac{\partial H}{\partial k}\Big|_{X,k}\frac{dk}{dt}$$

For simplification, assume X_o = constant so that $\frac{dX_o}{dt} = 0$.

Now,

$$\frac{dH}{dt} \text{ (on S)} = \frac{dH}{dt} \text{ (general)} \qquad \text{(Appendix I)}$$

$$\left[1 - \frac{(p-p_1)X_{AE}(1-X_{AE})}{(X_{AE} - X_o)} - \left[X_{AE}(p-p_1)+p_1\right]\left[1+\ell n\ \frac{X_{AE} - X_S}{X_{AE} - X_o}\right]\right] \frac{dX}{dt}$$

$$+ \frac{X_{AE}(1-X_{AE})(p-p_1)}{k\ (X_{AE} - X_o)} \left[- \frac{(p-p_1)(X_S-X_o)(2X_{AE}X_o - X_o - X_{AE}^2)}{(X_{AE} - X_o)}\right.$$

$$\left. + (X_S-X_o)(X_{AE}(p-p_1)+p_1) + (X_{AE}-X_o)\ \ell n\left(\frac{X_{AE} - X_S}{X_{AE} - X_o}\right)\right.$$

$$\left. \cdot \left[(2X_{AE}-X_S)(p-p_1) + p_1\right]\right] \frac{dk}{dt} = 0 \qquad (3.2.18)$$

For the special case where $p = p_1$, Equation (3.2.18) reduces to

$$\left[1-p_1\left(1+ \ell n\left(\frac{X_{AE} - X_S}{X_{AE} - X_o}\right)\right)\right] \frac{dX}{dt} = 0$$

which has two solutions

$$\frac{dX}{dt} = 0 \qquad \text{implies} \quad X = \text{Constant}_1$$

or

$$X = X_{AE} - (X_{AE} - X_o)\ e^{\frac{1-p}{p}}$$

But when $p = p_1$, X_{AE} is a constant and the second alternative solution is also $X = \text{Constant}_2$.

However, many numerical examples have been tried and it appears that the second solution is not satisfied.

For the general case ($p \neq p_1$) due to the complexity of Equation (3.2.18) for the optimal policy on the stationary path, the analytical solution cannot be at the moment completely derived. From here on, theoretical development together with a numerical scheme will be worked out for finding the optimal policy.

3.2.2 Second Kinetic Model (Order 1-2)

The rate was expressed as

$$\rho = \psi \left[K_1(1-X) - K_2 C_{A_o} X^2\right]$$

so

$$\frac{\partial \rho}{\partial k} = \frac{\psi}{k} \left[p_1 K_1 (1-X) - p_1 K_2 C_{A_o} X^2\right] \qquad (3.2.19)$$

With Equations (3.2.14) and (3.2.19) we have

$$H_S = X_S - \rho(X_s,k) \int_{X_o}^{X_s} \left[\frac{pK_1(1-X) - p_1 K_2 C_{Ao} X^2}{\rho^2}\right] dX \qquad (3.2.20)$$

In this section (3.2), the general criteria from the Maximum Principle has been used in our system equations. The necessary conditions for an optimum are represented in Equation (3.2.18) for the first kinetic model (Order 1-1).

Subdivisions 3.2.1 and 3.2.2 have been devoted to represent the Hamiltonian on the stationary policy for our two kinetic models being studied.

3.3 Endothermic Reaction

In this section, it is shown that for endothermic reactions of order (1-1), the optimal temperature policy must end on the upper constraint temperature in the following manner.

From Equation (3.2.10) since at the end of the process $\mu = 0$, we must have at the end

$$\left.\frac{\partial H}{\partial k}\right|_{\psi,\mu,t} = \left.\frac{\partial X}{\partial k}\right|_{\psi,X_o}$$

But with Equations (3.2.15) and (3.2.17) assuming $X_o = 0$ for the sake of

simplicity without loosing any generality

$$\left.\frac{\partial X}{\partial k}\right|_{\psi,X_o} = \frac{(p-p_I)(X_S)(1-X_{AE})}{k} + \frac{\psi(K_1+K_2)(X_{AE}-X_S)}{k}\left[X_{AE}(p-p_I)+p_I\right] \quad (3.3.1)$$

For an endothermic reaction, p is larger than p_I, and $\frac{\partial X}{\partial k}$ is positive because all the terms inside Equation (3.3.1) are positive and so at the end we will have $\frac{\partial H}{\partial k} > 0$. It means with Equation (3.2.8) that for an endothermic reversible reaction of order (1-1), the optimal temperature policy must end on the upper bound and obviously will be a rising temperature profile. The same conclusions holds for $p = p_I$. Notice that since $\frac{\partial X}{\partial k}$ is always positive, from Equation (3.2.15), X_I is always greater than the Hamiltonian.

This is easily generalized for any order of reactions because for all endothermic reaction, the conversion increase with temperature.

3.4 Exothermic Reaction

In this section it is shown that for exothermic reactions of order (1-1) the optimal temperature policy does not have to reach the upper constraint any more; also from theoretical developments it is shown that there exist for exothermic reaction a range of starting temperaturesfor a reactor where no optimal policy can be derived and the method to find these bound is explained.

For an exothermic reaction p is less than p_I and at the end

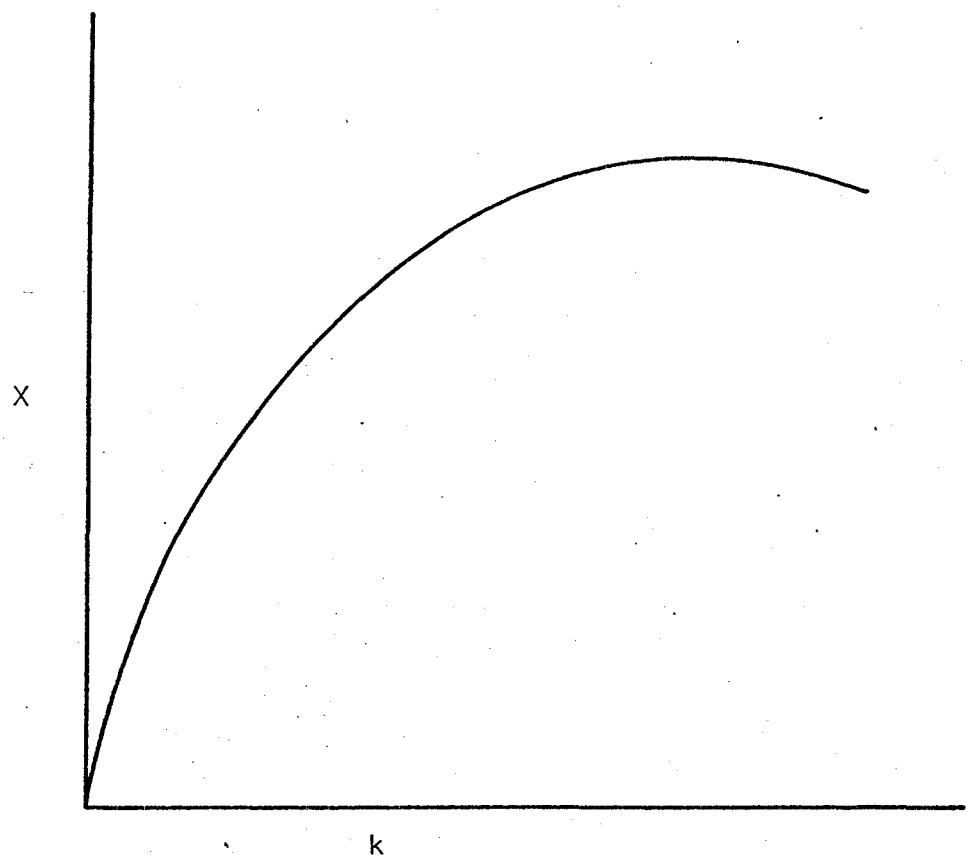
$$\frac{\partial H}{\partial k} = \frac{(p-p_I)(X_s(1-X_{AE})}{k} + \frac{\psi(K_1+K_2)(X_{AE}-X_S)}{k}\left[X_{AE}(p-p_I)+p_I\right]$$

$$= \quad \text{negative} \quad + \quad \text{positive} \ [\text{negative} + \text{positive}]$$

It is no longer a necessary condition to end on the upper constraint, because we cannot predict the sign of $\partial H/\partial k$ at the end. But since for some values of p and p_1 the policy would be to end on the upper constraint, it is expected that it will still be a rising temperature profile unless p = 0 which will be the limiting case.

3.4.1 Initial Temperature Limitation

For the exothermic reaction plotting the conversion versus k, keeping the activity constant, gives the kind of curve shown on Figure 18.



Schematic Diagram

Looking at the Hamiltonian on the stationary policy, we have

$$H_s = X_s - k \frac{\partial X}{\partial k}$$

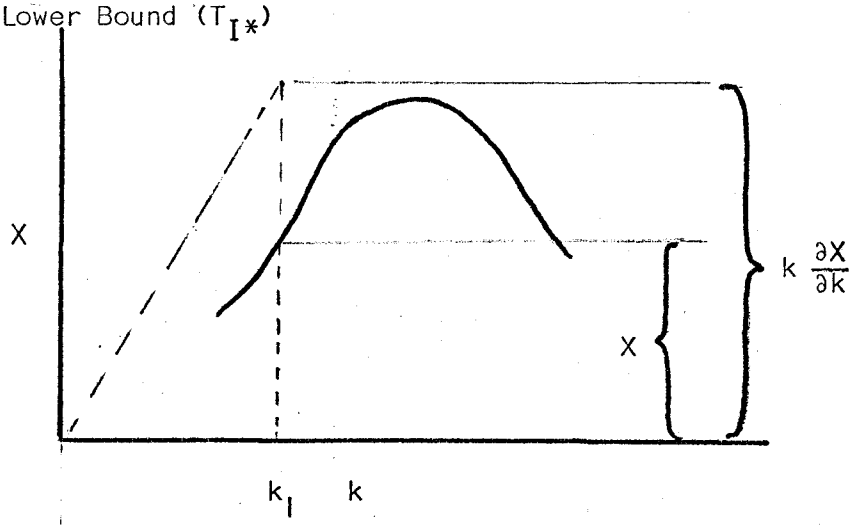
and also in general

$$H = X + \mu \phi \qquad \phi = -k\, g(\psi) \leq 0$$

Since ϕ is always negative and μ is always positive and zero at the end for a fixed time problem, we have $\mu\phi \leq 0$. It also implies that on any optimal policy, we must have $H \leq X$, and $H = X_f$ because at $t = \tau$, $\mu = 0$. Also X is always positive, so H has to be greater than or equal to zero.

It is easily shown that for an exothermic reaction, upper and lower bounds on the initial starting temperature can be found different from those imposed on the reactor, where we will not have any stationay policy because it does not satisfy the Maximum Principle.

A) Lower Bound (T_{I*})



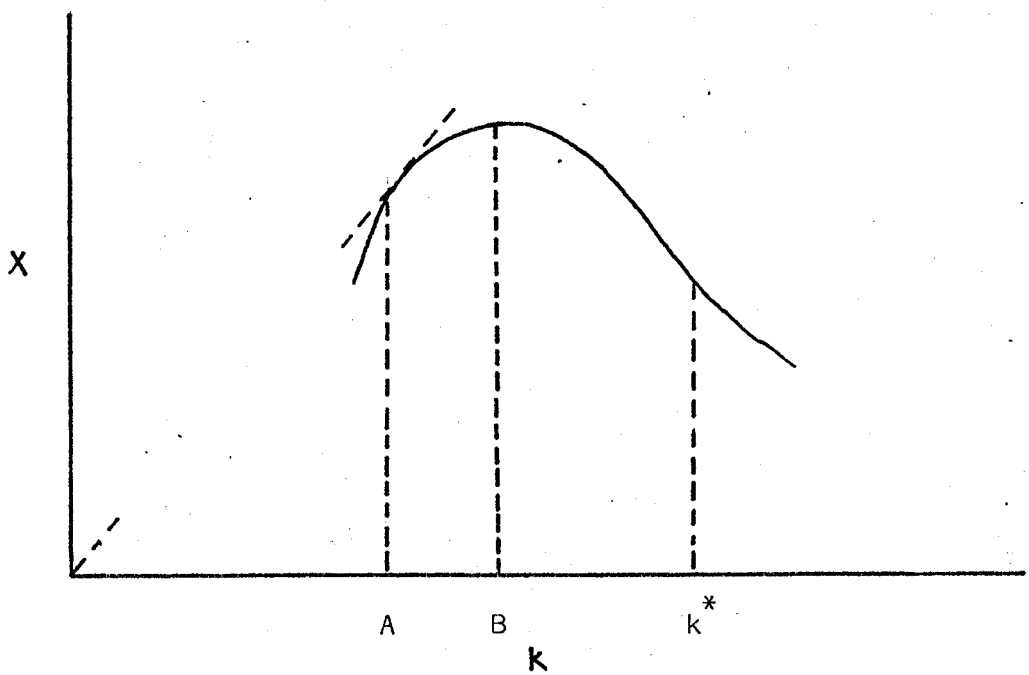
for $k_I = k_l$ we have $\qquad H_S = X - k \frac{\partial X}{\partial k}$

$= \text{negative}$

So this starting value of k_l does not satisfy the Maximum Principle.

However, if there is no point of inflexion, there will be no lower bound on the initial temperature, because X will be always greater than k ∂X/∂k.

If there is a point of inflexion, the lower bound on initial temperature is formed by the point of tangency from the origin where k ∂X/∂k is equal to X.



On the schematic diagram above, the lower and upper bound are respectively A and B.

Analytically these limits are easily calculated. For the low range this limitation arises when

$$X_i = k_i \frac{\partial X}{\partial k} \qquad (3.4.1)$$

With Equation (3.2.3)

$$X_i = X_{AE}(1-EXP(Y)) \tag{3.4.2}$$

where $Y = -\psi_i(K_1+K_2)$

By substitution of Equations (3.3.1) and (3.4.2) in (3.4.1) one has an equation of one unknown k_i

$$X_{AE}(1-EXP(Y))=X_{AE}[(1-EXP(Y)(p-p_1)(1-X_{AE})+(EXP(Y))\psi(K_1+K_2)[X_{AE}(p-p_1)+p_1] \tag{3.4.3}$$

If Equation (3.4.3) can be satisfied for a starting initial temperature, this temperature will be the lower bound.

The upper bound on the initial temperature is when $\frac{\partial X}{\partial K} = 0$, therefore, at this initial temperature, the initial conversion equals the value of the Hamiltonian and we are able to operate the reactor at this temperature for an infinitely short time because the conversion is decreasing and the Hamiltonian has to be kept constant.

This point is found analytically from Equations (3.3.1) and (3.4.2) to give

$$(1-EXP(Y)(p-p_1)(1-X_{AE}) = (-EXP(Y))[X_{AE}(p-p_1)+p_1]\psi_i(K_1+K_2) \tag{3.4.4}$$

Again by trial and error this equation is easily solved to yield the upper bound on initial temperature.

As an illustration of this phenomenon for an exothermic reaction, numerical solution for $p = 0.6$ and $p_1 = 0.8$ has given a maximum initial temperature of $850^{\circ}F$ for having a stationary policy, and no lower bound has been found numerically for this example. For values of $p = 1.2$ and $p_1 = 1.6$, minimum and maximum starting temperatures were $740^{\circ}F$ and $830^{\circ}F$. From the numerical examples run, it is believed that when the difference

between p and p_1 increases with p_1 increasing, the range of initial permissible temperature will decrease.

Now an interesting question is what would be the optimum policy, if there is one, to operate the reactor for an initial temperature higher than T_I^* ? Obviously there is no stationary policy, the only possibility remaining is a constrained policy. By way of contradiction the upper constraint policy is rejected in this manner.

Assume the policy is on the upper constraint. From Equation

(3.2.8) $\frac{\partial H}{\partial k} \geq 0$

We have

$$H = X + \mu\phi$$

$$\frac{\partial H}{\partial k} = \frac{\partial X}{\partial k} + \frac{\mu\phi}{k} \geq 0$$

Because $\frac{\partial X}{\partial k} < 0$ for an exothermic reaction where $T_I > T_I^*$, it implies that $\frac{\mu\phi}{k} > 0$ then $\mu < 0$. Since μ has to be zero at the final time $\frac{d\mu}{dt} > 0$. On the other hand, from Equation(3.2.2) we must have $\frac{d\mu}{dt} < 0$ at the end. Since μ is continuous (obtained from the solution of an ordinary differential equation), these two conclusions are in contradiction. Our hypothesis is then invalid and therefore this policy is rejected. A priori the lower constraint policy cannot be rejected.

For endothermic reaction, these restrictions on the upper initial temperature, do not appear because from Equations (3.3.1) $\frac{\partial X}{\partial k}$ is always positive.

In this latter section, it has been noted that for exothermic reactions, it is no longer a necessary condition that the optimal temperature policy end on the upper constraint, also in many cases there

exist severe restrictions on the starting temperature of a reactor to have an optimal policy.

CHAPTER IV

NUMERICAL SOLUTIONS

4.1 METHODS

In this scheme, Pontryagin's Maximum Principle is used, for any optimal stationary policy, by guessing a temperature and iterating so that the Hamiltonian remains constant. So we fix the initial temperature and activity, from equations (3.2.3) and (3.2.17), and calculate the initial conversion and the initial Hamiltonian. After this process is initiated, for a small time increment, assume the same temperature, and with it calculate the activity, the conversion and the Hamiltonian. If the constancy of the Hamiltonian is respected, increment the time, if not, assume another temperature until the calculated Hamiltonian for this temperature has surpassed the original Hamiltonian and with a Reguli-Falsi technique, find the exact temperature to satisfy the constancy of the Hamiltonian. This procedure is used repetitively.

4.2 Results

A) The first set of calculations were carried out for a reversible reaction $A \underset{k_2}{\overset{k_1}{\rightleftarrows}} B$ being first order in both directions for a hypothetical reactor where

$$F(X, T) = (X_{AE} - X)$$

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

$$E_C/R = 15.000^{\circ}K$$

$$k^* = 4.0 \quad (T^* = 900^{\circ}F)$$

$$k_* = 0.13 \quad (T_* = 700^{\circ}F)$$

$$X_o = 0.0$$

$$\psi_I = 1.0$$

The calculation method used here differs from that used in the irreversible case in the following way: for the irreversible case, a specified maximum conversion attainable for that reactor with the activity equal to one was used to calculate the maximum rate constant of reaction. So that K^* was a constant for any P value. For the reversible reaction, since

$$K_1^* = A\, k^{*\,p}$$

and

$$K_2^* = B\, k^{*\,p_1}$$

are of Arrhenius form, keeping the Arrhenius constants A and B constant; different values of p and p_1 would change K_1^* and K_2^*.

Figure 1 to 8 shows the general behavior of the system variables when there is no temperature constraint on the reactor.

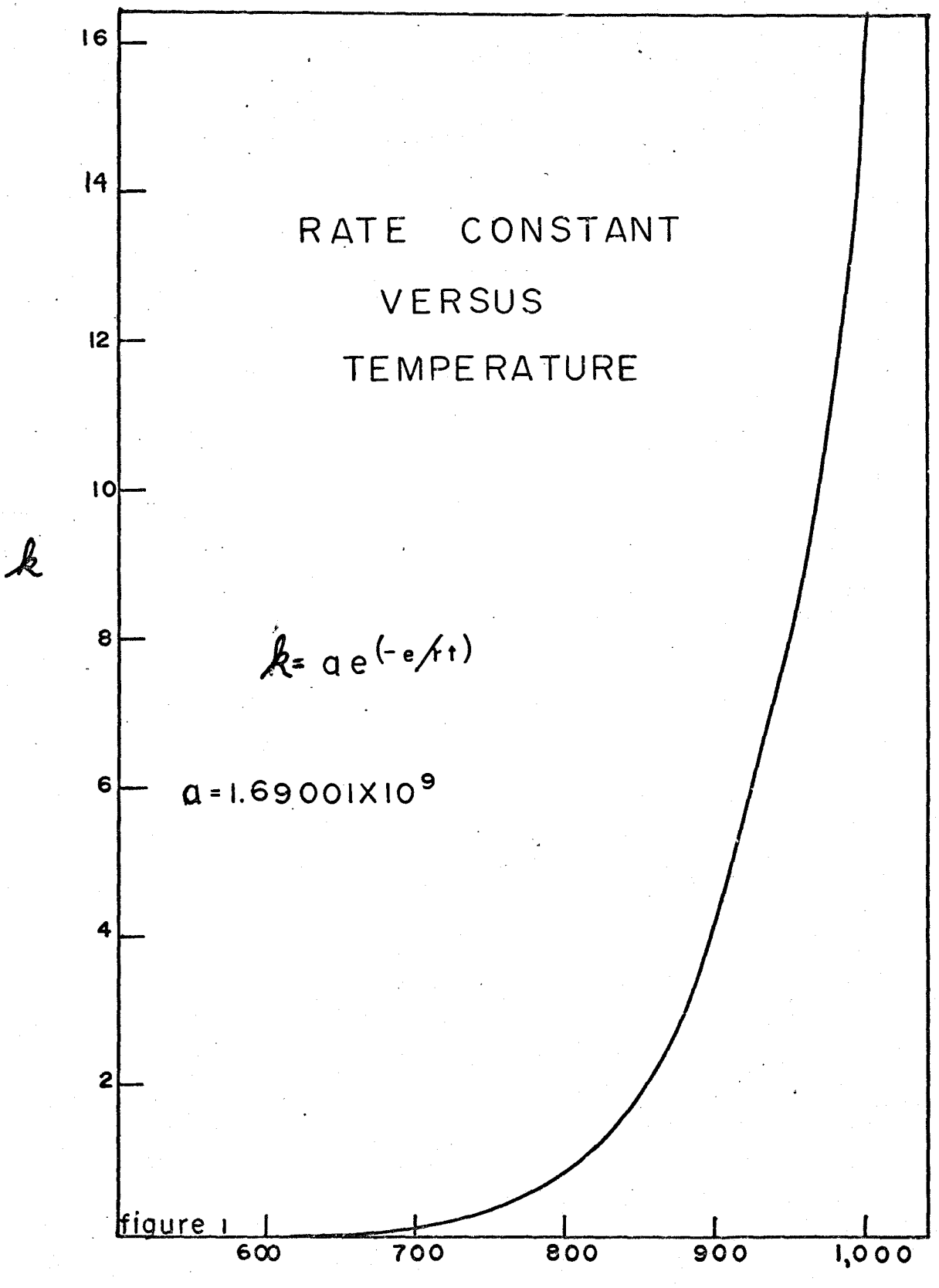

RATE CONSTANT
VERSUS
TEMPERATURE
$k = a e^{(-e/rt)}$
$a = 1.69001 \times 10^9$
k
16
14
12
10
8
6
4
2
600
700
800
900
1,000
TEMPERATURE ° F

figure 1

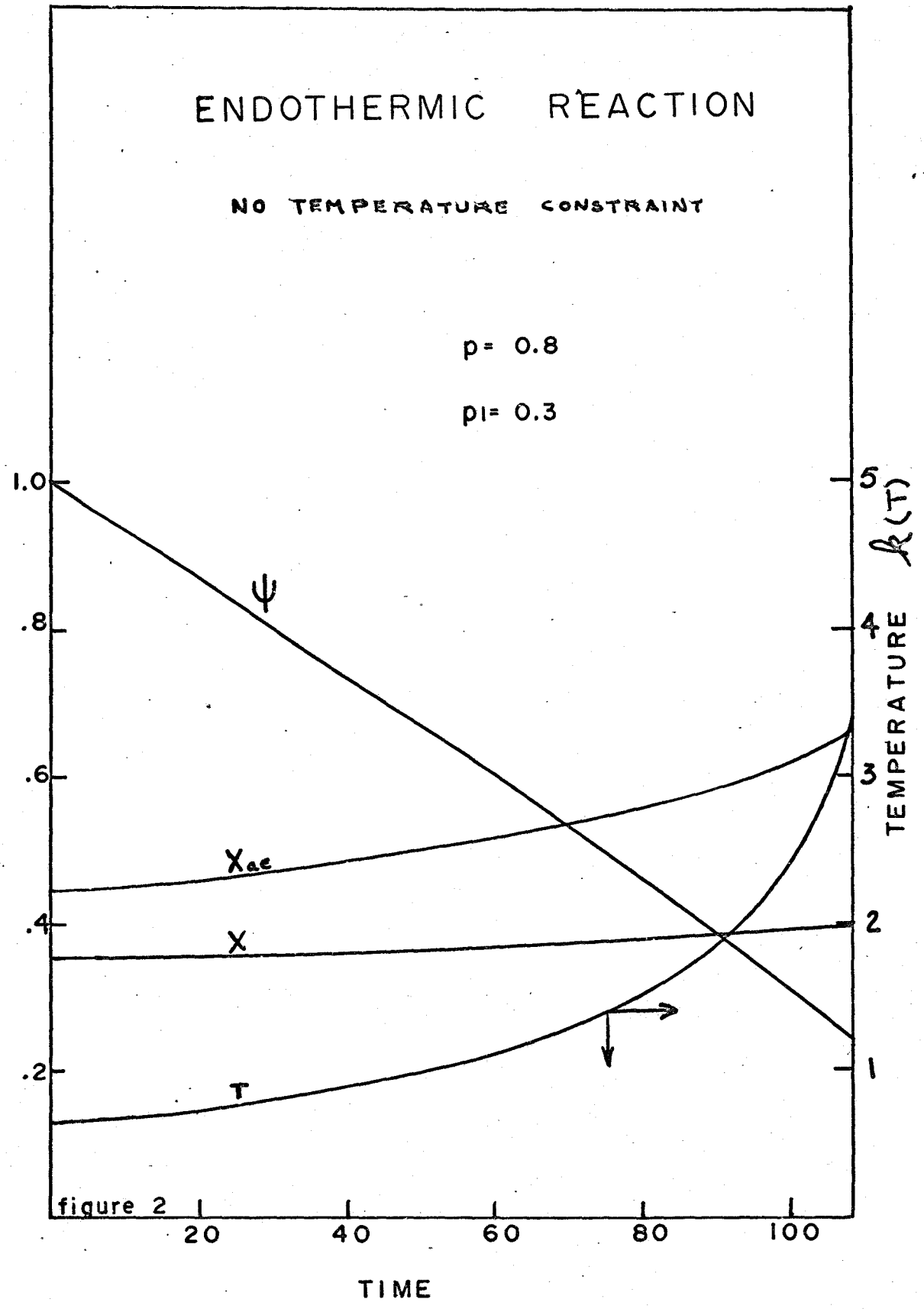

ENDOTHERMIC REACTION
NO TEMPERATURE CONSTRAINT
p= 0.8
pI= 0.3
1.0
.8
.6
.4
.2
ψ
Xae
X
T
5
4
3
2
1
TEMPERATURE k(T)
20
40
60
80
100
TIME

figure 2

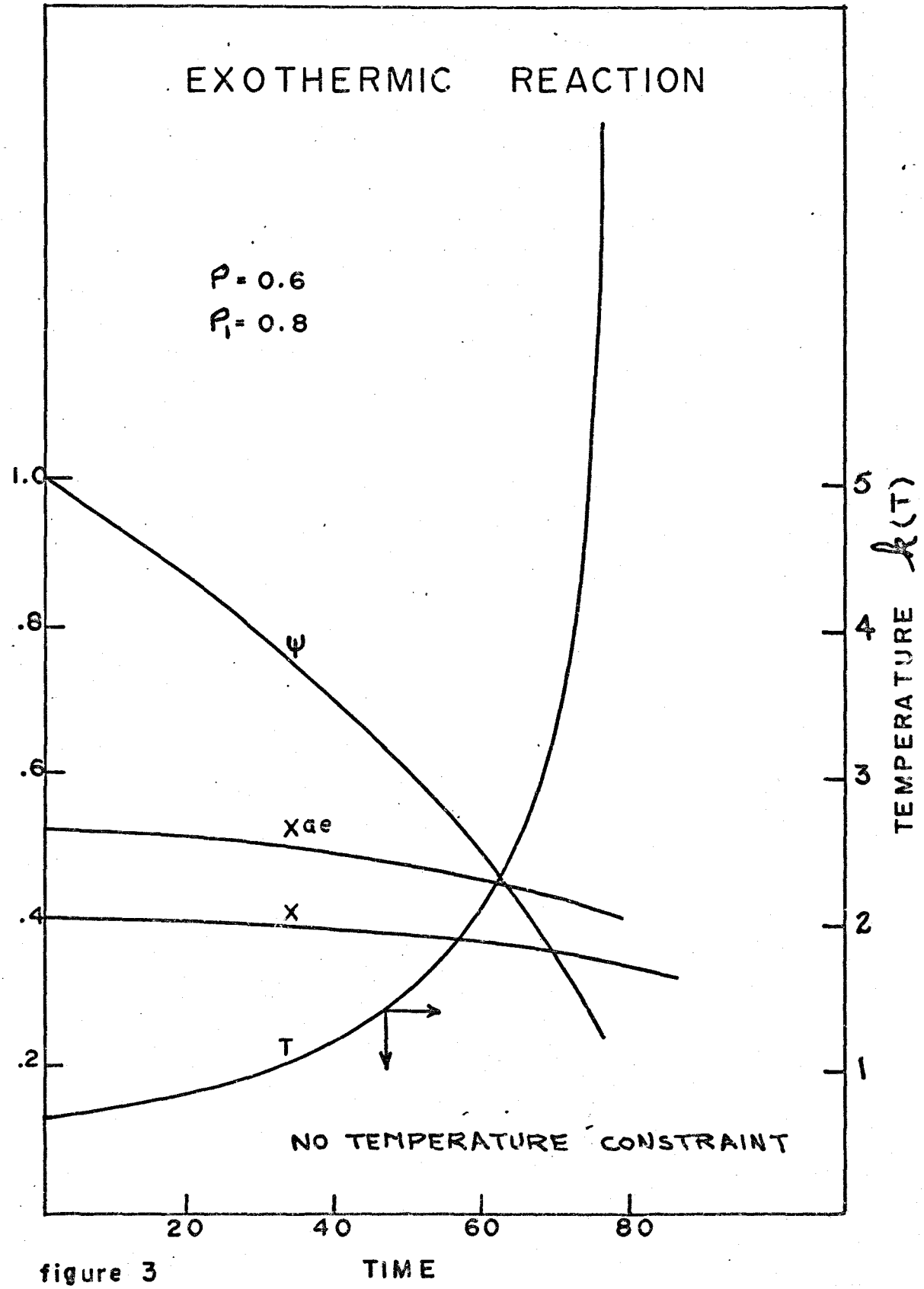

EXOTHERMIC REACTION
P = 0.6
P1 = 0.8
1.0
.8
.6
.4
.2
ψ
Xae
X
T
NO TEMPERATURE CONSTRAINT
20
40
60
80
TIME
5
4
3
2
1
TEMPERATURE k(T)

figure 3

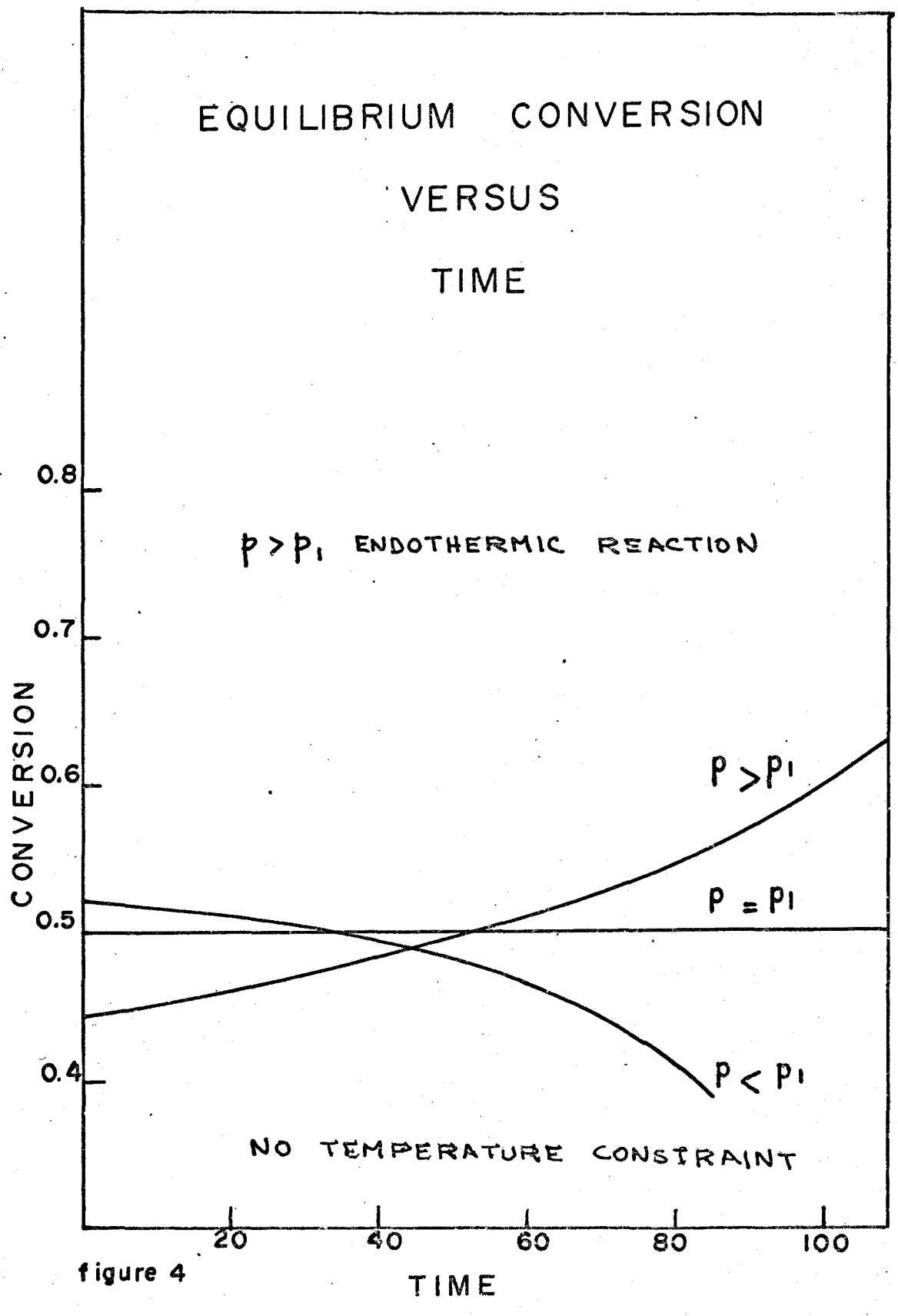

EQUILIBRIUM CONVERSION
VERSUS
TIME
P > P1 ENDOTHERMIC REACTION
P > P1
P = P1
P < P1
NO TEMPERATURE CONSTRAINT
CONVERSION
0.8
0.7
0.6
0.5
0.4
20
40
60
80
100
TIME

figure 4

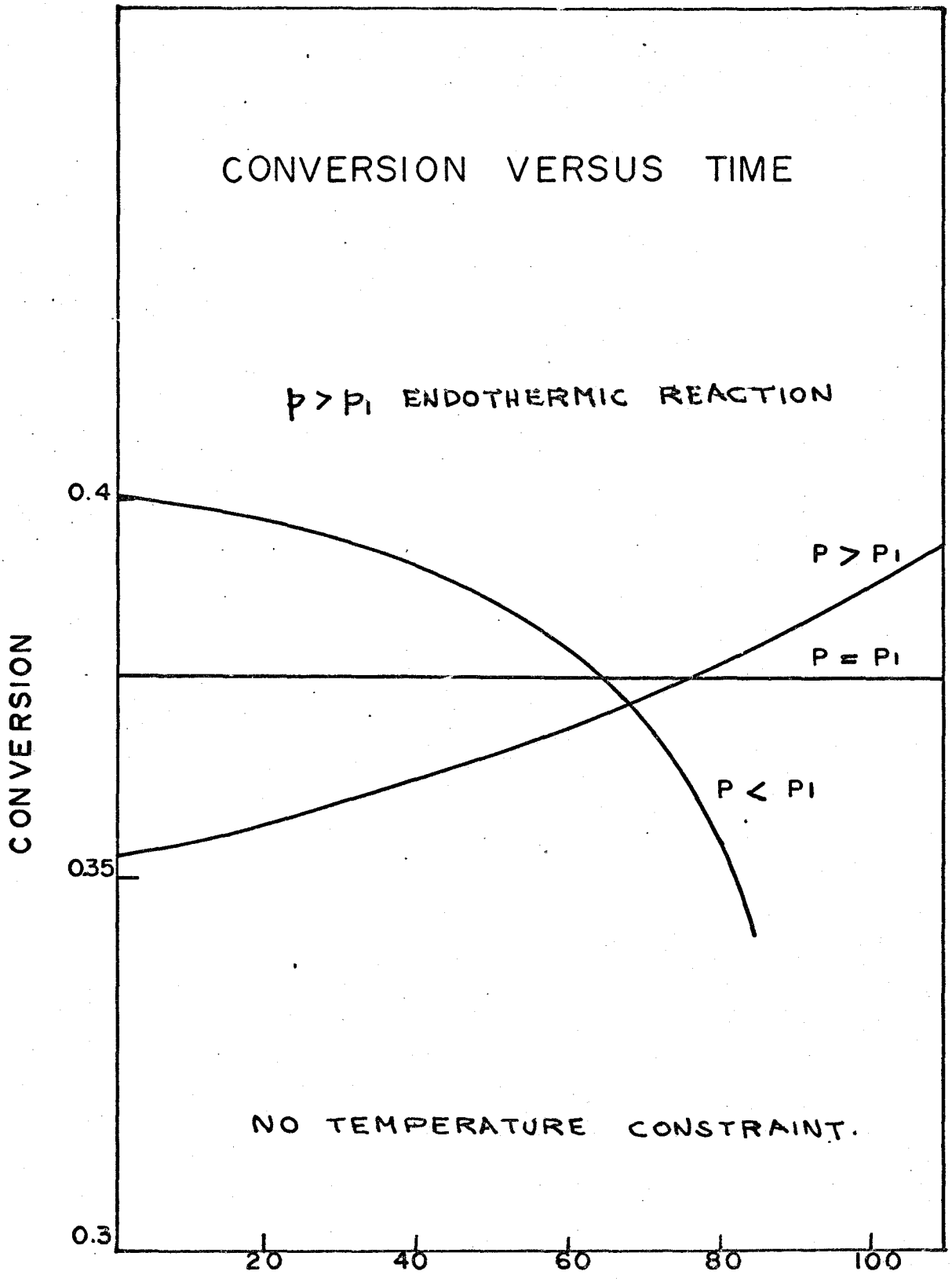

CONVERSION VERSUS TIME
P > P1 ENDOTHERMIC REACTION
0.4
0.35
0.3
CONVERSION
P > P1
P = P1
P < P1
NO TEMPERATURE CONSTRAINT.
20
40
60
80
100
TIME

figure 5

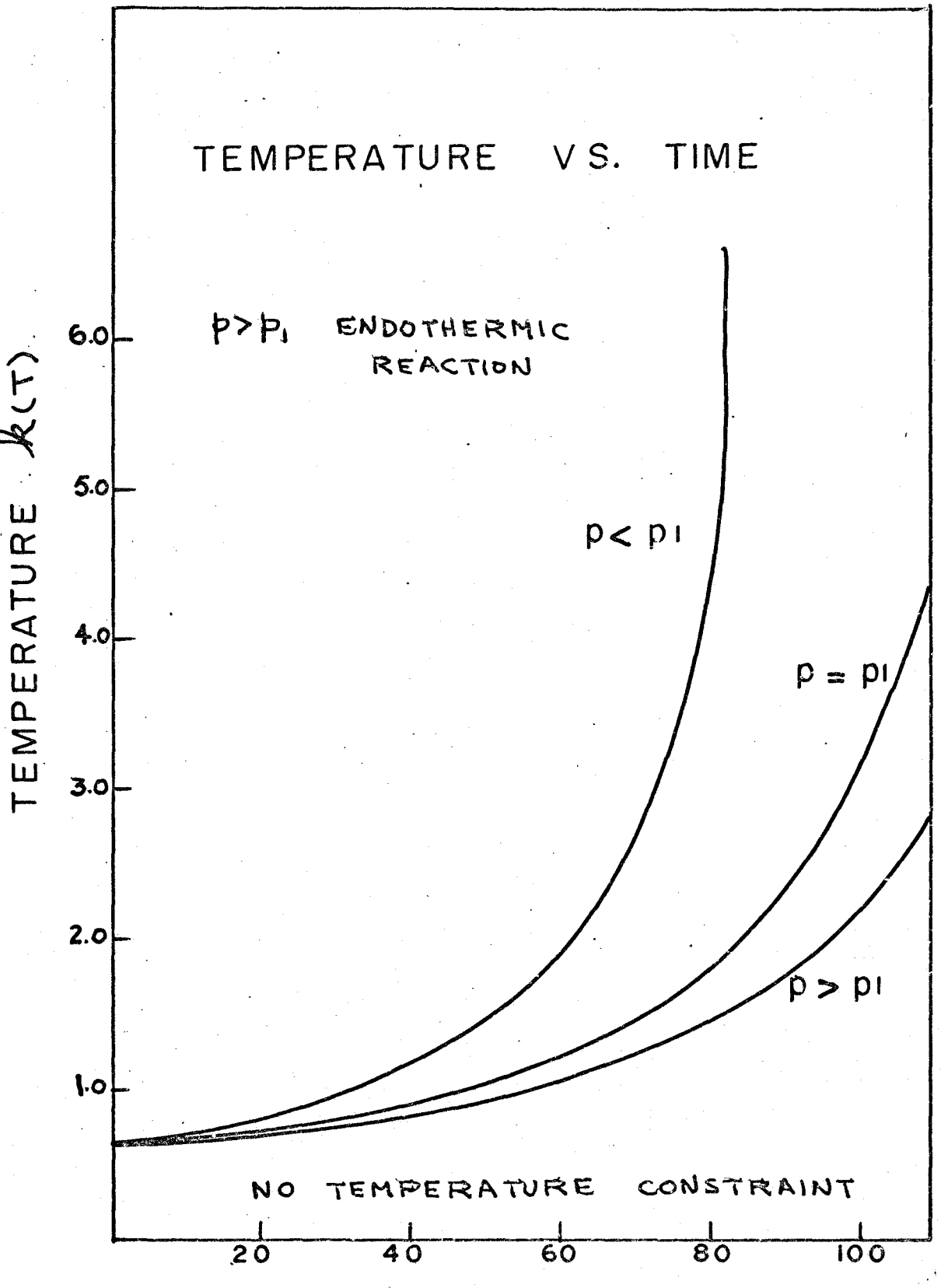

TEMPERATURE VS. TIME
p>p1 ENDOTHERMIC REACTION
p< p1
p = p1
p > p1
NO TEMPERATURE CONSTRAINT
TEMPERATURE k(T)
6.0
5.0
4.0
3.0
2.0
1.0
20
40
60
80
100
TIME

figure 6

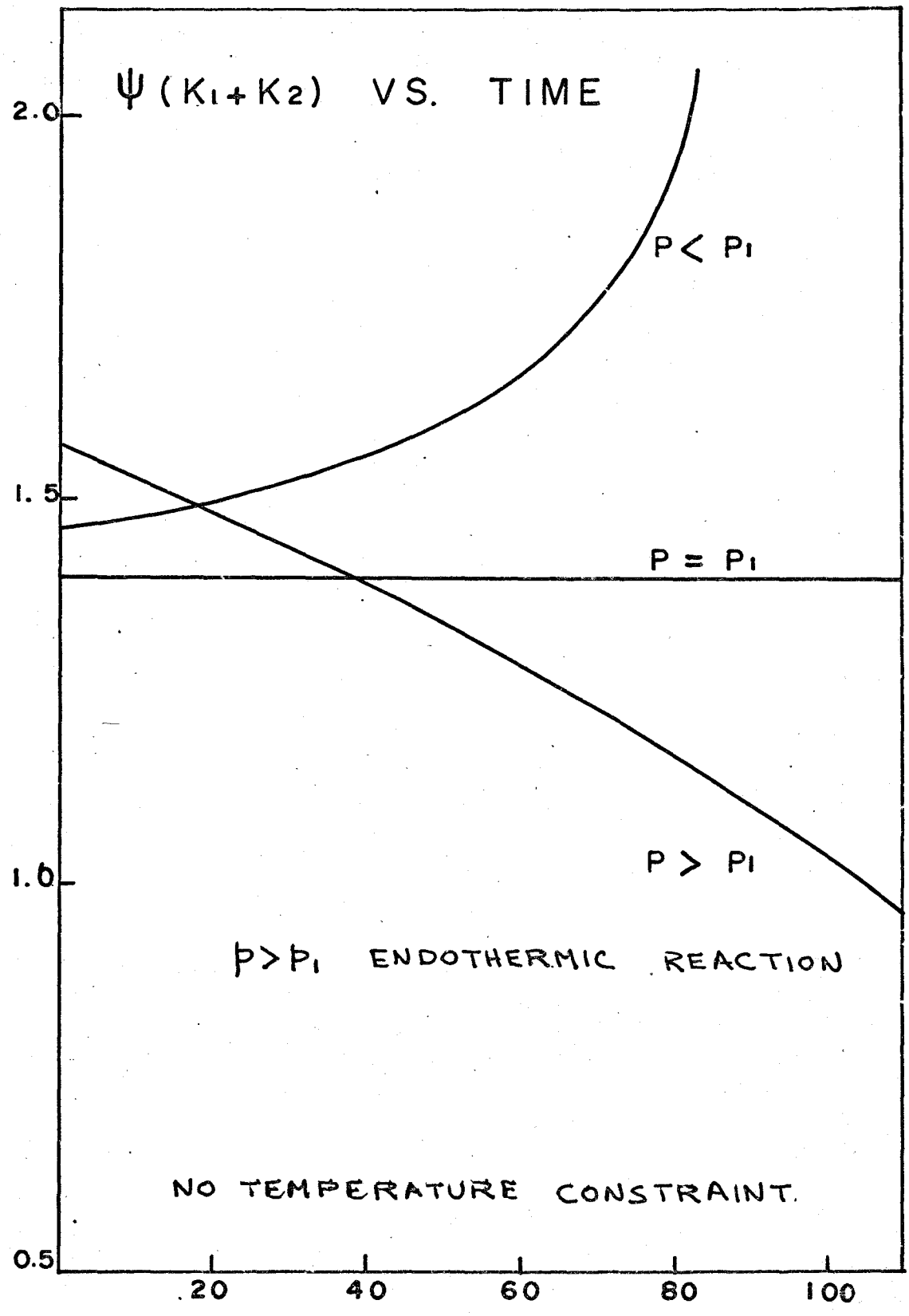

Ψ (K1 + K2) VS. TIME
2.0
1.5
1.0
0.5
P < P1
P = P1
P > P1
P>P1 ENDOTHERMIC REACTION
NO TEMPERATURE CONSTRAINT.
20
40
60
80
100
TIME

figure 7

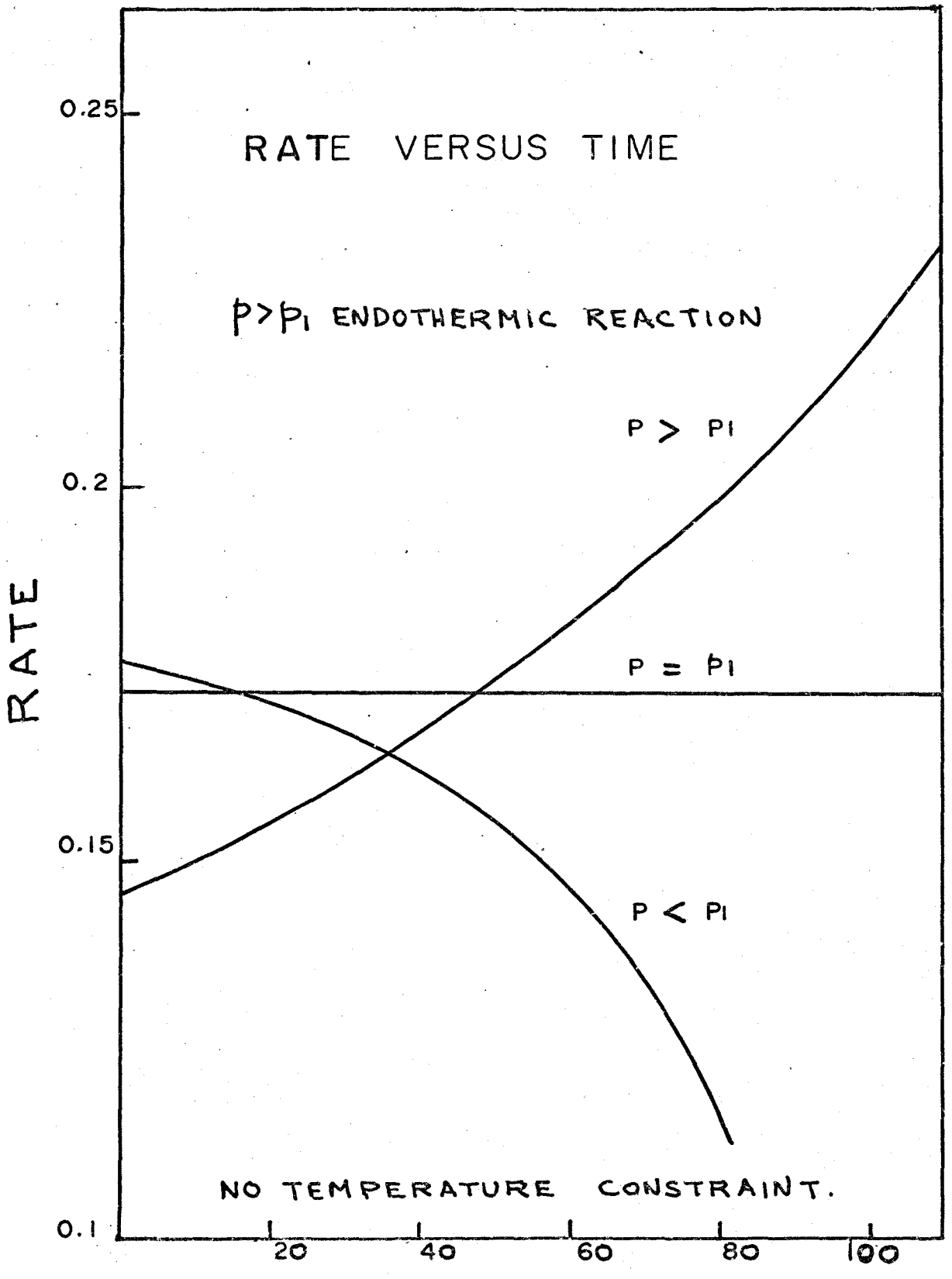

RATE VERSUS TIME
P>P1 ENDOTHERMIC REACTION
P > P1
P = P1
P < P1
NO TEMPERATURE CONSTRAINT.
RATE
TIME
0.25
0.2
0.15
0.1
20
40
60
80
100

figure 8

B) Sensitivity Calculation

In Figure 9, for an endothermic reaction, increasing the ratio of p/p_1 with p_1 = constant increases the total time (τ) and gives a more slowly rising temperature profile, however the policy always reaches the upper temperature constraint.

Figure 10 is for an exothermic reaction. Increasing the ratio of p/p_1 with p = constant increases the total time but has practically no effect on the temperature profile.

With Figures 11 and 12, for endothermic and exothermic reactions, an increase in the initial temperature decreases the total time of reaction.

Figure 13 is for the special case where $p=p_1$; the same phenomena is observed.

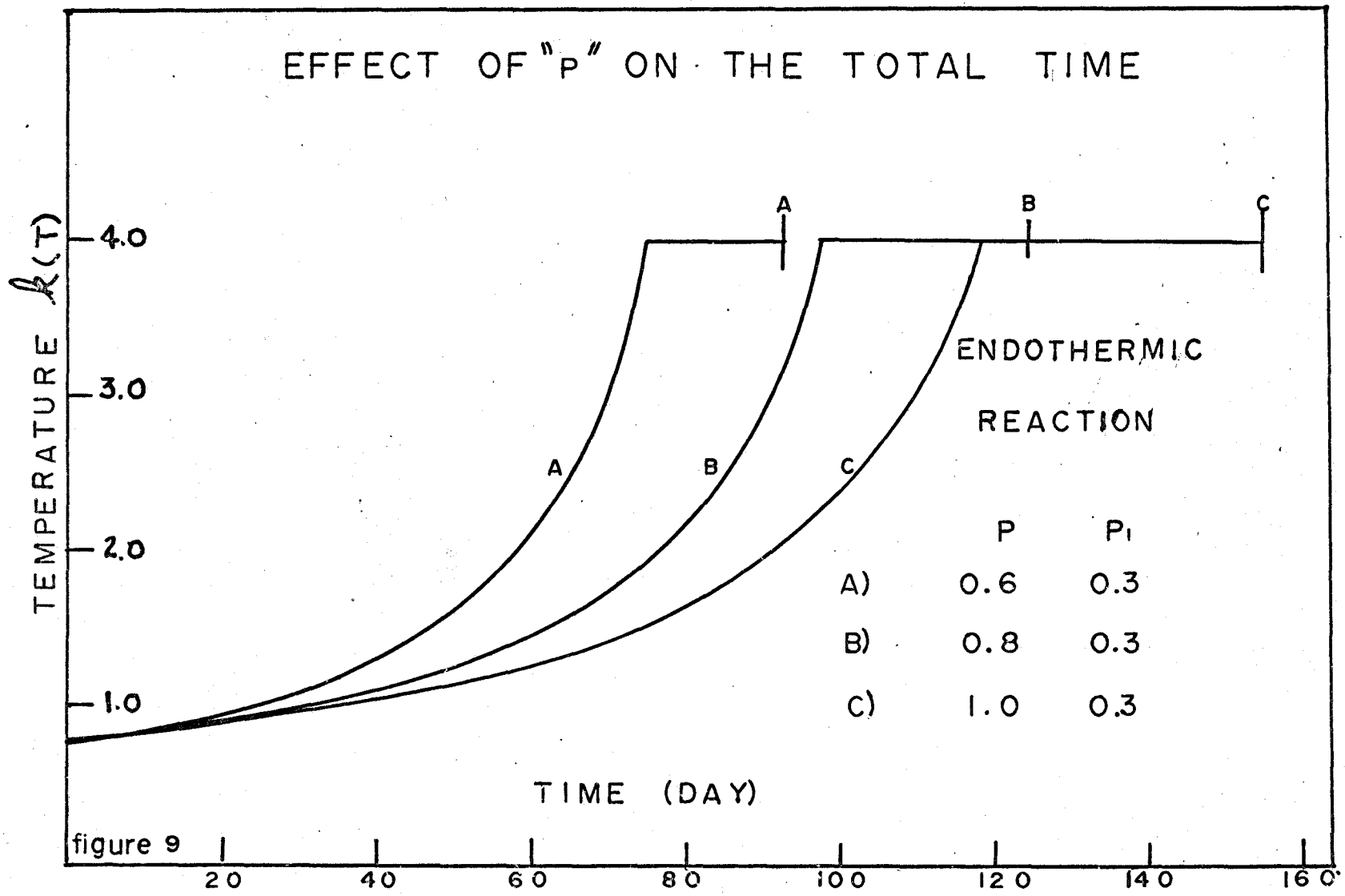

EFFECT OF "P" ON THE TOTAL TIME
TEMPERATURE k(T)
4.0
3.0
2.0
1.0
A
B
C
ENDOTHERMIC
REACTION
P
P1
A) 0.6 0.3
B) 0.8 0.3
C) 1.0 0.3
TIME (DAY)
20
40
60
80
100
120
140
160

figure 9

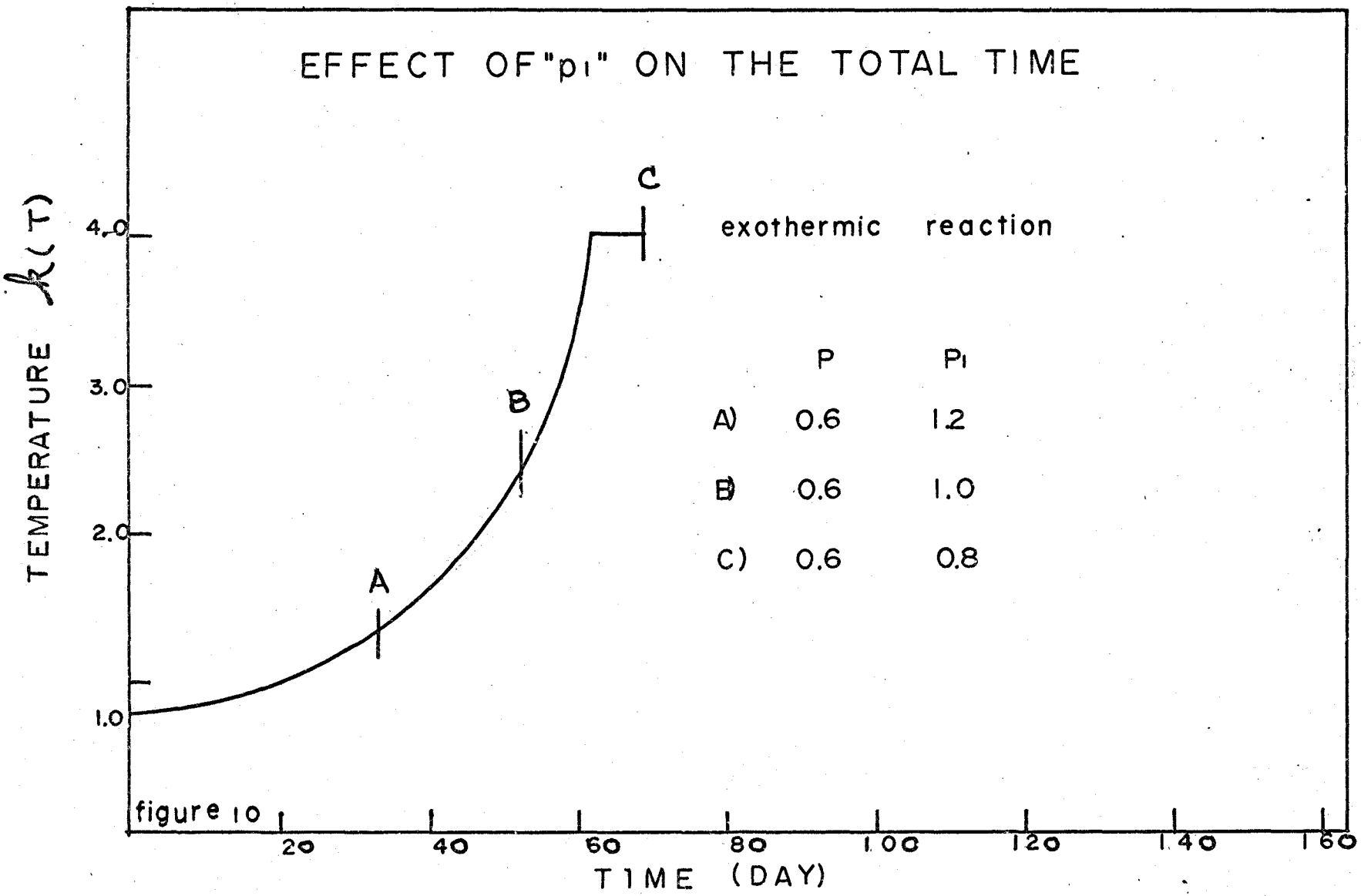

EFFECT OF "p1" ON THE TOTAL TIME
TEMPERATURE k(T)
4.0
3.0
2.0
1.0
A
B
C
exothermic reaction
P
P1
A) 0.6 1.2
B) 0.6 1.0
C) 0.6 0.8
20
40
60
80
100
120
140
160
TIME (DAY)

figure 10

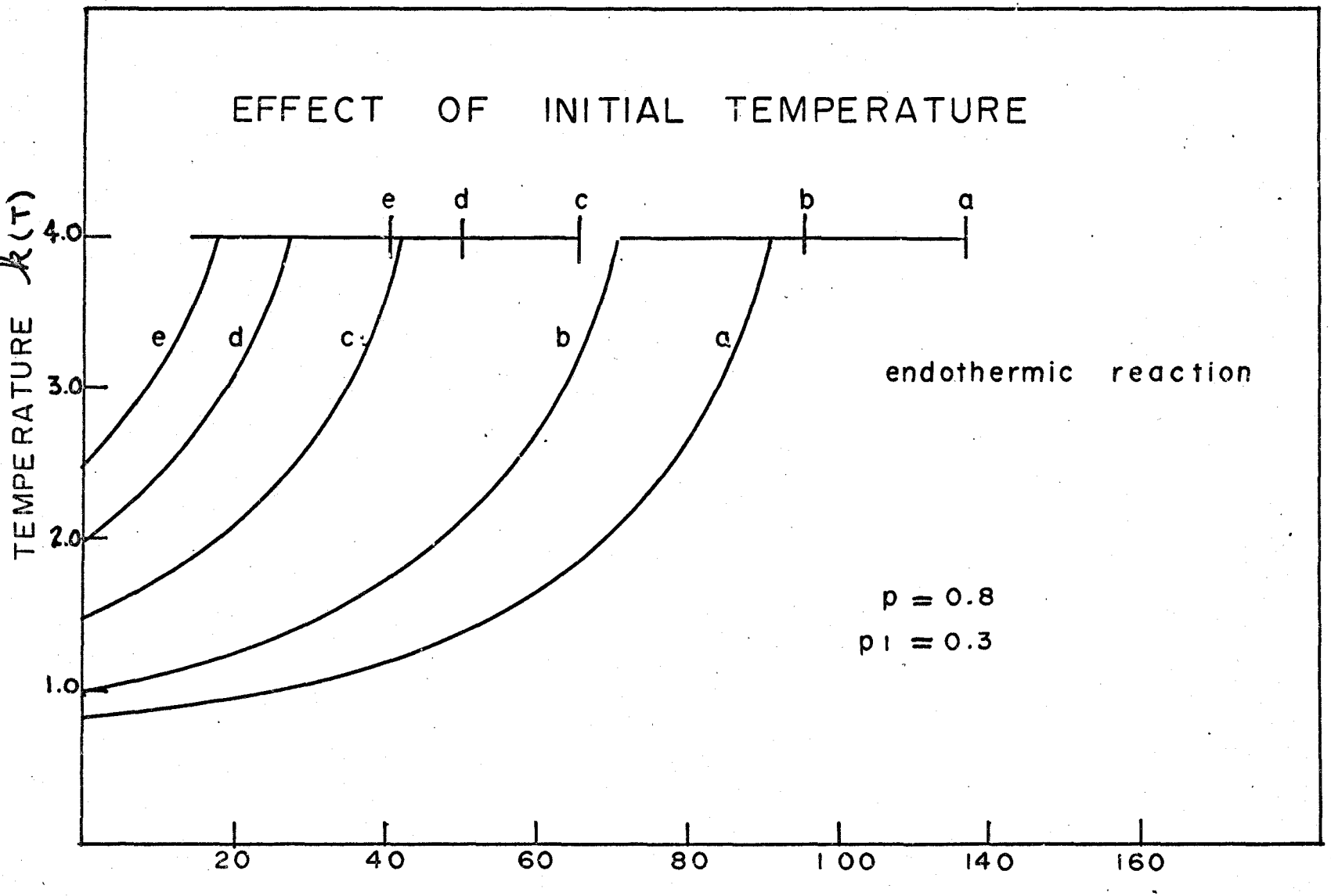

EFFECT OF INITIAL TEMPERATURE
TEMPERATURE R(T)
4.0
3.0
2.0
1.0
e
d
c
b
a
endothermic reaction
p = 0.8
p1 = 0.3
20
40
60
80
100
140
160
TIME

figure 11

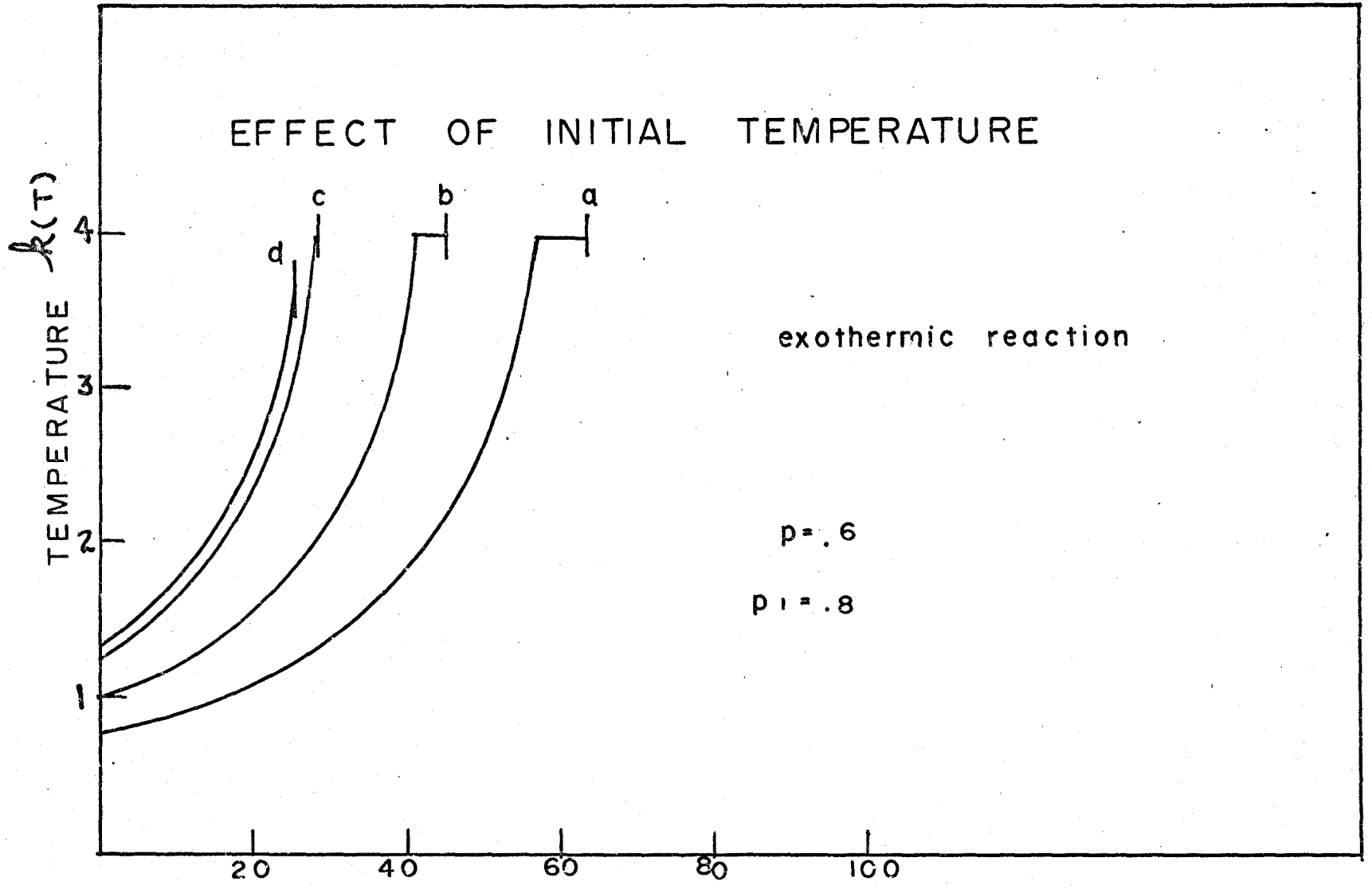

EFFECT OF INITIAL TEMPERATURE
TEMPERATURE R(T)
4
3
2
1
a
b
c
d
exothermic reaction
p = .6
p1 = .8
20
40
60
80
100
TIME

figure 12

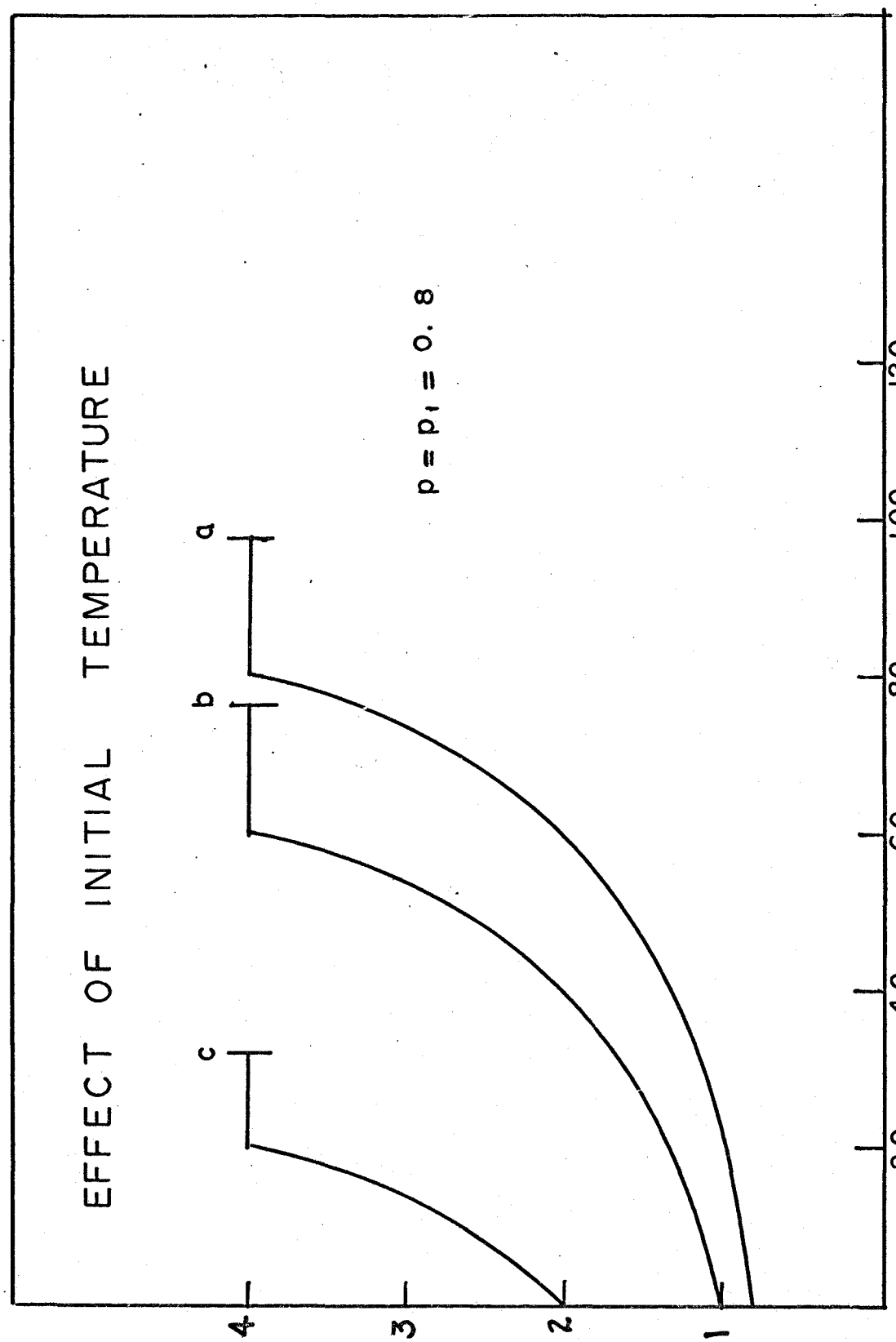

EFFECT OF INITIAL TEMPERATURE
$p = p_1 = 0.8$
a
b
c
TEMPERATURE $\gamma(T)$
1
2
3
4
20
40
60
80
100
120
TIME

figure 13

C) Endothermic Reaction

Figure 14 is the temperature profile with time which satisfies the conditions of optimality given by Pontryagin's Maximum Principle.

Figure 15 shows the equilibrium conversion and also the conversion (exit conversion) with time. Notice that when the upper temperature constraint is reached, the equilibrium conversion remains constant, but the conversion decrease because the temperature cannot be increased any more. However even if $(X_{AE} - X)$ increases rapidly after the temperature has hit the constraint, the rate now decreases, because the activity is decreasing faster than $(X_{AE} - X)$ does (Figure 16).

Figure 17 indicates that no matter what the initial temperature is, the initial conversion will always be greater than the Hamiltonian. The initial temperature of a stationary policy may be arbitrarily near the upper temperature constraint. This is explained theoretically because $\frac{\partial X}{\partial k}$ is always positive for an endothermic reaction.

Notice that Figure 17 is linear with k but has an exponential shape with temperature.

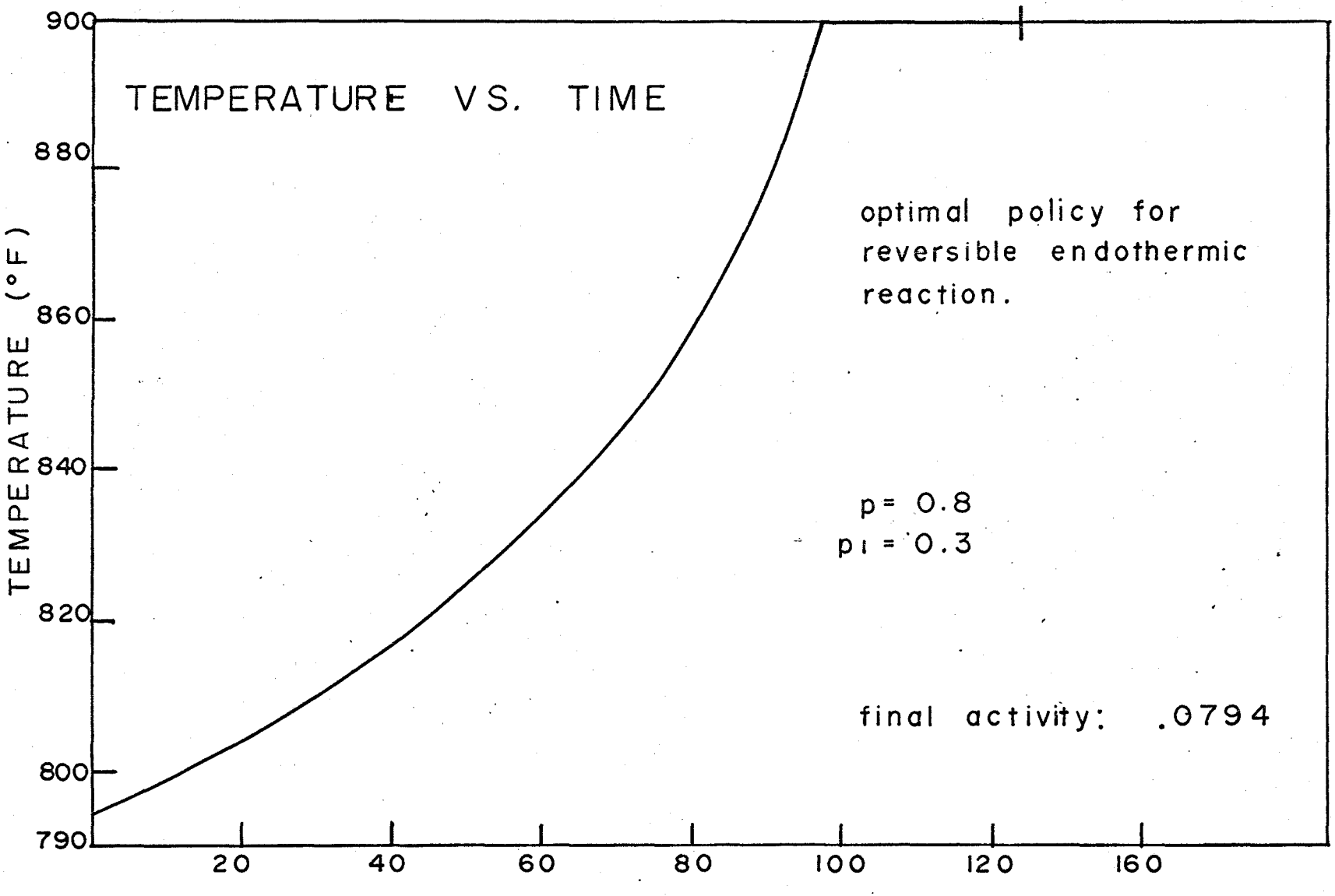

TEMPERATURE VS. TIME
optimal policy for reversible endothermic reaction.
p= 0.8
p1 = 0.3
final activity: .0794
TEMPERATURE (°F)
900
880
860
840
820
800
790
20
40
60
80
100
120
160
TIME (DAY)

figure 14

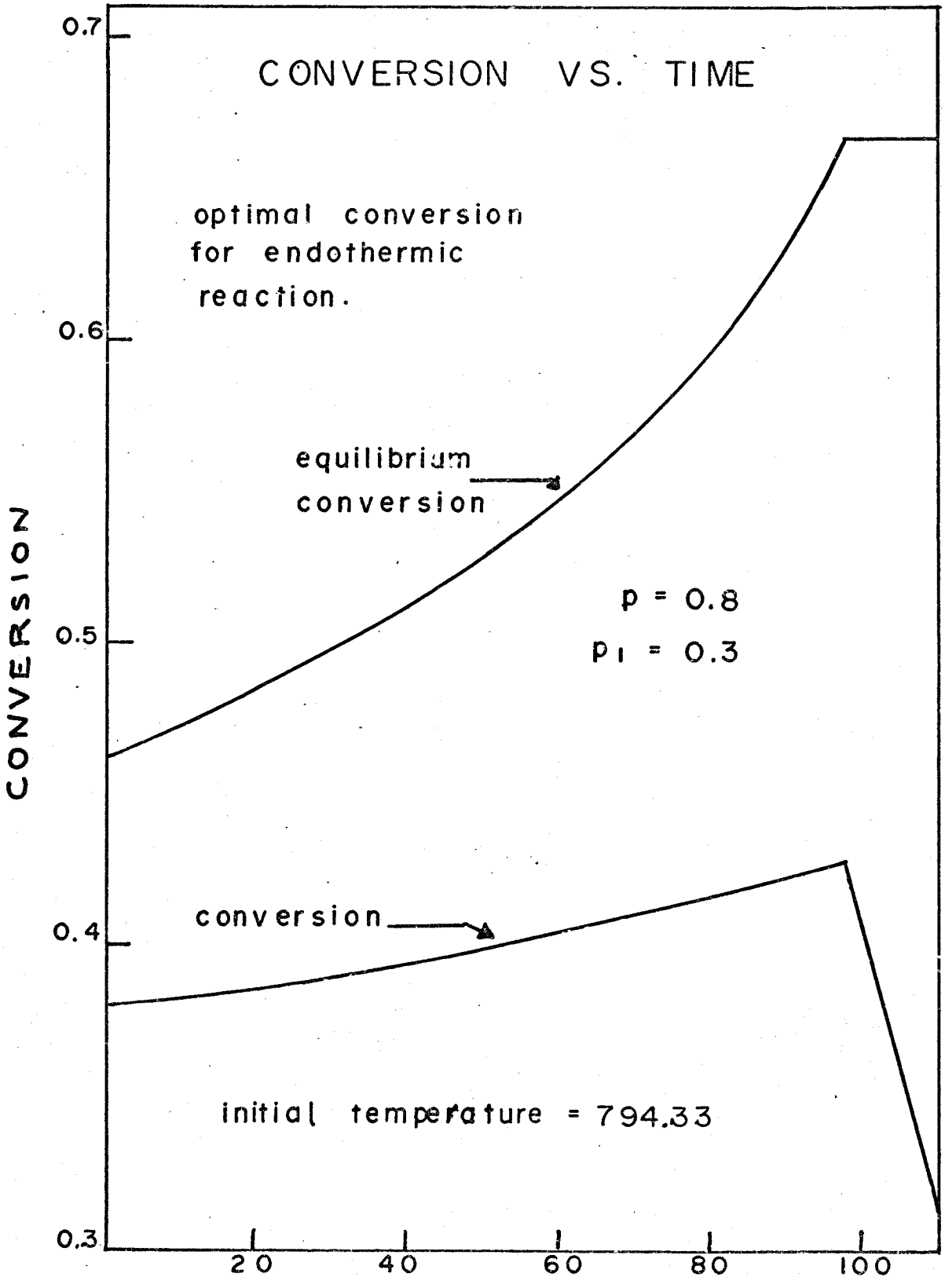

CONVERSION VS. TIME
optimal conversion for endothermic reaction.
equilibrium conversion
conversion
p = 0.8
p1 = 0.3
initial temperature = 794.33
CONVERSION
TIME
0.7
0.6
0.5
0.4
0.3
20
40
60
80
100

figure 15

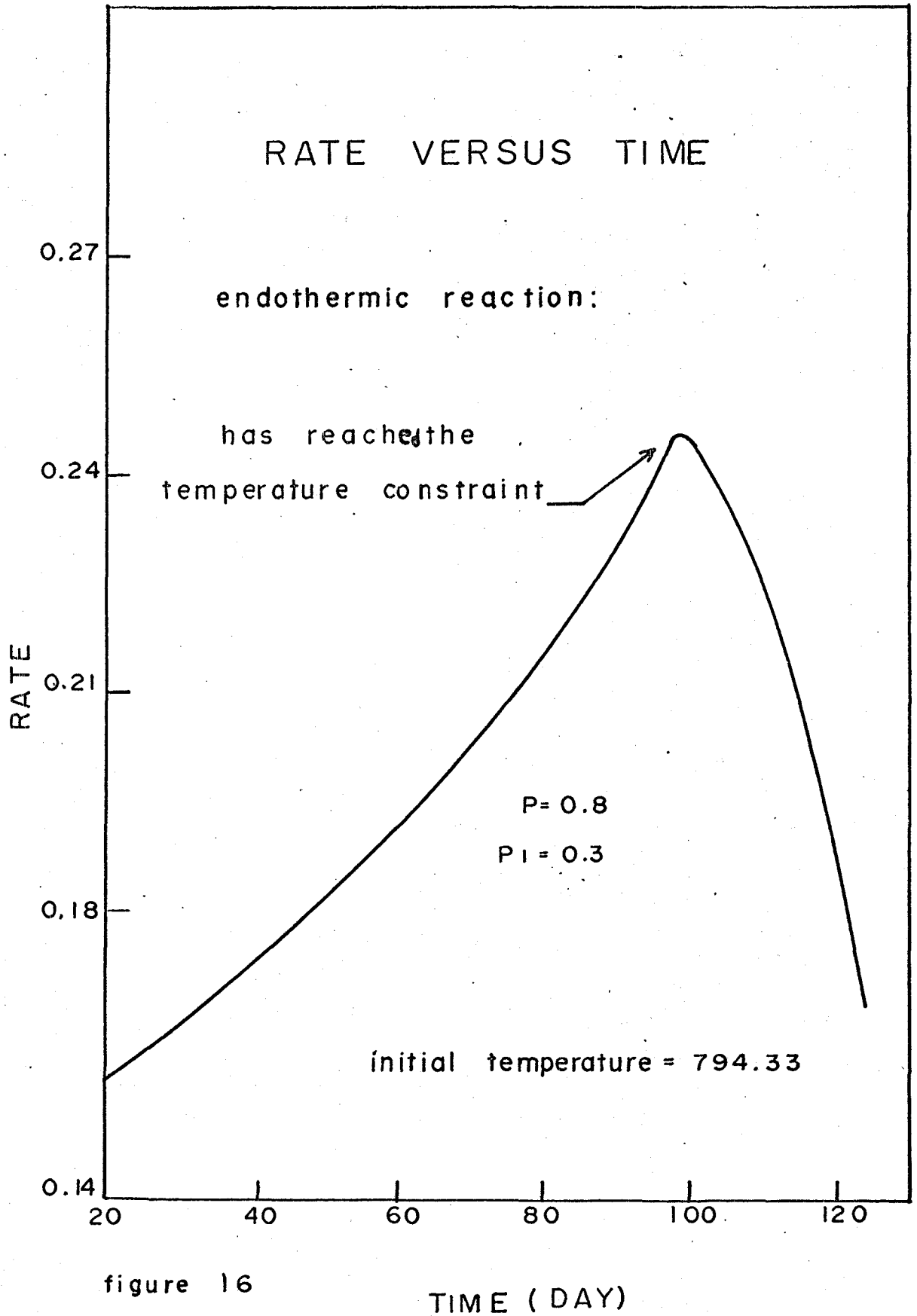

RATE VERSUS TIME
endothermic reaction:
has reached the
temperature constraint
P= 0.8
P1 = 0.3
initial temperature = 794.33
RATE
0.27
0.24
0.21
0.18
0.14
20
40
60
80
100
120
TIME (DAY)

figure 16

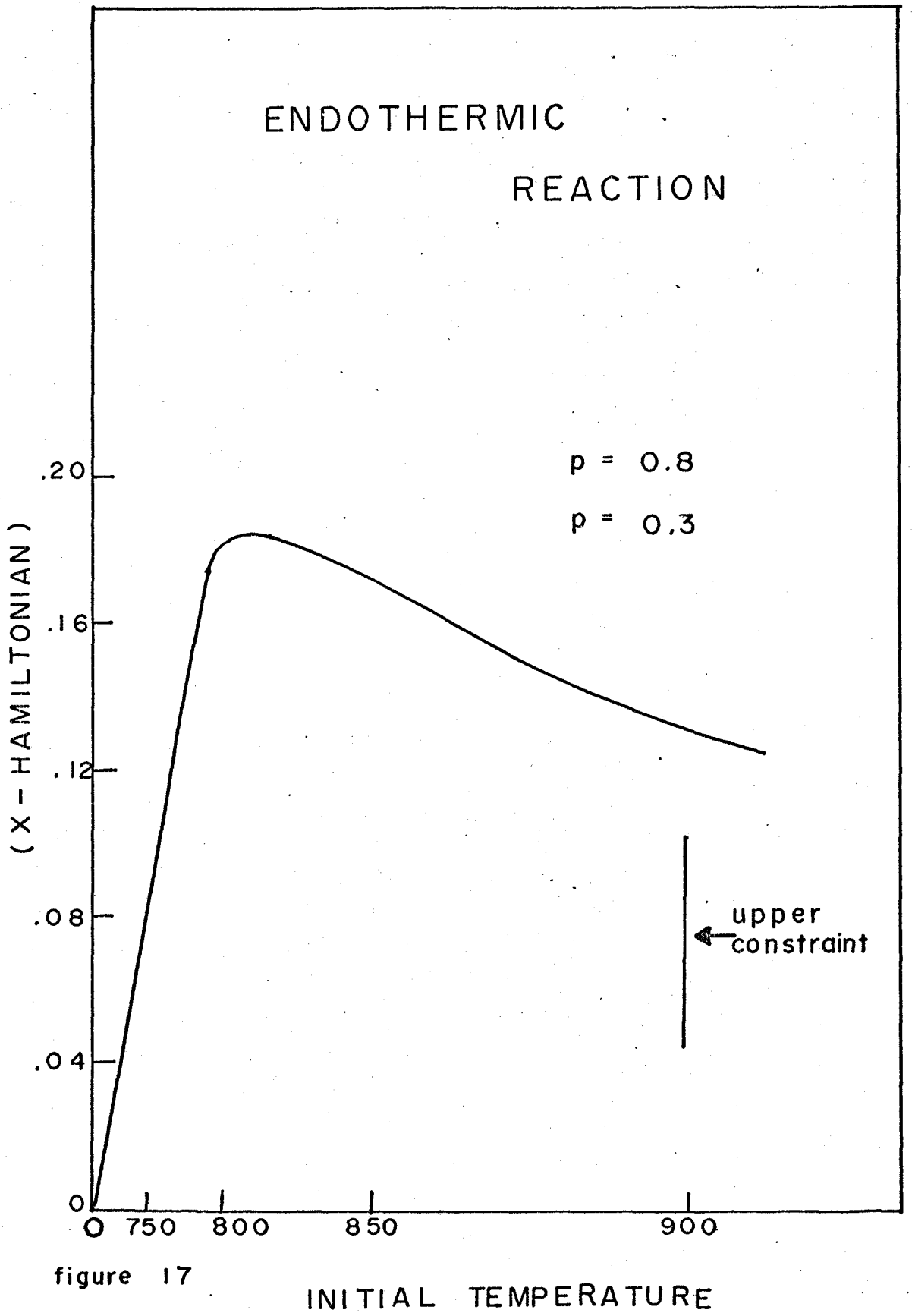

ENDOTHERMIC
REACTION
p = 0.8
p = 0.3
.20
.16
.12
.08
.04
0
(X - HAMILTONIAN)
upper
constraint
0
750
800
850
900
INITIAL TEMPERATURE

figure 17

D) Exothermic Reactions

The graph of conversion versus the rate of decay on Figure 18 is typical for p less than 1, having no inflexion point, and the point of tangency at k = 0; so there is no lower bound on initial starting temperature.

Figure 19 shows an upper bound of approximately 850°F on the initial temperature, where above that point, the initial conversion becomes lower than the Hamiltonian, which is not permissible. Figure 20 is the optimal temperature profile for an exothermic reversible reaction.

On Figures 21 and 22, the conversion and the rate show the inverse phenomena as observed for an endothermic reaction, which is reasonable.

Figure 23 compares the temperature profile for a first order reaction in both directions with a first order reaction forward and a second order reaction backward. Notice that for an order (1-2), the temperature rises more slowly but the operating time is longer. From this it is predictable that for an order (2-1) of reaction, the temperature would have to rise faster but for a shorter operating time.

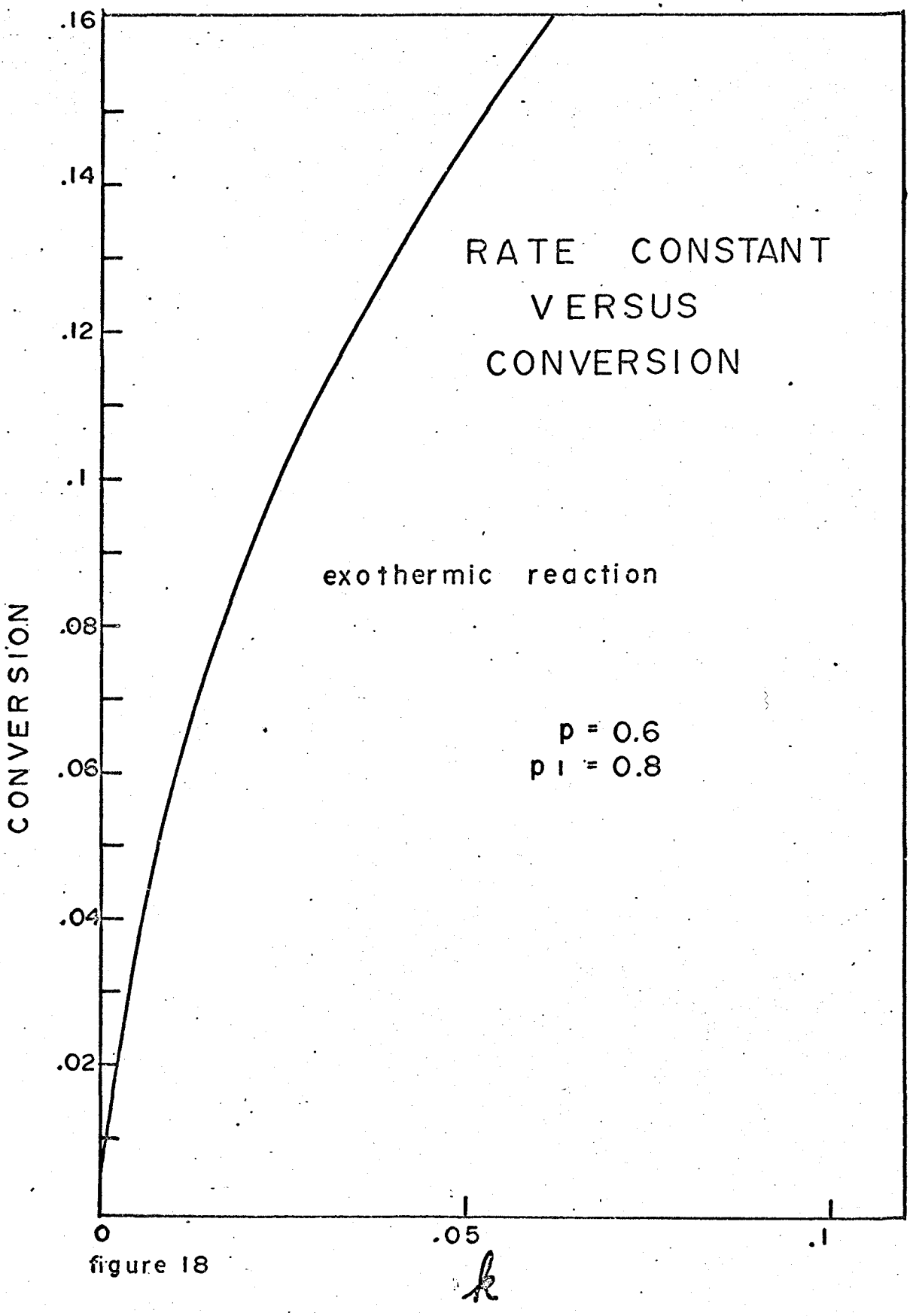

RATE CONSTANT
VERSUS
CONVERSION
exothermic reaction
p = 0.6
p1 = 0.8
CONVERSION
.16
.14
.12
.1
.08
.06
.04
.02
0
.05
.1
k

figure 18

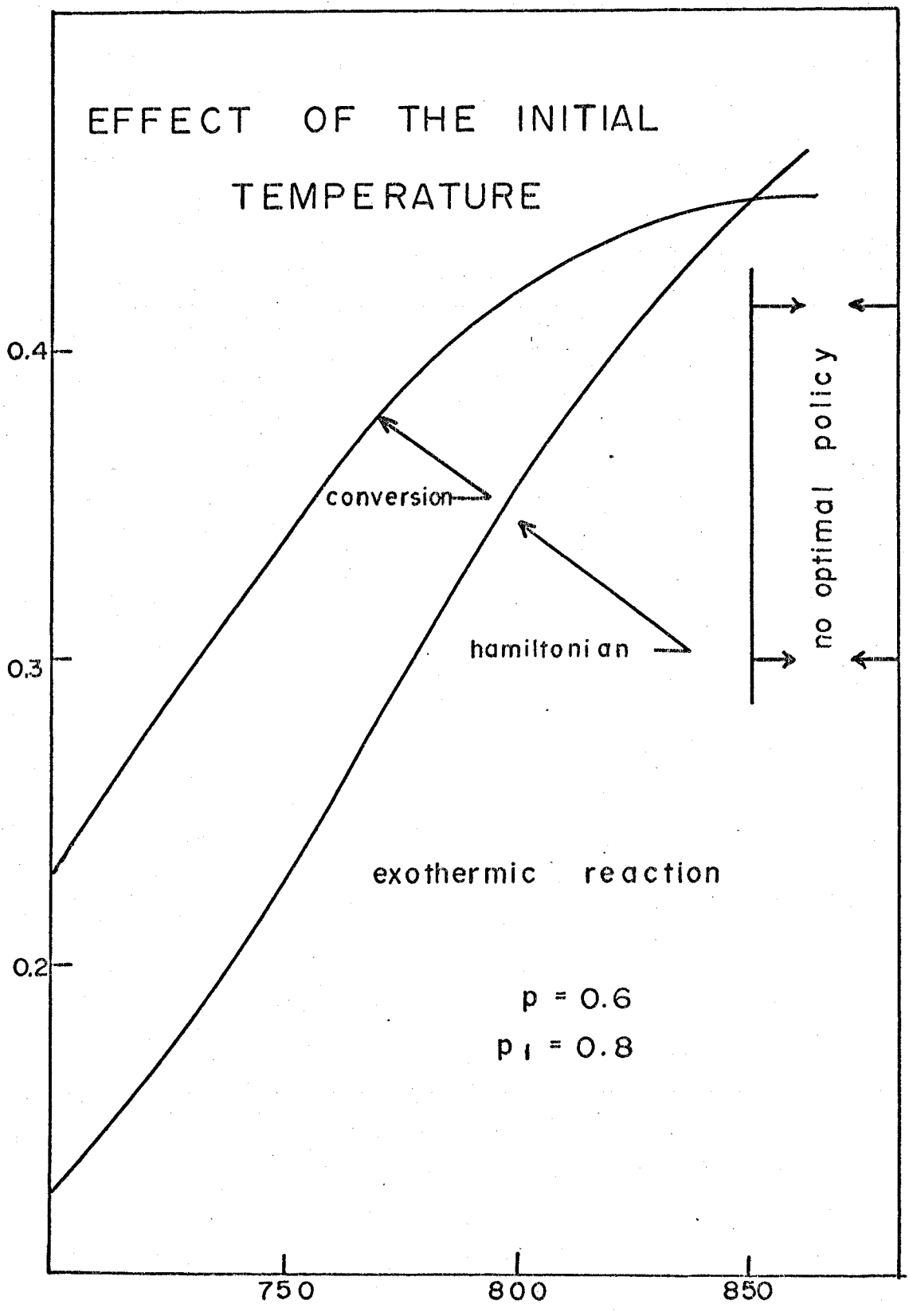

EFFECT OF THE INITIAL TEMPERATURE
0.4
0.3
0.2
conversion
hamiltonian
no optimal policy
exothermic reaction
p = 0.6
p1 = 0.8
750
800
850
INITIAL TEMPERATURE (°F)

figure 19

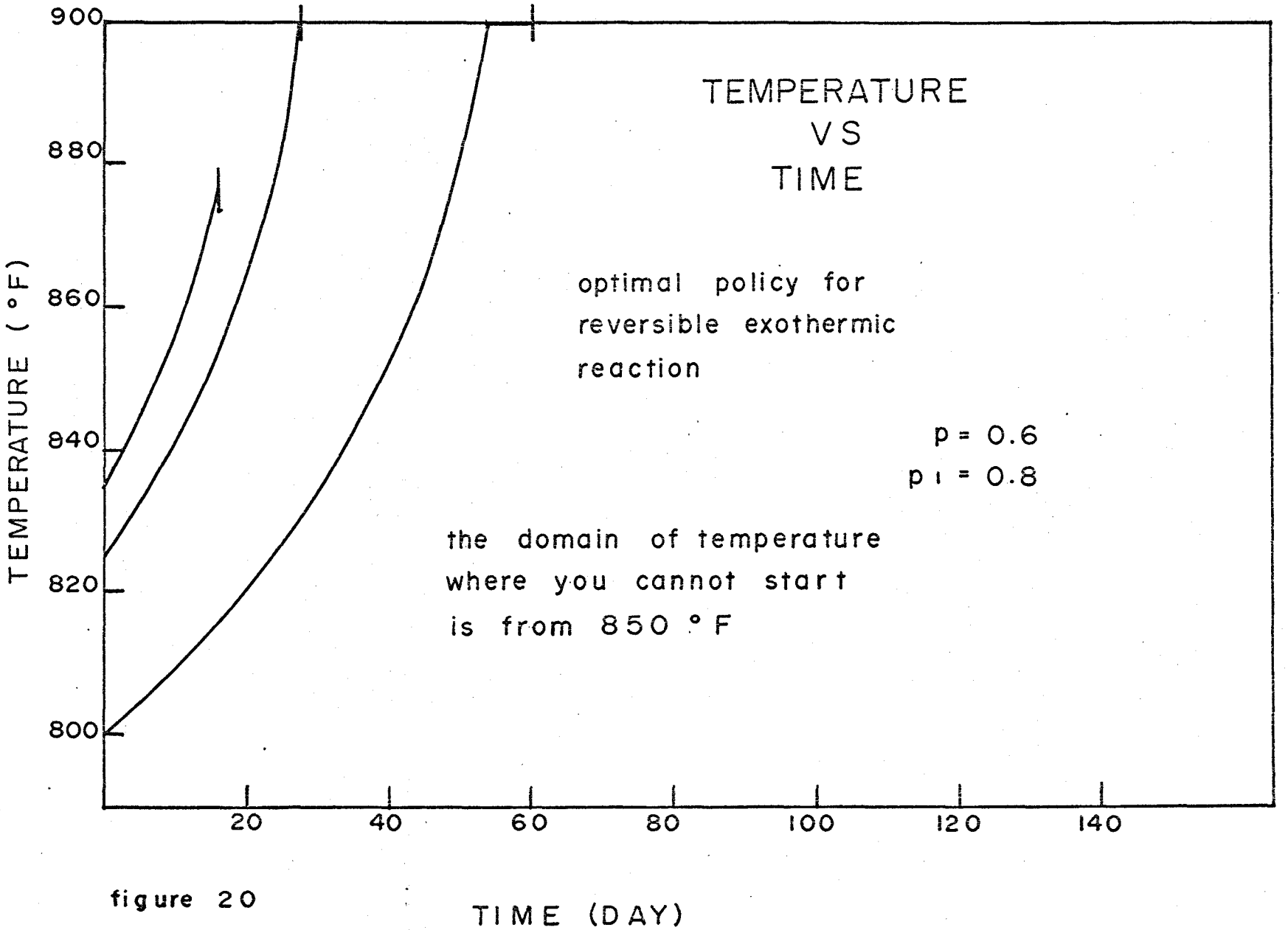

TEMPERATURE
VS
TIME
optimal policy for
reversible exothermic
reaction
p = 0.6
p ı = 0.8
the domain of temperature
where you cannot start
is from 850 °F
TEMPERATURE (°F)
900
880
860
840
820
800
20
40
60
80
100
120
140
TIME (DAY)

figure 20

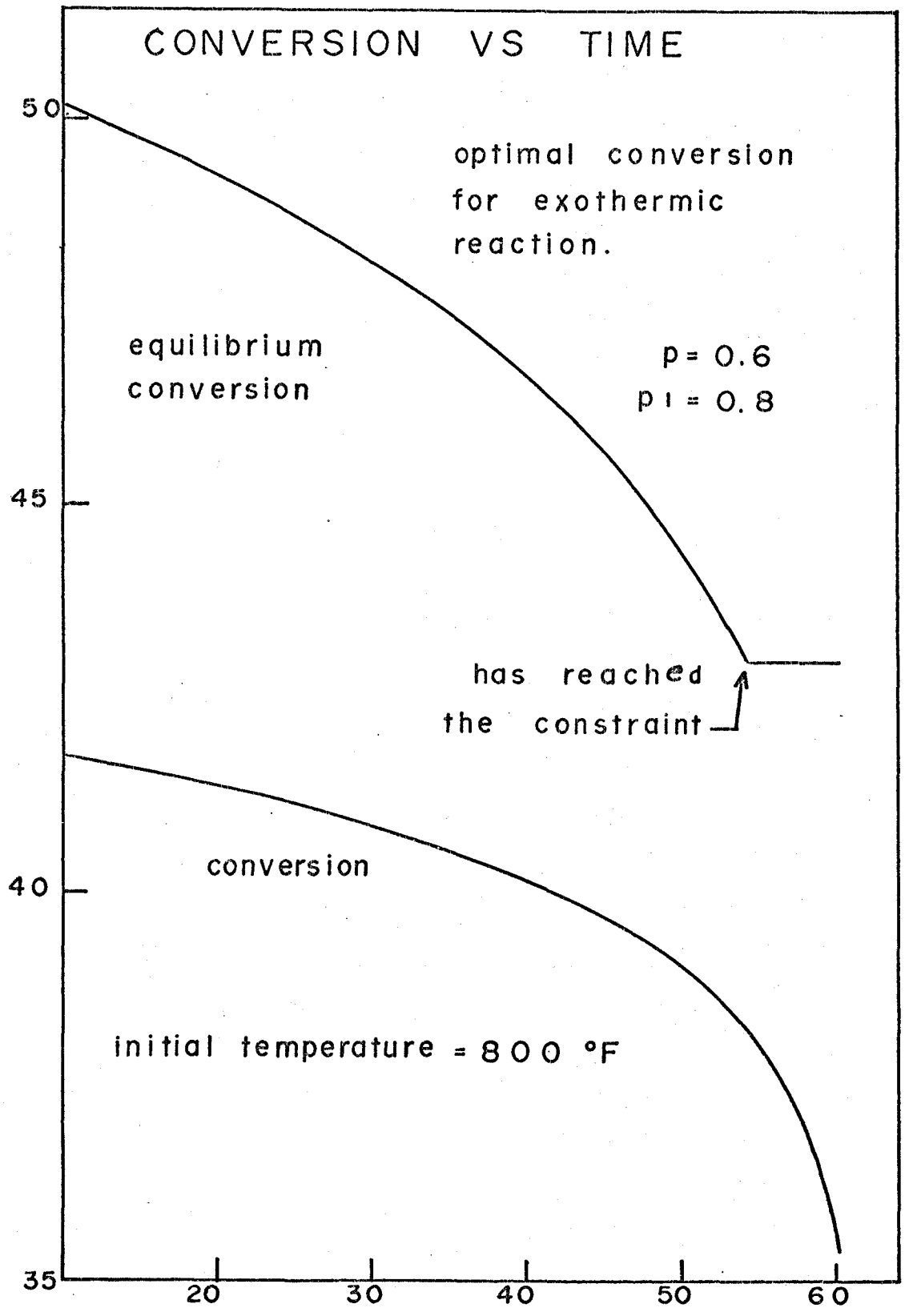

CONVERSION VS TIME
50
45
40
35
optimal conversion
for exothermic
reaction.
equilibrium
conversion
p = 0.6
p1 = 0.8
has reached
the constraint
conversion
initial temperature = 800 °F
20
30
40
50
60
TIME (DAY)

figure 21

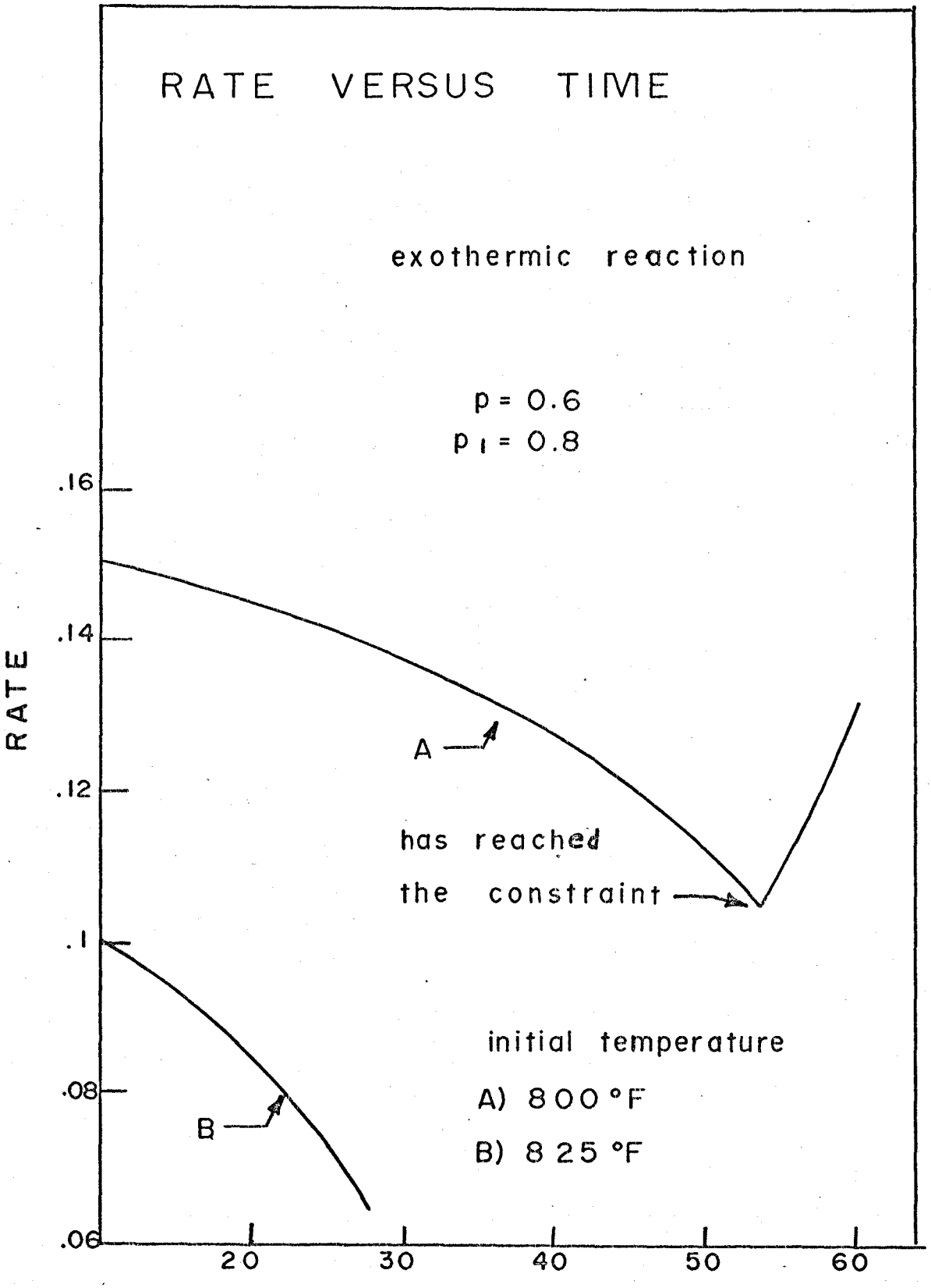

RATE VERSUS TIME
exothermic reaction
p = 0.6
p1 = 0.8
.16
.14
.12
.1
.08
.06
RATE
A
has reached
the constraint
initial temperature
A) 800 °F
B) 825 °F
B
20
30
40
50
60
TIME (DAY)

figure 22

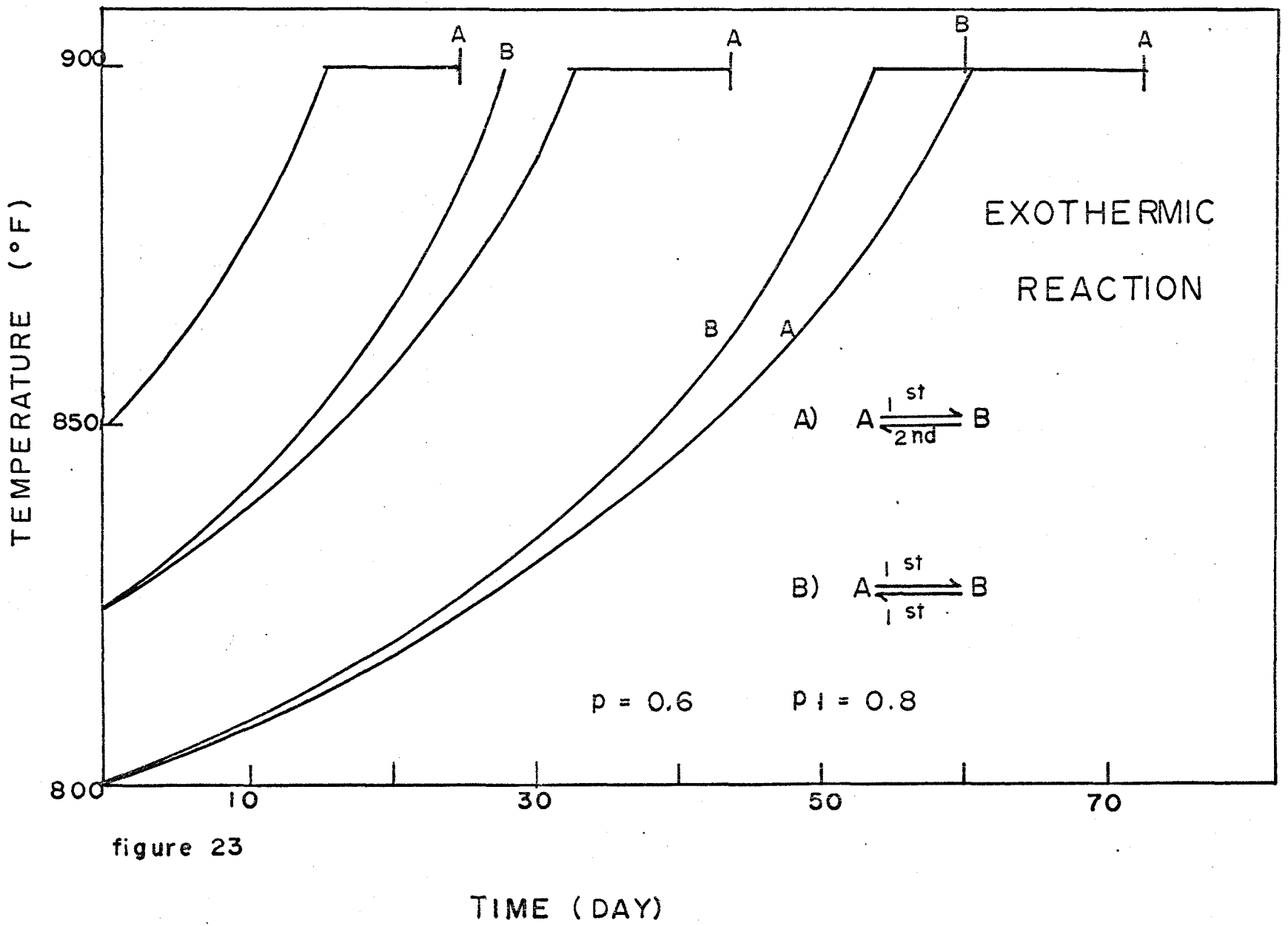

900
850
800
TEMPERATURE (°F)
10
30
50
70
TIME (DAY)
A
B
A
B
A
B
A
EXOTHERMIC
REACTION
A) A 1st 2nd B
B) A 1st 1st B
p = 0.6
p' = 0.8

figure 23

4.3 Conclusion and Discussion

Endothermic and exothermic reactions have a different behavior with respect to the starting temperature. Exothermic reactions are subject to a lower and an upper bound on the initial starting temperature while endothermic reactions have only a lower bound on the initial temperature, different from the bound imposed on the reactor. These bounds are also more restrictive on the initial starting temperature than the domain of temperature where $\frac{\partial^2 X}{\partial k^2} \leq 0$

For first order reactions, theoretical developments based on the maximum principle of Pontryagin have yielded such interesting conclusions as:

1. For endothermic reactions, the optimal temperature policy must always reach the upper temperature constraint while for exothermic reactions this is not necessary. This is easily extrapolated for any order of reaction.
2. For exothermic reactions, there exists a range of initial temperatures outside of which no optimal policy can start and it also excludes the isothermal policy on the upper temperature constraint.

Complete numerical solutions are given for reaction orders (1-1) and (1-2) using a simple algorithm.

The results shown are significant in the sense that much consideration should be devoted to the initial temperature at which to start a reactor.

The first kinetic model used of order (1-1) has always given the optimal policy.

However for a reaction order (1-2) in some cases even for these initial temperatures where the initial Hamiltonian was positive and greater than the initial conversion, this method was not able to find an optimal policy because after a small time increment the Hamiltonian decreases; and increasing or decreasing the temperature would decrease the Hamiltonian again. There seems to be no optimal policy for these starting temperatures, probably due to the high sensitivity of the Hamiltonian with respect to the conversion.

The programming method is very general and could be used for other kinetic models by making few changes in the listing.

SECTION V

SUMMARY AND FUTURE WORK

The problem of choosing a temperature policy with time to maximize the total conversion over a fixed total time τ in a reactor with uniform temperature and decaying catalyst has been solved. The reaction is reversible and has a factorable rate of decay which is independent of conversion, but the rate equation is not factorable.

The stationary policy is no longer constant conversion as it was for irreversible reactions, except for $p = p_1$, but it has to follow the equilibrium conversion more or less closely.

Fixing the initial temperature is equivalent to fixing the total time, so for each initial temperature there corresponds one and only one total time, the policy is unique for each value of τ and is a continuous function of time. The higher the initial temperature or X_s is, the lower the total time of operation is.

Future work could be done with the rate of catalyst decay expressed as a function of conversion, activity, and temperature. The derivations will not be the same because the function describing the activity with time would be a partial derivative.

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NOMENCLATURE

E - activation energy for reaction (E) and decay (E_C)

g - activity-dependent factor in decay rate, $0 \leq g(\psi) \leq 1$

H - Hamiltonian function

k - rate constant of decay rate, $k=k(T)$, also decision variable

K - rate constant of reaction rate, $K \sim k^p$

K_{EQ} - equilibrium rate constant

p - ratio E_1/E_C

p_1 - ratio E_2/E_C

S - stationary policy

t - time on stream

T - temperature

X - conversion of reaction, $0<X\leq 1$

X_o - inlet conversion

Z - space time through reactor $0 \leq \theta \quad (\theta \equiv 1)$

θ - space time of reactor $\equiv 1$

μ - adjoint variable to ψ

τ - total reaction time

ρ - rate of reaction

ϕ - rate of decay

ψ - catalyst activity, $\leq \psi_I$

u - order of the forward reaction

w - order of the backward reaction

Subscripts

f - final value, at $t = \tau$

S - value along arc of policy S

I - initial value

* - minimum attainable value

Superscripts

+ - value along optimal policy

* - maximum attainable value

APPENDIX

A.1 Proof that for constant inlet conversion, the Hamiltonian is constant with time.

From Equations (3.2.1), (3.2.2), (3.2.3), and (3.2.5) the time derivative of H along any optimal path is in general

$$\frac{\partial H}{\partial t} = \frac{\partial H}{\partial \psi}\frac{d\psi}{dt} + \frac{\partial H}{\partial \mu}\frac{d\mu}{dt} + \frac{\partial H}{\partial X_o}\frac{dX_o}{dt} + \frac{\partial H}{\partial k}\frac{dk}{dt}$$

The fourth term is always zero because on a stationary policy, the Hamiltonian is maximized with respect to the control k so $\frac{\partial H}{\partial k} = 0$ and on a constrained policy $\frac{dk}{dt} = 0$. Then

$$\frac{dH}{dt} = -kg(\psi)\frac{\partial H}{\partial \psi} + \frac{\partial H}{\partial \mu}\left(-\frac{\partial X}{\partial \psi} - \mu\frac{\partial \phi}{\partial \psi}\right) + \frac{\partial H}{\partial X_o}\frac{dX_o}{dt}$$

By Equation (3.2.5)

$$\frac{\partial H}{\partial \psi} = \frac{\partial X}{\partial \psi} + \mu\frac{\partial \phi}{\partial \psi}$$

and

$$\frac{\partial H}{\partial \mu} = \phi = -kg(\psi)$$

Therefore

$$\frac{dH}{dt} = -kg(\psi)\left[\frac{\partial X}{\partial \psi} + \mu\frac{\partial \phi}{\partial \psi}\right] - \frac{\partial H}{\partial \mu}\left[\frac{\partial X}{\partial \psi} + \mu\frac{\partial \phi}{\partial \psi}\right] + \frac{\partial H}{\partial X_o}\frac{dX_o}{dt}$$

$$\frac{dH}{dt} = \frac{\partial H}{\partial X_o}\frac{dX_o}{dt} \quad \text{(General)}$$

For constant inlet conversion $\frac{dX_o}{dt} = 0$ and H = constant.

Also from $H = X + \mu\phi$

$$\frac{\partial H}{\partial X_o} = \frac{\partial X}{\partial X_o}$$

and

$$I = \int_{X_o}^{X} \frac{dX}{\psi(K_1+K_2)(X_{AE}-X)}$$

Differentiating both sides with respect to X_o gives

$$\frac{\partial X}{\partial X_o} = \frac{\rho\ (X)}{\rho\ (X_o)}$$

and then

$$\frac{dH}{dt} = \frac{\rho(X)}{\rho(X_o)} \frac{dX_o}{dt}$$

A4312.
RUN(S)
SETINDF.
REDUCE.
LGO.

APPENDIX A.2.1

```
'       6400 END RECORD
      PROGRAM TST (INPUT,OUTPUT,TAPE5=INPUT,TAPE6=OUTPUT)
C     ****************************************************************
C     ****************************************************************
*     CATALYST DECAY REACTOR SINGLE BED (OPTIMAL POLICY ) WRITTEN BY
*     JEAN-GUY DROUIN MC.MASTER UNIVERSITY THE 4 TH. MARCH 1969
*     EQUATION USED$D(PSI)/DT=-K*PSI**M      PSI*KK=INT(DX/(1-X)**N)
C     ****************************************************************
C     ****************************************************************
C     ******************     SYMBOLS      ****************************
C     ****************************************************************
C     AKU= INITIAL RATE CONSTANT OF DECAY RATE
C     AKKU= INITIAL RATE CONSTANT OF REACTION
C     AKI= MINIMUM RATE CONSTANT OF DECAY RATE
C     AKKI= MINIMUM RATE CONSTANT OF REACTION
C     AKU= MAXIMUM RATE CONSTANT OF DECAY RATE
C     AKKU= MAXIMUM RATE CONSTANT OF REACTION
C     EC= ACTIVATION ENERGY   EC/R
C     XA= MAXIMUM CONVERSION   (ACTIVITY=1.0 WITH MAX. TEMPERATURE )
C     TETA= SPACE TIME OF REACTOR
C     XE= INITIAL CONVERSION
C     M= ORDER OF DECAY RATE
C     N= ORDER OF REACTION
C     P= RATIO E/EC
C     TO= MAXIMUM TEMP.(K) CORRESPONDING TO AKU
C     PSI= INITIAL ACTIVITY
C     PSIO= INITIAL ACTIVITY ON THE STATIONARY PATH
C     PSI1= INITIAL ACTIVITY ON THE UPPER CONSTRAINT
C     TAI= TIME ON THE LOWER CONSTRAINT
C     TSOS= TIME SPENT ON THE STATIONARY PATH
C     TOU= TIME ON THE UPPER CONSTRAINT
C     TR= TIME TO REPLACE THE CATALYST
C     ****************************************************************
C     ****************************************************************
      DIMENSION T(8),X(8),PSIT(8),PSIU(8)
      COMMON M,P,AKI,AKU,AKKI,AKKU,PSI,PSIO,PSI1,XE,XS,TETA,PM,EE,N
      COMMON TAI,TSOS,TAUX,AKO,TO,BEAM1,BEAM2,FGH,XY,DEF,FF
       DO 4444 MOOSE=1,10
      READ(5,200)AKU,AKI,EC,XA,PSI,TETA,XE
      READ(5,201)M,N,P,XS,TO
      A=N-1
      B=1.-XS
      C=1.-XE
      D=1.-XA
      EE=M-1
      CD=C**A
      FF=1./(-EE)
      FG=D**A
      DE=B**A
      CDE=ALOG(B)
      DEF=ALOG(C)
      EDC=ALOG(D)
      XY=1./P-M+1.
      IF(N-1)2,3,2
```

```
    2 AKKU=(1./FG-1./CD)/(A*TETA)
      AKK0=(1./DE-1./CD)/(A*PSI*TETA)
      GO TO 4
    3 AKKU=-(EDC-DEF)/TETA
      AKK0=-(CDE-DEF)/(PSI*TETA)
    4 AK0=(AKK0/AKKU)**(1./P)*AKU
      AKKI=(AKI/AKU)**P*AKKU
      IF(AK0-AKI)5,6,6
    5 AK0=AKI
      AKK0=AKKI
*     ON THE LOWER CONSTRAINT TILL X=XS
      GO TO 112
    6 FP=-N*DE
      PM=1./(1.+PSI*AKK0*FP)
      AA=1.+PSI*AKK0*FP
      IF(AA)8,7,7
    7 IF(P-PM)8,9,9
    9 FPXA=-N*FG
      PMXA=1./(1.+AKKU*FPXA*PSI)
      IF(P-PMXA)10,11,11
*     AT 11 THE POLICY IS ON C*U
   11 WRITE(6,300)
      AK0=AKU
      AKK0=AKKU
      GO TO 8
   10 WRITE(6,301)
      WRITE(6,321)
       GO TO 4444
    8 IF(XS-XA)12,12,13
   13 WRITE(6,302)
      AK0=AKU
      PSI0=PSI
      AKK0=AKKU
      PSI1=PSI0
      TAI=0.0
      TSOS=0.0
      GO TO 22
*     FIND PSI0 ON THE STATIONARY PATH=PSI IF NO C*I
   12 TAI=0.0
      PSI0=PSI
      PSI1=AKK0*PSI0/AKKU
      FGH=PSI0**(1./P)
      GO TO 19
  112 IF(N-1)14,15,14
   15 PSI0=(-CDE+DEF)/(TETA*AKK0)
      GO TO 16
   14 PSI0=(1./DE-1./CD)/(TETA*AKK0*A)
   16 FGH=PSI0**(1./P)
      PSI1=AKK0*PSI0/AKKU
*     FIND TAI=0.0 IF NO C*I
      IF(M-1)17,18,17
   18 TAI=1./AKI*ALOG(PSI/PSI0)
      GO TO 19
   17 TAI=(PSI0**(-EE)-PSI**(-EE))/(-EE)/(-AKI)
*     FIND THE TIME ON THE CONSTANT CONVERSION
   19 AAA=1./P-EE
      IF(ABS(AAA)-1.0E-5)20,21,21
   20 TSOS=ALOG(PSI1/PSI0)/(-AK0*FGH)
```

```
      GO TO 22
   21 TSOS=(PSI1**XY-PSI0**XY)/(XY*(-AK0*FGH))
   22 XF=XS-P*AKKU*PSI0*B**N
      IF(XF)50,51,51
   50 WRITE(6,303)
      WRITE(6,321)
      GO TO 4444
*     FIND PSIF BECAUSE AKKU IS CTE.
   51 IF(N-1)60,61,60
   61 PSIF=-(ALOG(1.-XF)-DEF)/(TETA*AKKU)
      GO TO 62
   60 PSIF=(1./(1.-XF)**A-1./CD)/(TETA*AKKU)
*     FIND TOTAL TIME TAUX
   62 IF(M-1)24,23,24
   23 TAUX=TSOS+TAI-ALOG(PSIF/PSI1)*1./AKU
      GO TO 125
   24 TAUX=TSOS+TAI-(PSIF**(-EE)-PSI1**(-EE))/((-EE)*AKU)
*     FIND INTEGRAL OF X DT
  125 WRITE(6,304)PSI,PSI0,PSI1
      WRITE(6,305)P,N,AK0,AKK0
      WRITE(6,306)M,TETA,XA
      WRITE(6,307)PSIF,XF,XS
      TOU=TAUX-TSOS-TAI
      ATOU=TOU/3600.
      ATAI=TAI/3600.
      ATSOS=TSOS/3600.
      ATAUX=TAUX/3600.
      WRITE(6,308)ATAI
      WRITE(6,309)ATSOS
      WRITE(6,310)ATOU
      WRITE(6,311)ATAUX
      WRITE(6,313)
      WRITE(6,312)
      CALL POLCAI(PROFIT)
      WRITE(6,314)
      WRITE(6,312)
      CALL POLCST(EC,DOLLAR)
      WRITE(6,315)
      WRITE(6,312)
      CALL POLCAU(CENT)
      TOTAL=PROFIT+DOLLAR+CENT
      WRITE(6,316)PROFIT
      WRITE(6,317)DOLLAR
      WRITE(6,318)CENT
      WRITE(6,319)TOTAL
      TR=(TOTAL/XF-TAUX)/3600.
      WRITE(6,320)TR
      WRITE(6,321)
       IF(MOOSE-10)4444,4445,4445
 4444 CONTINUE
  200 FORMAT(2E10.3,5F10.0)
  201 FORMAT(2I10,3F10.0)
  300 FORMAT(10X,62HTHE POLICY IS ON THE UPPER CONSTRAINT......P GREATER
     1 THEN PMXA)
  301 FORMAT(10X,55HXS HAS BEEN TAKEN TOO BIG..... P LESS THEN PM AND P
     1MXA)
  302 FORMAT(10X,69HTHE POLICY IS ON THE UPPER CONSTRAINT..... BECAUSE X
     1S GREATER THEN XA)
```

```
  303 FORMAT(10X,75HGIVE THE TOTAL TIME OR CHOOSE A GREATER XS.....BECAU
     1SE XF WOULD BE NEGATIVE)
  304 FORMAT(5X,4HPSI=,F10.5,10X,5HPSI0=,F10.5,10X,5HPSI1=,F10.5)
  305 FORMAT(5X,4H  P=,F10.5,10X,5H   N=,I10,10X,4HAK0=,E12.5,5HAKK0=,E1
     12.5)
  306 FORMAT(5X,4H  M=,I10,10X,5HTETA=,F10.5,10X,4H XA=,F10.5)
  307 FORMAT(5X,5HPSIF=,F10.7,10X,4H XF=,F10.7,10X,4H XS=,F10.5)
  308 FORMAT(10X,38HTIME IN HOURS ON THE LOWER CONSTRAINT=,F15.5)
  309 FORMAT(10X,38HTIME IN HOURS ON THE STATIONARY  PATH=,F15.5)
  310 FORMAT(10X,38HTIME IN HOURS ON THE UPPER CONSTRAINT=,F15.5)
  311 FORMAT(10X,38HTOTAL TIME IN HOURS TO OPERATE        =,F15.5)
  312 FORMAT(12X,8HACTIVITY,16X,8HTIME(HR),16X,10HCONVERSION,16X,14HTEMP
     1ERATURE(K))
  313 FORMAT(5X,23HON THE LOWER CONSTRAINT,//)
  314 FORMAT(5X,22HON THE STATIONARY PATH,//)
  315 FORMAT(5X,23HON THE UPPER CONSTRAINT,//)
  316 FORMAT(10X,31HPROFIT ON THE LOWER CONSTRAINT=,E15.7,/)
  317 FORMAT(10X,32HPROFIT ON THE STATIONARY POLICY=,E15.7,/)
  318 FORMAT(10X,31HPROFIT ON THE UPPER CONSTRAINT=,E15.7,///)
  319 FORMAT(10X,13HTOTAL PROFIT=,E15.7,//)
  320 FORMAT(10X,13HTR. FOR MAX.=,E15.7)
  321 FORMAT(1H1)
 4445 STOP
      END
*
      SUBROUTINE POLCAI(PROFIT)
      DIMENSION T(4),X(4),PSIT(4)
      COMMON M,P,AKI,AKU,AKKI,AKKU,PSI,PSI0,PSI1,XE,XS,TETA,PM,EE,N
      COMMON TAI,TSOS,TAUX,AK0,T0,BEAM1,BEAM2,FGH,XY,DEF,FF
      IF(TAI)1,1,2
    1 PROFIT=0.0
      BEAM1=0.0
      RETURN
    2 L=100
      AN=L
      TI=TAI/AN
      PROFIT=0.0
      B=1./PSI**EE
      C=-EE*AKI
      AM=M
      D=1./(1.-AM)
      AA=ALOG(1.-XE)
      BB=1./(1.-XE)**(N-1)
      T(1)=0.0
      JJ=L/2
      DO 9 J=1,JJ
      DO 8 I=1,3
      IF(M-1)3,4,3
    4 PSIT(I)=PSI*EXP(-AKI*T(I))
      GO TO 5
    3 PSIT(I)=(B+(-C*T(I)))**FF
    5 IF(N-1)6,7,6
    7 X(I)=1.-EXP(AA-PSIT(I)*AKKI*TETA)
      GO TO 10
    6 S=N-1
      X(I)=1.-((S)*TETA*PSIT(I)*AKKI+(1.-XE)**(-S))**(1./(-S))
   10 T(I+1)=T(I)+TI
    8 CONTINUE
```

```
      PROFIT=PROFIT+TI/3.*(X(1)+4.*X(2)+X(3))
      T(1)=T(3)
    9 CONTINUE
      CALL TIMEX(TAI,DTIME)
      TT=0.0
      DO 21 J=1,100
      I=1
      IF(TT-TAI)22,28,28
   22 IF(M-1)23,24,23
   24 PSIT(I)=PSI*EXP(-AKI*TT)
      GO TO 25
   23 PSIT(I)=(B+(-C*TT))**FF
   25 IF(N-1)26,27,26
   27 X(I)=1.-EXP(AA-PSIT(I)*AKKI*TETA)
      GO TO 30
   26 X(I)=1.-((-S)*TETA*PSIT(I)*AKKI+(1.-XE)**(-S))**(1./(-S))
   30 ATT=TT/3600.
      WRITE(6,321)PSIT(I),ATT,X(I)
      TT=TT+DTIME
      IF(J-100)21,15,15
   21 CONTINUE
   28 BEAM1=TT
      TT=TAI
      J=100
      GO TO 22
   15 RETURN
  321 FORMAT(10X,F12.5,10X,F12.5,10X,F12.5)
      END
*
      SUBROUTINE POLCST(EC,DOLLAR)
      COMMON M,P,AKI,AKU,AKKI,AKKU,PSI,PSI0,PSI1,XE,XS,TETA,PM,EE,N
      COMMON TAI,TSOS,TAUX,AK0,T0,BEAM1,BEAM2,FGH,XY,DEF,FF
      IF(TSOS)27,27,28
   27 DOLLAR=0.0
      BEAM2=BEAM1
      RETURN
   28 R=1.0
      BB=-AK0*FGH*XY
      CTE=PSI1*AKKU
      AA=PSI0**XY
      BBB=P*M-(1.+P)
      DOLLAR=XS*TSOS
      CALL TIMEX(TSOS,DTIME)
      CALL TIMO(BEAM1,DTIME,TAI,T)
      DO 50 I=1,100
      IF(T-TAI-TSOS)31,39,39
   31 IF(ABS(BBB)-1.E-5)33,34,34
   33 PSITT=PSI0*EXP(-AK0*FGH*(T-TAI))
      GO TO 35
   34 PSITT=(AA+BB*(T-TAI))**(1./XY)
   35 AKK=CTE/PSITT
      TEMP=T0/(1.-R*T0/(EC*P)*ALOG(AKK/AKKU))
      CCT=T/3600.
      WRITE(6,322)PSITT,CCT,XS,TEMP
      T=T+DTIME
      IF(I-100)50,37,37
   50 CONTINUE
   39 BEAM2=T
```

```
      T=TAI+TSOS
      I=100
      GO TO 31
   37 RETURN
  322 FORMAT(10X,F12.5,10X,F12.5,10X,F12.5,10X,F12.5)
      END
*
      SUBROUTINE POLCAU(CENT)
      DIMENSION PSIU(4),X(4),T(4)
      COMMON M,P,AKI,AKU,AKKI,AKKU,PSI,PSI0,PSI1,XE,XS,TETA,PM,EE,N
      COMMON TAI,TSOS,TAUX,AK0,T0,BEAM1,BEAM2,FGH,XY,DEF,FF
      L=100
      AN=L
      TI=(TAUX-TSOS-TAI)/AN
      CENT=0.0
      T(1)=TSOS+TAI
      AA=PSI1**(-EE)
      CC=DEF
      JJJ=L/2
      DO 39 J=1,JJJ
      DO 38 I=1,3
      IF(M-1)33,34,33
   34 PSIU(I)=PSI1*EXP((T(I)-TSOS-TAI)*(-AKU))
      GO TO 35
   33 PSIU(I)=(AA+(EE*AKU)*(T(I)-TAI-TSOS))**FF
   35 IF(N-1)36,37,36
   37 X(I)=1.-EXP(CC-TETA*PSIU(I)*AKKU)
      GO TO 410
   36 S=N-1
      X(I)=1.-((S)*TETA*PSIU(I)*AKKU+(1.-XE)**(-S))**(1./(-S))
  410 T(I+1)=T(I)+TI
   38 CONTINUE
      CENT=CENT+TI/3*(X(1)+4.*X(2)+X(3))
      T(1)=T(3)
   39 CONTINUE
      TIME=TAUX-TSOS-TAI
      CALL TIMEX(TIME,DTIME)
      SOS=TAI+TSOS
      CALL TIMO(BEAM2,DTIME,SOS,TT)
      I=1
      DO 41 J=1,100
      IF(TT-TAUX)42,48,48
   42 IF(M-1)43,44,43
   44 PSIU(I)=PSI1*EXP((TT-TSOS-TAI)*(-AKU))
      GO TO 145
   43 PSIU(I)=(AA+(EE*AKU)*(TT-TAI-TSOS))**FF
  145 IF(N-1)46,47,46
   47 X(I)=1.-EXP(CC-TETA*PSIU(I)*AKKU)
      GO TO 411
   46 X(I)=1.-((S)*TETA*PSIU(I)*AKKU+(1.-XE)**(-S))**(1./(-S))
  411 BBTT=TT/3600.
      WRITE(6,323)PSIU(I),BBTT,X(I)
      TT=TT+DTIME
      IF(J-100)41,45,45
   41 CONTINUE
   48 TT=TAUX
      J=100
      GO TO 42
```

```
   45 RETURN
  323 FORMAT(10X,F12.5,10X,F12.5,10X,F12.5)
      END
*
      SUBROUTINE TIMEX(TIME,DTIME)
      DIMENSION NO(15)
      IF(TIME-10*3600.)7,8,8
    8 CHECK=TIME/(10.*3600.)
      NO(1)=IFIX(CHECK)
      DO 1 IN=2,15
      NO(IN)=NO(IN-1)/10.
      IF(NO(IN))2,2,1
    1 CONTINUE
      WRITE(6,324)
      STOP
    2 NXX=10**(IN-2)
      NUM=NO(IN-1)*NXX
      NOM=NUM+NXX
      ANUM=NUM
      DIFF1=(CHECK-ANUM-0.5*NXX)
      IF(DIFF1)3,4,4
    3 DTIME=ANUM
      GO TO 5
    4 ANOM=NOM
      DTIME=ANOM
      GO TO 5
    7 DTIME=3600.0
      RETURN
    5 DTIME=DTIME*3600.0
      RETURN
  324 FORMAT(10X,14HERROR IN TIMEX)
      END
*
      SUBROUTINE TIMO(BEAM,DTIME,SOS,T)
      DO 99 KK=1,10000
      IF(BEAM-SOS)55,77,77
   77 BEAM=BEAM-DTIME
   99 CONTINUE
   55 T=BEAM+DTIME
      RETURN
      END
*
'        6400 END RECORD
 1.160E-06 3.540E-09 15000.    0.9        1.0        1.0        0.0
         0          1  0.5     0.557     900.0
 1.160E-06 3.540E-09 15000.    0.9        1.0        1.0        0.0
         0          1   1.0     0.250     900.0
 1.160E-06 3.540E-09 15000.    0.9        1.0        1.0        0.0
         0          1  1.5     0.532     900.0
 1.160E-06 3.540E-09 15000.    0.9        1.0        1.0        0.0
         0          1   0.5       0.9    900.0
 1.160E-06 3.540E-09 15000.    0.9        1.0        1.0        0.0
         0          1   0.1     0.673     900.0
 1.160E-06 3.540E-09 15000.    0.9        1.0        1.0        0.0
         0          1   1.5       .761    900.0
 1.160E-06 3.540E-09 15000.    0.9        1.0        1.0        0.0
         0          1 1.0       0.9       900.0
'        6400 END FILE
```

A4312,LC4000,T200.
RUN(S)
SETINDF.
REDUCE.
LGO.

APPENDIX A.2.2.

```
'         6400 END RECORD
      PROGRAM TST (INPUT,OUTPUT,TAPE5=INPUT,TAPE6=OUTPUT)
C     ***************************************************************
C     ***************************************************************
C     THIS PROGRAM FINDS THE BEST ISOTHERMAL POLICY FOR IRREVERSIBLE REAC
C     EQUATIONS USED.... D(PSI)/DT=-K*PSI**M
C                        RATE=K(T)*PSI*(1.-X)**N
C     ***************************************************************
C     ***********************SYMBOLS*********************************
C     AKI= MINIMUM RATE CONSTANT OF DECAY RATE
C     AKU= MAXIMUM RATE CONSTANT OF DECAY RATE
C     EC= ACTIVATION ENERGY   EC/R
C     XA= MAXIMUM CONVERSION   (ACTIVITY=1.0 WITH MAX. TEMPERATURE )
C     XE= INITIAL CONVERSION
C     TETA= SPACE TIME OF REACTOR
C     P= RATIO E/EC
C     PSI= ACTIVITY
C     M= ORDER OF DECAY RATE
C     N= ORDER OF REACTION
C     TO= MAXIMUM TEMP.(K) CORRESPONDING TO AKU
C     TAUX= TOTAL TIME IN DAYS
C     ***************************************************************
C     ***************************************************************
      DIMENSION T(4),X(4),PSIT(4)
      COMMON M,N,TAUX,PSI,XE,P,AKI,TETA,AKU,XA
      COMMON TO,R,EC,CTE,TEMP
      COMMON ACT
      MOOSE=0
      DO 500 MOOSE=1,50
      READ(5,100)AKU,AKI,EC,XA,PSI,TETA,XE
      READ(5,104)M,N
      READ(5,101)P,TAUX
      READ(5,105)TO,R,EC
      TAUX=TAUX*86400.0
      CTE=AKU/EXP(-EC/(R*TO))
      AKSUP=PSI**(1.-M)/(TAUX*(1.-M))
      IF(M.GT.0) GO TO 1
      TEMP1=-EC/R/ALOG(AKI/CTE)
      TEMP2=-EC/R/ALOG(AKSUP/CTE)
      IF(AKSUP.GT.AKU) GO TO 1
      IF(AKSUP.LT.AKI) GO TO 2
      AKU=AKSUP
    1 ARGMIN=AKI
      ARGMAX=AKU
      WRITE(6,120)
      CALL SEARCH(ARGMIN,ARGMAX,PROFIT)
      BTAUX=TAUX/86400.0
      WRITE(6,102)BTAUX,TEMP,ACT,PROFIT,M,N,P
      IF(MOOSE.EQ.50) GO TO 3
      GO TO 500
    2 TAUXM=PSI**(1-M)/((1-M)*AKI)
      BTAUXM=TAUXM/86400.0
      WRITE(6,106)BTAUX,BTAUXM
  500 CONTINUE
```

```
  3 STOP
100 FORMAT(2E10.3,5F10.0)
101 FORMAT(2F10.0)
102 FORMAT(5X,E12.5,10X,E12.5,10X,E12.5,10X,E12.5,10X,I2,10X,I2,5X,F5.
   12,///)
104 FORMAT(2I10)
105  FORMAT(3F10.0)
106 FORMAT(5X,58HTHE TOTAL TIME IS TOO LONG EVEN FOR THE LOWEST TEMPER
   1ATURE,20HYOUR TOTAL TIME IS =,E12.4,7H IN DAY,//,37HAND THE MAXIMU
   2M TIME PERMISSIBLE IS =,E12.4,///)
120 FORMAT( 6X,12HTIME IN DAYS, 6X,14HTEMPERATURE(K), 4X,8HACTIVITY,10
   1X,6HPROFIT,8X,14HORDER OF DECAY,10X,17HORDER OF REACTION,5X,7HP VA
   2LUE)
    END
    SUBROUTINE SEARCH(ARGMIN,ARGMAX,PROFIT)
    COMMON M,N,TAUX,PSI,XE,P,AKI,TETA,AKU,XA,TAUXM,L,NF,RTAUX
    COMMON TO,R,EC,CTE,TEMP
    COMMON ACT
    NFLAG=0
    TO=1.6180339887
    TMIN=ARGMIN
    TMAX=ARGMAX
  4 T2=TMIN+(TMAX-TMIN)/TO
    T1=TMIN+(TMAX-T2)
    CALL INTG(T1,P1)
    CALL INTG(T2,P2)
    PMAX=P2
    TTMAX=T2
    IF(NFLAG)6,5,6
  5 DO 23 I=1,50
  6 IF(P2-P1)13,19,9
  9 IF(T1-T2)10,10,11
 10 TMIN=T1
    GO TO 12
 11 TMAX=T1
 12 T1=TMIN+(TMAX-T2)
    CALL INTG(T1,P1)
    GO TO 23
 13 IF(T1-T2)17,17,16
 16 TMIN=T2
    GO TO 18
 17 TMAX=T2
 18 T2=TMAX-(T1-TMIN)
    CALL INTG(T2,P2)
    GO TO 23
 19 ROS=T1-T2
    IF(ABS(ROS)-1.0E-14)37,37,60
 60 IF(ROS)20,37,21
 20 TMIN=T1
    TMAX=T2
    GO TO 22
 37 TTMAX=T1
    GO TO 39
 21 TMIN=T2
    TMAX=T1
 22 NFLAG=1
    GO TO 4
 23 CONTINUE
```

```
   39 IF(P1-P2)40,40,41
   40 PROFIT=P2
      RETURN
   41 PROFIT=P1
      RETURN
      END
      SUBROUTINE INTG(T1,P1)
      DIMENSION T(4),X(4),PSIT(4)
      COMMON M,N,TAUX,PSI,XE,P,AKI,TETA,AKU,XA
      COMMON T0,R,EC,CTE,TEMP
      COMMON ACT
      EE=M-1
      AA=ALOG(1.-XE)
      AKOP=T1
      A=N-1
      C=1.-XE
      D=1.-XA
      IF(N-1)2,13,2
    2 AKKU=(1./D**A-1./C**A)/(A*TETA)
      GO TO 14
   13 AKKU=-(ALOG(D)-ALOG(C))/TETA
   14 AKKOP=AKKU*(AKOP/AKU)**P
      L=100
      AN=L
   32 TI=TAUX/AN
      PROFIT=0.0
      B=1./PSI**EE
      C=-EE*AKI
      AM=FLOAT(M)
      BB=1./(1.-XE)**(N-1)
      T(1)=0.0
      JJ=L/2
      DO 9 J=1,JJ
      DO 8 I=1,3
      IF(M-1)3,4,3
    4 PSIT(I)=PSI*EXP(-AKOP*T(I))
      GO TO 5
    3 PSIT(I)=(B+EE*AKOP*T(I))**(1./(-EE))
    5 IF(N-1)6,7,6
    7 X(I)=1.-EXP(AA-PSIT(I)*AKKOP*TETA)
      GO TO 10
    6 S=N-1
      X(I)=1.0-((S)*TETA*PSIT(I)*AKKOP+BB)**(1.0/(-S))
   10 T(I+1)=T(I)+TI
    8 CONTINUE
      PROFIT=PROFIT+TI/3.*(X(1)+4.*X(2)+X(3))
      T(1)=T(3)
    9 CONTINUE
      P1=PROFIT
      TEMP=-EC/R/ALOG(AKOP/CTE)
      ACT=PSIT(I)
      RETURN
      END
      6400 END RECORD
 1.160E-06 3.540E-09 15000.     0.9        1.0        1.0        0.0
         0          1
1.5         30.0
900.0       1.0         15000.0
```

ORD11

APPENDIX A.2.3

```
100. ************************************************************************
110. OPTIMAL POLICY FOR A REVERSIBLE REACTION(FIRST ORDER ON BOTH DIR-
120. ECTIONS) GIVEN THE INITIAL TEMPERATURE(F) WRITTEN BY JEAN-GUY
130. DROUIN ,AUGUST 1968
140. ************************************************************************
150.
160.                              SYMBOLS
170.
180.
190. TI=STARTING TEMPERATURE(F)
200. AP=ACTIVATION ENERGY RATIO E1/EC
210. AP1=    "          "          "  E2/EC
220. TS=UPPER BOUND ON TEMPERATURE(F)
230. CTE=ARRHENIUS CONSTANT
240. PSI=INITIAL ACTIVITY
250. PSIF=FINAL ACTIVITY
260. DTIME=TIME INCREMENTATION(ARBITRARY UNITS)
270. DELTAK=RATE CONSTANT INCREMENTATION
280. XAE=EQUILIBRIUM CONVERSION
290. X=CONVERSION
300. INITIAL CONVERSION=0.0
310. HAM=HAMILTONIAN
320. TAUX=TOTAL TIME OF OPERATION
330.
340. ************************************************************************
350. ************************************************************************
360.
370 COMMON TIME,PSI,AP,AP1,A,B,PSIT,X,XAE,HAM
380 COMMON IKL,DTIME,DELTAK,DIR
390 COMMON AKK1,AKK2,COM,KRS
400 READ,TI,AP,AP1,TS
410 E=15700.
420 CTE=1.69301E+9
430 TII=(TI-32)*5./9.+273.
440 TSS=(TS-32)*5./9.+273.
450 AK=CTE*EXP(-E/TII)
460 AKU=CTE*EXP(-E/TSS)
470 PSI=1.
480 DTIME=.01
490 LL=0
500 DELTAK=.5
510 A=1.
520 B=1.
530 TAUX=100.
540 KRS=1
550 IKL=0
560 LIST=0
570 NN=1
580 IJK=1
590 EPS=1.0E-5
```

ORD11 CONTINUED

```
600 TIME=0.0
610 ZZ=DTIME
620 AKK1=AK**AP*A
630 AKK2=AK**AP1*B
640 XAE=AKK1/(AKK1+AKK2)
650 X=XAE*(1.-EXP(-PSI*(AKK1+AKK2)))
660 HAM0=X-(AP-AP1)*(1.-XAE)*X+(XAE-X)*ALOG((XAE-X)/XAE)*(XAE*(AP-AP1
670 +)+AP1)
680 COW=HAM0
690 HAM=HAM0
700 RATEI=PSI*(AKK1+AKK2)*(XAE-X)
710 AAA=X/XAE
720 CC=XAE-X
730 PRINT,"PSI      TEMP(F)      X      XAE      (XAE-X)      X/XAE  HAM  TIME"
740 PRINT41,PSI,TI,X,XAE,CC,AAA,HAM,TIME
750 41 FORMAT(F7.5,F8.3,6F7.5)
760 IF(HAM-X)2,613,613
770 613 PRINT,"INITIAL TEMPERATURE IS TOO HIGH"
780 STOP
790 PRINT,↑↑,"INITIAL RATE =",RATEI
800 IF(HAM)105,106,106
810 105 PRINT,"INITIAL TEMPERATURE IS TOO LOW"
820 STOP
830 106 CONTINUE
840 2 TIME=TIME+DTIME
850 I=0
860 J=0
870 DIR=AK
880 CALL PROCES(AK)
890 20 IF((HAM-HAM0)-EPS)10,12,13
900 13 IF(J-1)50,60,50
910 60 AK1=AK-DELTAK
920 AK2=AK
930 32 CALL PROCES(AK1)
940 HAM1=HAM
950 CALL PROCES(AK2)
960 HAM2=HAM
970 CALL REGULI(HAM1,HAM2,AK1,AK2,HAM0,AK)
980 IF(AK-AKU)92,94,94
990 92 CONTINUE
1000 IKL=0
1010 PSI=PSIT
1020 GO TO 12
1030 94 CED=AK-AKU
1040 LL=1
1050 DE=AKU-AK1
1060 TIME=TIME-DTIME
1070 XX=DTIME*DE/(DE+CED)
1080 TIME=TIME+XX
1090 DTIME=XX
```

ORD11 CONTINUED

```
1100 LIST=1
1110 NN=10
1120 102 CALL PROCES(AKU)
1130 IF(IJK-1)49,48,49
1140 48 PSIF=-ALOG(1.-COW/XAE)/(AKK1+AKK2)
1150 TAUX=TIME+ALOG(PSIT/PSIF)/AKU
1160 IJK=2
1170 49 CONTINUE
1180 AK=AKU
1190 PSI=PSIT
1200 GO TO 12
1210 50 I=1
1220 AK=AK-DELTAK
1230 CALL PROCES(AK)
1240 GO TO 20
1250 10 IF(I-1)30,40,30
1260 40 AK1=AK+DELTAK
1270 AK2=AK
1280 GO TO 32
1290 30 J=1
1300 AK=AK+DELTAK
1310 CALL PROCES(AK)
1320 GO TO 20
1330 12 BBB=Y/XAE
1340 CC=XAE-Y
1350 RS=PSIT*(AKK1+AKK2)
1360 RST=PSIT*AK
1370 RATE=RS*CC
1380 IF(LL-1)500,400,500
1390 500 IF(X-COW)300,400,400
1400 300 PRINT,"CONVERSION IS LOWER THAN THE HAMILTONIAN"
1410 PRINT,PSIT,TEMP,X,XAE,CC,BBB,HAM,TIME
1420 STOP
1430 400 CONTINUE
1440 IF(NN-10)89,69,69
1450 69 CONTINUE
1460 TEMP=-E/ALOG(AK/CTE)-273.
1470 TEMP=TEMP*9./5.+32.
1480 PRINT51,PSIT,TEMP,X,XAE,CC,BBB,HAM,TIME
1490 51 FORMAT(F7.5,F8.3,6F7.5)
1500 PRINT,↑
1510 PRINT,"ACTIVITY BY AK =",RST
1520 PRINT,"ACTIVITY BY AKK1+2=",RS
1530 PRINT,"RATE=",RATE,↑↑
1540 IF(TIME-TAUX)77,78,78
1550 77 NN=1
1560 IF(LIST-1)2,125,2
1570 89 NN=NN+1
1580 BOSS=NN
1590 IF(LIST-1)2,125,2
```

ORD11 CONTINUED

```
1600 125 IF(KRS-1)225,245,225
1610 245 DTIME=ZZ-XX
1620 DIR=AKU
1630 TIME=TIME+DTIME
1640 KRS=2
1650 MN=BOSS
1660 GO TO 102
1670 225 TIME=TIME+ZZ
1680 DTIME=ZZ
1690 GO TO 102
1700 78 PRINT,↑↑,"TOTAL TIME=",TAUX,"FINAL ACTIVITY=",PSIF
1710 STOP
1720 END
1730 SUBROUTINE PROCES(AK)
1740 COMMON TIME,PSI,AP,AP1,A,B,PSIT,X,XAE,HAM
1750 COMMON IKL,DTIME,DELTAK,DIR
1760 COMMON AKK1,AKK2,COW,KRS
1770 4 PSIT=PSI*EXP(-(AK+DIR)/2.*DTIME)
1780 AKK1=AK**AP*A
1790 AKK2=AK**AP1*B
1800 XAE=AKK1/(AKK1+AKK2)
1810 X=XAE*(1.-EXP(-PSIT*(AKK1+AKK2)))
1820 IF(KRS-2)7,8,8
1830 7 CONTINUE
1840 HAM=X-(AP-AP1)*(1.-XAE)*X+(XAE-X)*ALOG((XAE-X)/XAE)*(XAE*(AP-AP1
1850 +)+AP1)
1860 GO TO 18
1870 8 HAM=COW
1880 18 IF(IKL)122,122,123
1890 123 CONTINUE
1900 PRINT,"HAMILTONIAN = ",HAM,"  CONTROL K = ",AK
1910 122 CONTINUE
1920 RETURN
1930 15 STOP
1940 END
1950 SUBROUTINE REGULI(HAM1,HAM2,AK1,AK2,HAM0,ARG3)
1960 COMMON TIME,PSI,AP,AP1,A,B,PSIT,X,XAE,HAM
1970 EPS1=1.0E-5
1980 FUNC1=HAM1-HAM0
1990 FUNC2=HAM2-HAM0
2000 ABC=FUNC1*FUNC2
2010 IF(ABC)1,1,2
2020 1 ARG1=AK1
2030 ARG2=AK2
2040 GO TO 53
2050 2 PRINT,"STOP IN REGULI TEMPERATURE IS TOO LOW"
2060 STOP
2070 53 ARG3=ARG1+FUNC1*(ARG2-ARG1)/(FUNC1-FUNC2)
2080 CALL PROCES(ARG3)
2090 FUNC3=HAM-HAM0
```

ORD11 CONTINUED

```
2100 DIFF=FUNC3
2110 IF(ABS(DIFF)-EPS1)58,58,57
2120 58 RETURN
2130 57 BB=FUNC1*FUNC3
2140 IF(BB)61,58,59
2150 59 ARG1=ARG3
2160 FUNC1=FUNC3
2170 GO TO 53
2180 61 ARG2=ARG3
2190 FUNC2=FUNC3
2200 GO TO 53
2210 END
2220 $DATA
2230 400. .6 .8 900.
```

ORD12

APPENDIX A.2.4

```
100. ************************************************************************
110. OPTIMAL POLICY FOR A REVERSIBLE REACTION OF ORDER 1-2, GIVEN THE
120. INITIAL TEMP.(F),BY J.G.DROUIN  AUGUST 1969
130. ************************************************************************
140.
150.                          SYMBOLS
160.
170.
180. TI=STARTING TEMPERATURE(F)
190. AP=ACTIVATION ENERGY RATIO E1/EC
200. AP1=   "       "          "  E2/EC
210. TS=UPPER BOUND ON TEMPERATURE(F)
220. CTE=ARRHENIUS CONSTANT
230. PSI=INITIAL ACTIVITY
240. PSIF=FINAL ACTIVITY
250. DTIME=TIME INCREMENTATION(ARBITRARY UNITS)
260. DELTAK=RATE CONSTANT INCREMENTATION
270. XAE=EQUILIBRIUM CONVERSION
280. X=CONVERSION
290. INITIAL CONVERSION =0.0
300. HAM=HAMILTONIAN
310. TAUX=TOTAL TIME OF OPERATION
320.
330. ************************************************************************
340. ************************************************************************
350.
360 COMMON TIME,PSI,AP,AP1,A,B,PSIT,X,XAE,HAM
370 COMMON IKL,DTIME,DELTAK,DIR
380 COMMON AKK1,AKK2,COW,KRS,CA0
390 COMMON X0
400 READ,TI,AP,AP1,TS
410 E=15000.
420 CA0=1.
430 X0=0.
440 CTE=1.69001E+9
450 TII=(TI-32)*5./9.+273.
460 TSS=(TS-32)*5./9.+273.
470 AK=CTE*EXP(-E/TII)
480 AKU=CTE*EXP(-E/TSS)
490 PSI=1.
500 DTIME=.01
510 LL=0
520 DELTAK=.5
530 A=1.
540 B=1.
550 TAUX=100.
560 KRS=1
570 IKL=0
580 LIST=0
590 NN=1
```

ORD12 CONTINUED

```
600 IJK=1
610 EPS=1.0E-5
620 TIME=0.0
630 ZZ=DTIME
640 AKK1=AK**AP*A
650 AKK2=AK**AP1*B
660 PSIT=PSI
670 CALL HAMM
680 HAM0=HAM
690 COV=HAM0
700 HAM=HAM0
710 RATEI=PSI*(AKK1*(1.-X)-AKK2*CA0*X*X)
720 PRINT373
730 373 FORMAT(4X,4HPSI ,10X,7HTEMP(F),10X,1HX,10X,3HHAM,10X,4HTIME)
740 PRINT,PSI,TI,X,HAM,TIME
750 PRINT,↑↑,"INITIAL RATE =",RATEI
760 IF(HAM)105,106,106
770 106 IF(HAM-X)2,613,613
780 613 PRINT,"INITIAL TEMPERATURE(F) IS TOO HIGH"
790 STOP
800 105 PRINT,"INITIAL TEMP(F) IS TOO LOW"
810 STOP
820 2 TIME=TIME+DTIME
830 I=0
840 J=0
850 DIR=AK
860 CALL PROCES(AK)
870 20 IF(HAM-HAM0)10,12,13
880 13 IF(J-1)50,60,50
890 60 AK1=AK-DELTAK
900 AK2=AK
910 32 CALL PROCES(AK1)
920 HAM1=HAM
930 CALL PROCES(AK2)
940 HAM2=HAM
950 CALL REGULI(HAM1,HAM2,AK1,AK2,HAM0,AK)
960 IF(AK-AKU)92,94,94
970 92 IKL=0
980 PSI=PSIT
990 GO TO 12
1000 94 CED=AK-AKU
1010 LL=1
1020 DE=AKU-AK1
1030 TIME=TIME-DTIME
1040 XX=DTIME*DE/(DE+CED)
1050 TIME=TIME+XX
1060 DTIME=XX
1070 LIST=1
1080 NN=10
1090 102 CALL PROCES(AKU)
```

ORD12 CONTINUED

```
1100 IF(IJK-1)49,48,49
1110 48 SS=AKU**AP*A
1120 SST=AKU**AP1*B
1130 DAM=SQRT(4.*SS*SST*CA0+SS*SS)
1140 ZRS=-SS-DAM
1150 ZRST=-SS+DAM
1160 RSU=-2.*SST*CA0
1170 PSIF=1./DAM*ALOG((RSU*COW+ZRS)*(RSU*X0+ZRST)/(RSU*COW+ZRST)/(RSU
1180 +*X0+ZRS))
1190 TAUX=TIME+ALOG(PSIT/PSIF)/AKU
1200 IJK=2
1210 49 AK=AKU
1220 PSI=PSIT
1230 GO TO 12
1240 50 I=1
1250 AK=AK-DELTAK
1260 CALL PROCES(AK)
1270 GO TO 20
1280 10 IF(I-1)30,40,30
1290 40 AK1=AK+DELTAK
1300 AK2=AK
1310 GO TO 32
1320 30 J=1
1330 AK=AK+DELTAK
1340 CALL PROCES(AK)
1350 GO TO 20
1360 12 CONTINUE
1370 RATE=PSIT*(AKK1*CA0*(1.-X)-AKK2*CA0*CA0*X*X)
1380 IF(LL-1)500,400,500
1390 500 IF(X-COW)300,400,400
1400 300 PRINT,"CONVERSION IS LOWER THAN THE HAMILTONIAN"
1410 PRINT,PSIT,TEMP,X,HAM,TIME
1420 STOP
1430 400 IF(NN-10)89,69,69
1440 69 CONTINUE
1450 TEMP=-E/ALOG(AK/CTE)-273.
1460 TEMP=TEMP*9./5.+32.
1470 PRINT,PSIT,TEMP,X,HAM,TIME
1480 PRINT,↑
1490 PRINT,"RATE=",RATE,↑↑
1500 IF(TIME-TAUX)77,78,78
1510 77 NN=1
1520 IF(LIST-1)2,125,2
1530 89 NN=NN+1
1540 BOSS=NN
1550 IF(LIST-1)2,125,2
1560 125 IF(KRS-1)225,245,225
1570 245 DTIME=ZZ-XX
1580 DIR=AKU
1590 TIME=TIME+DTIME
```

ORD12 CONTINUED

```
1600 KRS=2
1610 NN=BOSS
1620 GO TO 102
1630 225 TIME=TIME+ZZ
1640 DTIME=ZZ
1650 GO TO 102
1660 78 PRINT,↑↑,"TOTAL TIME=",TAUX,"FINAL ACTIVITY=",PSIF
1670 STOP
1680 END
1690 SUBROUTINE PROCES(AK)
1700 COMMON TIME,PSI,AP,AP1,A,B,PSIT,X,XAE,HAM
1710 COMMON IKL,DTIME,DELTAK,DIR
1720 COMMON AKK1,AKK2,COM,KRS,CA0
1730 4 PSIT=PSI*EXP(-(AK+DIR)/2.*DTIME)
1740 AKK1=AK**AP*A
1750 AKK2=AK**AP1*B
1760 CALL HAMM
1770 18 IF(IKL)122,122,123
1780 123 CONTINUE
1790 PRINT,"HAMILTONIAN = ",HAM,"  CONTROL K = ",AK
1800 122 RETURN
1810 15 STOP
1820 END
1830 SUBROUTINE REGULI(HAM1,HAM2,AK1,AK2,HAM0,ARG3)
1840 COMMON TIME,PSI,AP,AP1,A,B,PSIT,X,XAE,HAM
1850 EPS1=1.0E-5
1860 FUNC1=HAM1-HAM0
1870 FUNC2=HAM2-HAM0
1880 ABC=FUNC1*FUNC2
1890 IF(ABC)1,1,2
1900 1 ARG1=AK1
1910 ARG2=AK2
1920 GO TO 53
1930 2 PRINT,"STOP IN REGULI TEMP. IS TOO LOW"
1940 STOP
1950 53 ARG3=ARG1+FUNC1*(ARG2-ARG1)/(FUNC1-FUNC2)
1960 CALL PROCES(ARG3)
1970 FUNC3=HAM-HAM0
1980 DIFF=FUNC3
1990 IF(ABS(DIFF)-EPS1)58,58,57
2000 58 RETURN
2010 57 BB=FUNC1*FUNC3
2020 IF(BB)61,58,59
2030 59 ARG1=ARG3
2040 FUNC1=FUNC3
2050 GO TO 53
2060 61 ARG2=ARG3
2070 FUNC2=FUNC3
2080 GO TO 53
2090 END
```

ORD12 CONTINUED

```
2100 SUBROUTINE HAMM
2110 COMMON TIME,PSI,AP,AP1,A,B,PSIT,X,XAE,HAM
2120 COMMON IKL,DTIME,DELTAK,DIR
2130 COMMON AKK1,AKK2,COW,KRS,CA0
2140 COMMON X0
2150 RIX=AKK1*AKK2*CA0
2160 FOX=SORT(4.*RIX+AKK1*AKK1)
2170 CAT=AKK2*CA0*(-2.)
2180 POT1=-AKK1-FOX
2190 POT2=-AKK1+FOX
2200 DAD=(CAT*X0+POT1)/(CAT*X0+POT2)
2210 ERR=EXP(PSIT*FOX)
2220 ERR1=DAD*ERR
2230 X=(POT2*ERR1-POT1)/(CAT*(1.-ERR1))
2240 IF(KRS-2)7,8,8
2250 7 CONTINUE
2260 SINT1=1./FOX*ALOG((CAT*X+POT1)/((CAT*X+POT2)*DAD))
2270 Q=-4.*RIX-AKK1*AKK1
2280 SINT11=(SINT1*CAT/Q+(-CAT*X+AKK1)/(-Q*X))*AP*AKK1
2290 DATE=AKK1*(1.-X)-AKK2*CA0*X*X
2300 SINT2=AKK1*(X-2.)/(Q*X)+AKK1/Q*SINT1
2310 SINT22=SINT2*(-AP)*AKK1
2320 SINT3=((AKK1*AKK1+2.*RIX)*X-AKK1*AKK1)/(-AKK2*CA0*Q*X)+2.*AKK1
2330 +/Q*SINT1
2340 SINT33=SINT3*(-AP1)*AKK2*CA0
2350 HAM=X-DATE*(SINT11+SINT22+SINT33)
2360 RETURN
2370 8 HAM=COW
2380 RETURN
2390 END
2400 $DATA
2410 800. .6 .8 900.
```