A PROCESS MODEL FOR A CONTINUOUS STIRRED TANK REACTOR

by

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ABSTRACT

The purpose of this investigation was to develop a mathematical model describing the dynamic behavior of a continuous stirred tank reactor and to confirm the validity of the model by comparing the results predicted by the simulated process with experimental data. The response of the process model when it was placed under control action was compared with the experimental reactor under the same conditions for proportional, reset, and combined proportional-reset control settings.

As a preliminary experiment, a sulfuric acid-water system was chosen for study, and the temperature of the reaction mixture was selected as the variable to be controlled. A laboratory scale reactor was constructed and temperature response data was obtained for step changes in inlet water flow rate, inlet water temperature, and inlet cooling water flow rate. The process was simulated on the analog computer and the open loop response of the model compared with that of the experimental reactor. The maximum deviation between the temperatures predicted by the model and the experimental process was 5 percent and the average deviation for the transient period was less than 1 percent.

The performance of a proportional-reset controller was simulated on the analog computer and incorporated into the process model. Runs were made using the computer model with control action placed on the flow rate of water being added to the reactor and on the cooling water flow rate. The inlet water flow rates varied from 0 ml/min. to 510 ml/min., and the cooling water flow rate varied from 0 ml/min. to 1000 ml/min. The set point temperature ranged from 80 to 120°F and the controller settings varried from 0.1 to 100 for the proportional band and from 0 to 1 for the reset rate. The results showed that effective control could be achieved only by placing control action on the cooling water flow rate.

The results of this study showed that for complex reaction systems and for processes which exhibit non-linear behavior, an analog simulation would provide more significant information with less effort than other methods presently being used.

INTRODUCTION

When designing a new chemical process, particularly the control system, problems arise which cannot be solved using information based on previous experience (3). Some of the more important problems are:

1. Control of the process to obtain the desired results.
2. Maintaining stability of the system.
3. The determination of optimum start-up conditions.

In most situations, the solutions to these problems are not available until the process is in operation, and then only after much time and money have been expended getting the plant on stream.

The purpose of this research was to explore some of the various methods which are available that can make the designing of a control system, particularly for a continuous stirred tank reactor, more of a routine operation rather than a trial and error problem. There are several techniques which are currently in use. Most of these are extremely difficult to perform. In a paper by Foss (2) a good summary of the various techniques involved in control system analysis is given.

In this paper, Foss deals with the stability of a continuous stirred tank reactor which is producing a product by a first order chemical reaction. A schematic diagram of the reactor in question is shown in Figure 1. To begin with, the basic differential equations describing the dynamic behavior of the system under study are derived. The equations describing the particular reactor in question follow.

$$\frac{Vdx}{dt} = q(X_o - X) + VX(Ae^{-E/RT}) \quad (1)$$

$$VPC_p\frac{dT}{dt} = qC_pP(T_o - T) - UA(T - T_c) + VX(\Delta H)Ae^{-E_A/RT} \quad (2)$$

where:

A = Area of cooling coil, cm^2

E = Energy of activation, cal/g-mol

ΔH = Heat of reaction, cal/g mol

P = Density of reaction mixture, gm/ml

p = Pre-exponentralfactor

q = Flow rate of reactant, ml/min

R = gas constant, ^oC/cal/g mol

T = Temperature of reactor, ^oC

T_o = Temperature of reactant stream, ^oC

T_c = Mean cooling water temperature, ^oC

t = Time, minutes

Figure 1. Continuous Stirred Tank Reactor

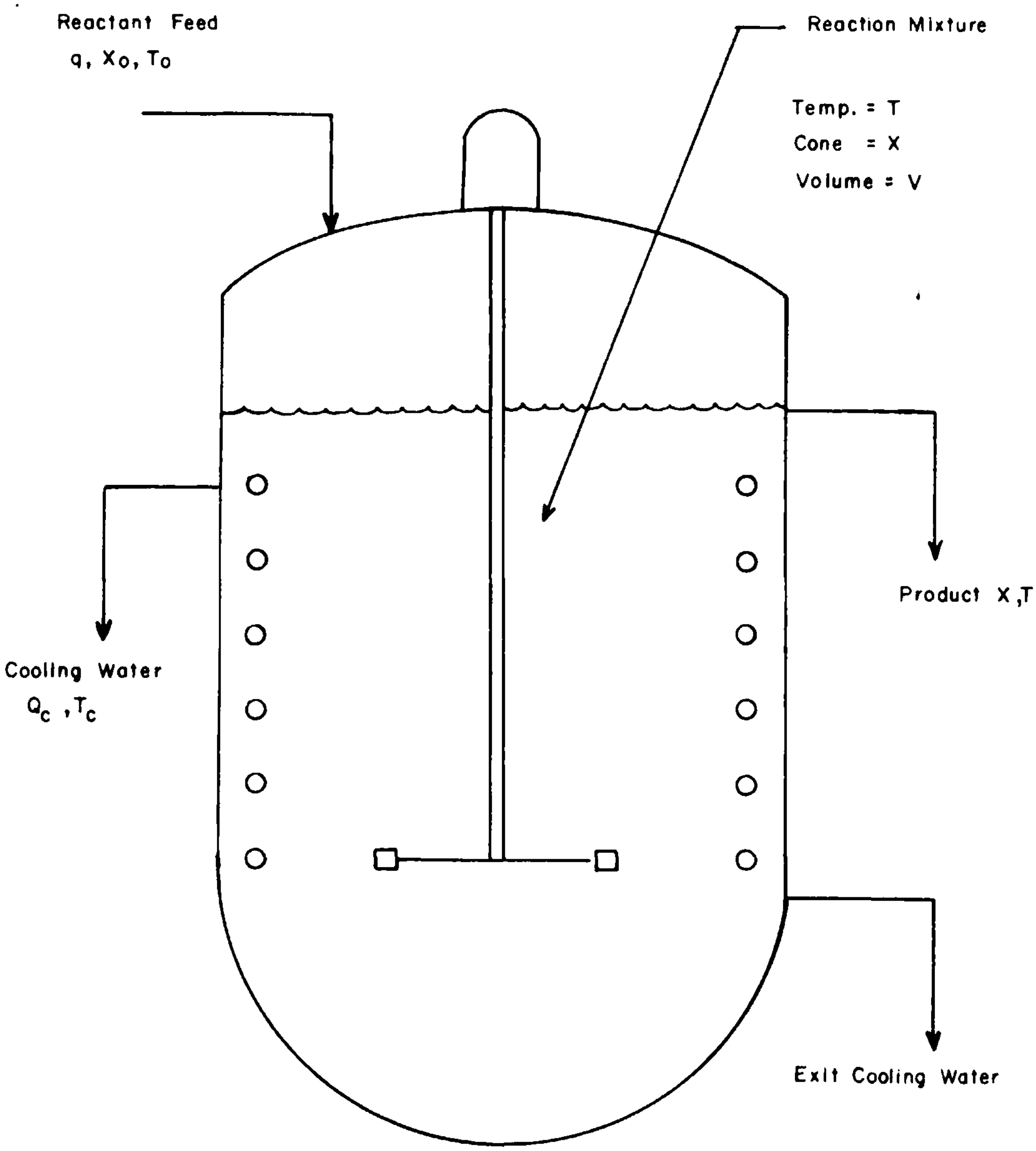

Reactant Feed
q, X_0, T_0
Reaction Mixture
Temp. = T
Cone = X
Volume = V
Product X,T
Cooling Water
Q_c ,T_c
Exit Cooling Water

Figure 1

U = Overall heat transfer coefficient, $\frac{\text{cal}}{\text{min. } ^{\circ}\text{C cm}^2}$

V = Reactor volume, cm^3

X = Concentration of reactant in mixture, g mol/ml

X_o = Concentration of reactant in incoming stream, g mol/ml.

These equations are then transformed into the Laplace domain and put into transfer function form. To obtain transfer functions from the differential equations, the perturbation method is carried out. This involves examining the dynamic behavior of the system in relation to small (infinitesimal) fluctuations about a steady state value. Because only very small deviations are considered, the non-linear effects may be neglected and the equations linearized. An example of this method will be given in a future section. One of the transfer functions derived by Foss, showing the effect of a change in the reactant flow rate on the concentration in the reactor is shown below.

$$\frac{\bar{X}^*}{\bar{q}^*} = \frac{\frac{X_o - X_{ss}}{q}\left(1 + . \; -Y + \frac{V}{q} S\right) + \frac{T_o - T_{ss}}{q}\left(- \frac{V}{q} \frac{X_s E}{R T_{ss}^2} K_s\right)}{\left(1 + \alpha + \frac{V}{q} S\right)\left(1 + \beta - \gamma + \frac{V}{q} S\right) + \alpha\gamma} \qquad (3)$$

$$\alpha = \frac{V}{q} A e^{-E/RT} \qquad \beta = UA/qC_p$$

$$\gamma = \frac{V}{q} \frac{E}{R T_{ss}^2} \frac{(-\Delta H) X_{ss}}{P C_p} A e^{-E_A/RT}$$

Foss then states that the usual stability criteria such as the Nyquist, Bode, and root locus methods can be applied to this and other similar transfer functions. He also states that these transfer functions are valid only for the particular steady state values about which they are linearized. He then states that little or no experimental work has been performed to verify these and other process models, and that there is much work to be done in this field.

This investigation was based primarily on the paper just described. It was proposed to extend research similar to the above to include experimental verification. It was necessary first to pick a suitable reaction system for study and to design and build an apparatus for gathering data, second to propose a model for the process, and third, to compare the predicted results with the experimental data and determine what information could be obtained from the model.

It was desired to find a system for study which was simple enough so that the model would not be extremely complicated, and still provide meaningful data. An ideal reaction system for the purposes outlined above should meet the following specifications:

1. The reactants should be easy to obtain and inexpensive enough so that relatively large quantities could be used in the study.
2. Non-corrosive and non-toxic reactants should be used if possible.
3. The reaction should lend itself to continuous analysis.
4. The reaction kinetics should be fully understood.

SELECTION OF EXPERIMENTAL PROCESS AND SYSTEM PARAMETERS

The search for a reaction for use in this study began with the process of searching for a first order chemical reaction, one whose behavior is described by the following equation.

$$\frac{dC}{dt} = -kC \tag{4}$$

where: C = Concentration of a reactant, g moles/ml.

K = Reaction rate constant, sec^{-1}

t = Time, sec.

Hougen and Watson (4) reported that the decomposition of hydrogen peroxide in a dilute sodium hydroxide solution could be classified as a first order reaction. This particular reaction was investigated to determine if it could be used as a reaction system for study. A simple analytical procedure for determining the percentage of hydrogen peroxide in aqueous solution was available. This method involved the addition of a sample of the reaction mixture to a volume of sulfuric acid, followed by titration with a standardized potassium permanganate solution (6). The reaction was run under the conditions specified by Hougen and Watson and found to approximate first order behavior. However, the reaction rate constant was found to be sensitive to changes in hydroxide concentration. When concentrations other than the specified were tried, the reaction rate was found to decrease. Maximum rate was obtained when the reaction was run in 0.04 molar sodium hydroxide, which was the original concentration. This suggests that the reaction is not truly first order but merely approximates first order characteristics at the specified conditions. The experimental data is shown in Table 3 in the appendix. In order to use this reaction in the continuous reactor, a method would have had to be found to keep the hydroxide concentration constant. This would have induced undesirable complications into the system. Therefore, it was decided to eliminate the possibility of using the peroxide in the continuous reactor. Also it was found that there was no method available of continuously monitoring the concentration of peroxide in the reaction mixture. Further investigation revealed that there was no immediately obvious first order reaction which met the specifications outlined above.

At this time it was decided that the real problem was not that a complex, higher order reaction could not be dealt with in the process model, but that direct continuous analysis of concentration required far more elaborate equipment than was available. To convert the existing Honeywell controller to accept a type of input other than an emf signal from a thermocouple was beyond the scope of this investigation. At this time it was decided that a "simulated" chemical reaction would be simpler to carry out and would serve the intended purposes just as well as a conventional commercial reaction. The advantage of the "simulated" reaction was that the need for elaborate analytical equipment was eliminated. A description of the process studied in this investigation follows.

When concentrated, commercial grade sulfuric acid is added to a more dilute solution of acid and water, a known quantity of heat is evolved. The amount of heat which is evolved (the heat of solution) is determined by the concentration of acid in the reactor before and after mixing. In a continuous reactor this corresponded to the relative flow rates of acid and water and to the initial concentration of acid. It was possible to obtain an analytical expression to relate these variables to the rate of heat evolution.

When developing an appropriate model for predicting the heat effects associated with the addition of a stream of water and a stream of acid to a reactor containing a mixture of acid and water, four separate effects were considered. First, heat was evolved when acid was added, second a smaller amount of heat was evolved when water was added to the mixture, third and fourth, sensible heat was contained in the acid and water streams, respectively. This investigation was primarily limited to solutions which contain more water than acid. In view of this, the heat effect of adding water to an acid-water mixture was neglected in the development of the model. From enthalpy concentration data (5) the curve of figure 2 was drawn. As can be seen, this curve, representing the heat effect associated with the addition of one mole of sulfuric acid to a solution of any given concentration, can be approximated by a straight line. Equation 5 represents this approximation.

$$-(\Delta H) = -20{,}000 + 19{,}400 Z_A \qquad (5)$$

where: ΔH = Heat of solution, cal/g mole.

Z_A = Mass fraction sulfuric acid.

Figure 2. Heat of solution for sulfuric acid-water solutions versus mass fraction sulfuric acid.

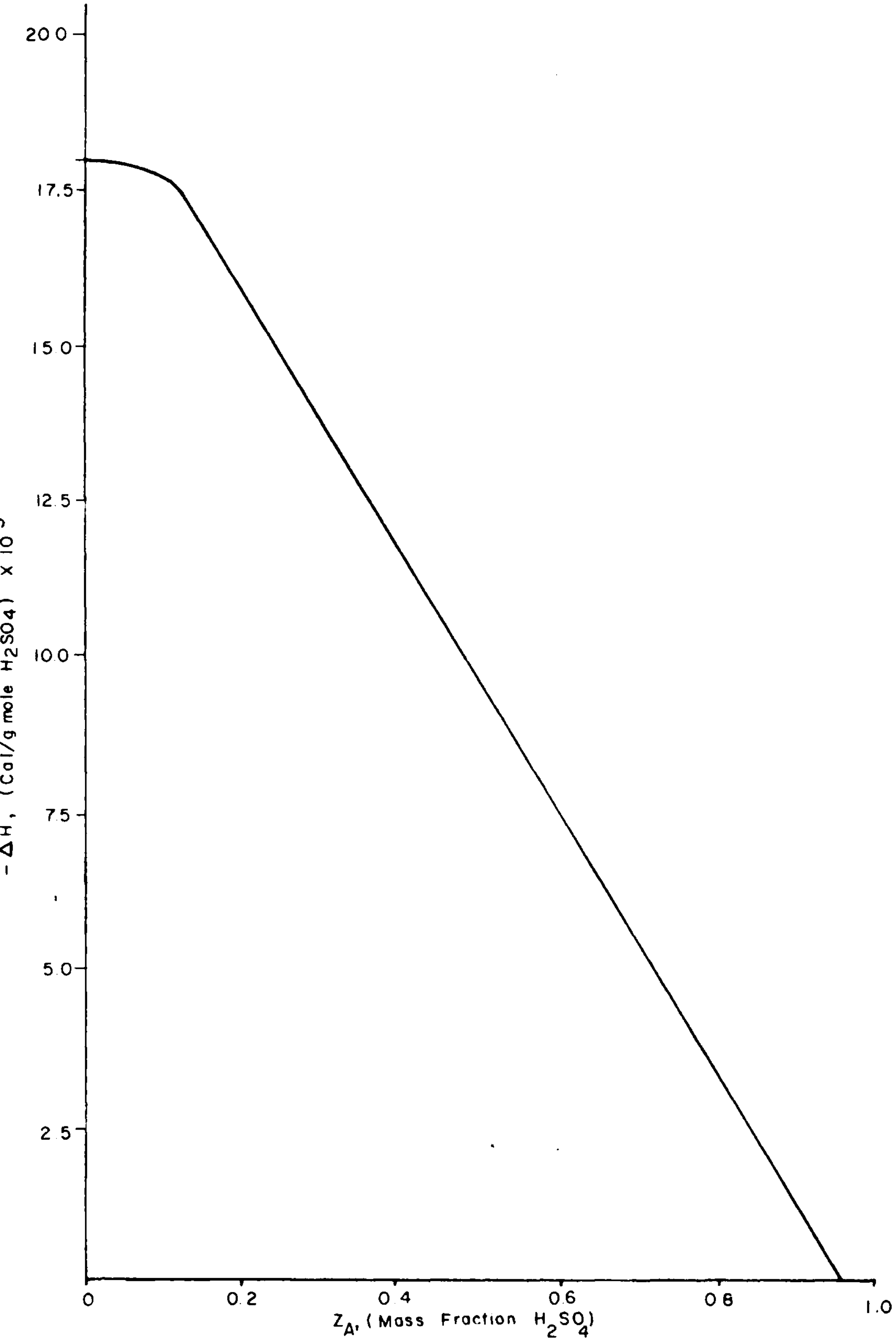

20.0
17.5
15.0
12.5
10.0
7.5
5.0
2.5
- ΔH, (Cal/g mole H2SO4) x 10-3
0
0.2
0.4
0.6
0.8
1.0
ZA, (Mass Fraction H2SO4)

Figure 2

This linear approximation failed for acid concentrations below about 10 percent. In this dilute range, a constant ΔH is used. It was later determined that the linear model was, in fact, sufficient for most dilute solutions, producing only a small error.

With the acid-water system, it was possible to maintain a desired temperature of the reaction mixture by adjusting the following variables.

1. Flow rate of acid.
2. Flow rate of water.
3. Water temperature.
4. Acid temperature.
5. Heat removal rate from the reactor.

How then did this simulated reaction measure up to the specifications set previously for an ideal reaction system?

1. The reactants were cheap and easy to obtain.
2. Sulfuric acid was toxic and corrosive.
3. Continuous measurement of the conditions in the reactor was possible because it was only necessary to measure the temperature of the reaction mixture.
4. The reaction kinetics were fully understood.

The first and particularly the third points made above justify the use of the acid-water system. The fact that sulfuric acid was toxic and corrosive presented no particular problem since the system was designed to resist the acid and extreme care was observed in the operation of the system.

A schematic diagram of the reactor to be modeled is shown in figure 3. The differential equations for the system and a sample transfer function derived by the perturbation method are presented below.

$$\frac{VdC_A}{dt} = P_A Q_A - (Q_A + Q_F)C_A \tag{6}$$

$$VPC_p \frac{dT}{dt} = Q_A P_A C_{pA}(T_{oA} - T) + Q_F P_F (T_{oF} - T)$$
$$- UA(T - T_c) + (BC_A + D)\frac{Q_A P_A}{M_A} \tag{7}$$

where:

A = Area of cooling coil, cm^2

C_A = Concentration of acid, g/ml

C_p = Heat capacity of reaction mixture, cal/gram-^oC

C_{pA} = Heat capacity of sulfuric acid, cal/gram-^oC

C_{pF} = Heat capacity of water, cal/gram-^oC

Figure 3. Schematic diagram of the experimental reactor.

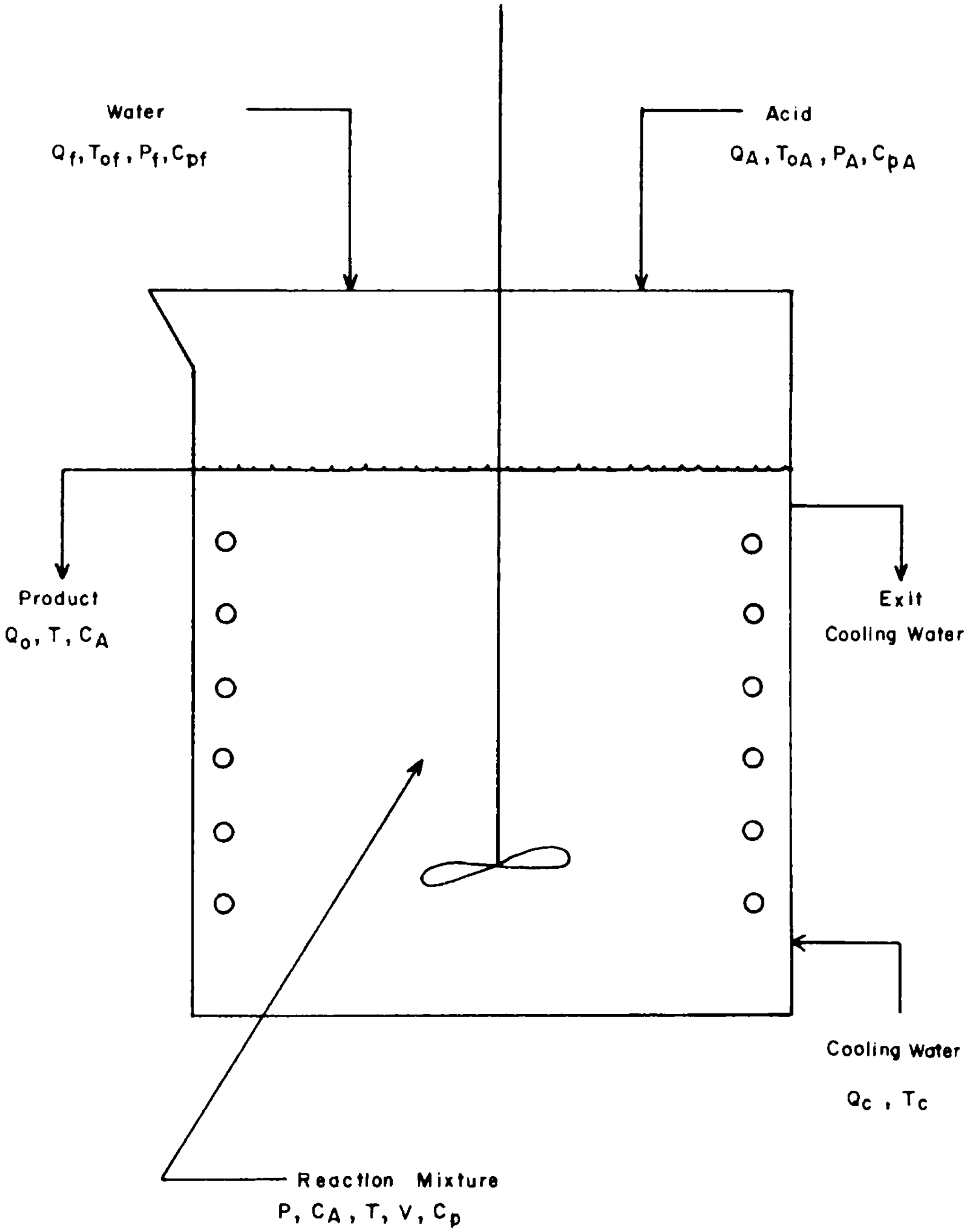

Water
Q_f, T_{of}, P_f, C_{pf}
Acid
Q_A, T_{oA}, P_A, C_{pA}
Product
Q_o, T, C_A
Exit
Cooling Water
Cooling Water
Q_c , T_c
Reaction Mixture
P, C_A, T, V, C_p

Figure 3

M_A = Molecular weight of sulfuric acid, grams/mole

P = Density of reaction mixture, grams/ml

P_A = Density of sulfuric acid, grams/ml

P_F = Density of water, grams/ml

Q_A = Flow rate of acid, ml/min

Q_F = Flow rate of water, ml/min

T = Temperature of reaction mixture, ^oC

T_c = Mean cooling water temperature, ^oC

T_{oA} = Temperature of acid, ^oC

T_{oF} = Temperature of water, ^oC

t = Time, minutes

U = Overall heat transfer coefficient of cooling coils, $\frac{\text{cal}}{\text{min } ^oC \text{ cm}^2}$

V = Volume of reactor, cm^3

To obtain the transfer function, these equations are linearized about a steady state value (designated by a subscript ss). By expanding in a Taylor series and dropping all high order terms, we can obtain

$$\frac{VdC_A}{dt} = F(C_A, Q_A, Q_F) \tag{8}$$

$$C_A^* = C_A - C_{Ass} \tag{9}$$

$$\frac{VdC_A^*}{dt} = \frac{\partial F}{\partial C_A}\bigg|_{ss} C_A^* + \frac{\partial F}{\partial Q_A}\bigg|_{ss} Q_A^* + \frac{\partial F}{\partial Q_F}\bigg| Q_F^* \tag{10}$$

$$\frac{dC_A^*}{dt} = \frac{-Q_{oss}}{V} C_A^* - \frac{C_{Ass}Q_F^*}{V} + \frac{P_A - C_{Ass}}{V} Q_A^* \tag{11}$$

Taking the Laplace transform for a variable Q_F,

$$SC_A^* = \frac{-Q_{oss}}{V} \bar{C}_A^* - \frac{C_{Ass}}{V} \bar{Q}_F^* \tag{12}$$

By similar treatment of equation 7, and substitution of equation 12 for $\bar{C}_A^*$, the following transfer function showing the effect on $\bar{T}^*$ of a small change in $\bar{Q}_F^*$ was obtained.

$$\frac{\bar{T}^*}{\bar{Q}_F^*} = \frac{\frac{P_F C_{pF} T_{oF_{ss}}}{VPC_p} S + \frac{P_F C_{pF} T_{oF_s} Q_{oss}}{V^2 PC_p} - \frac{Q_A P_A B}{MV^2 PC_p} C_{Ass}}{S + Q_{o_s}/V)\ (S + \frac{UA}{VPC_p} + Q_{Ass} P_A C_{pA} + Q_{F_{ss}} P_F C_{pF})} \tag{13}$$

Due to the complexity of the transfer functions developed above, the application of the standard stability criterion proves to be an arduous task even for this relatively simple process. Using the basic differential equations which describe the system, it was advantageous to simulate the system on an analog computer. From the analog simulation, the following information can be obtained.

1. The limits within which the process can be controlled.
2. The variables that should be controlled.
3. The type of control action which should be used.
4. Suitable controller settings.
5. The optimum start-up conditions.

In this particular system there were five variables which could be controlled to give the set point temperature; these were acid flow rate, water flow rate, acid temperature, water temperature, and coolant flow rate. With the analog simulation it was a simple matter to adjust these parameters and note their effect on the reactor temperature. By using a circuit which simulated the action of a controller, the effect of controlling the different variables was explored and the correct variable to be controlled chosen. The optimum controller settings could then be determined by inspection or, if necessary, by methods such as the Zigler-Nichols. The analog program used in this investigation is shown in figures 4, 5, and 6. Table 1 shows what the significant potentiometers represent.

Figure 4. Controller section of analog computer circuit.

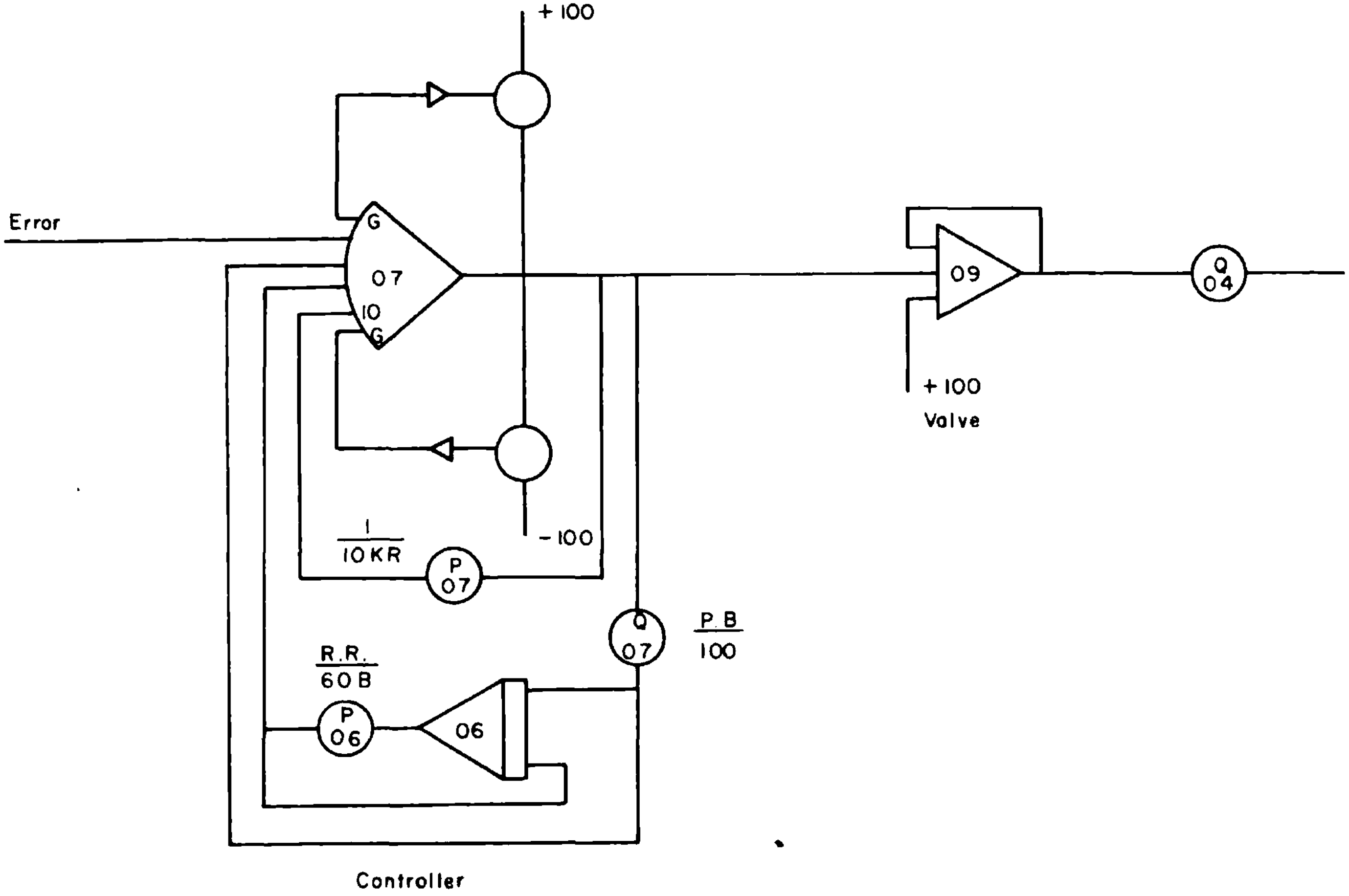
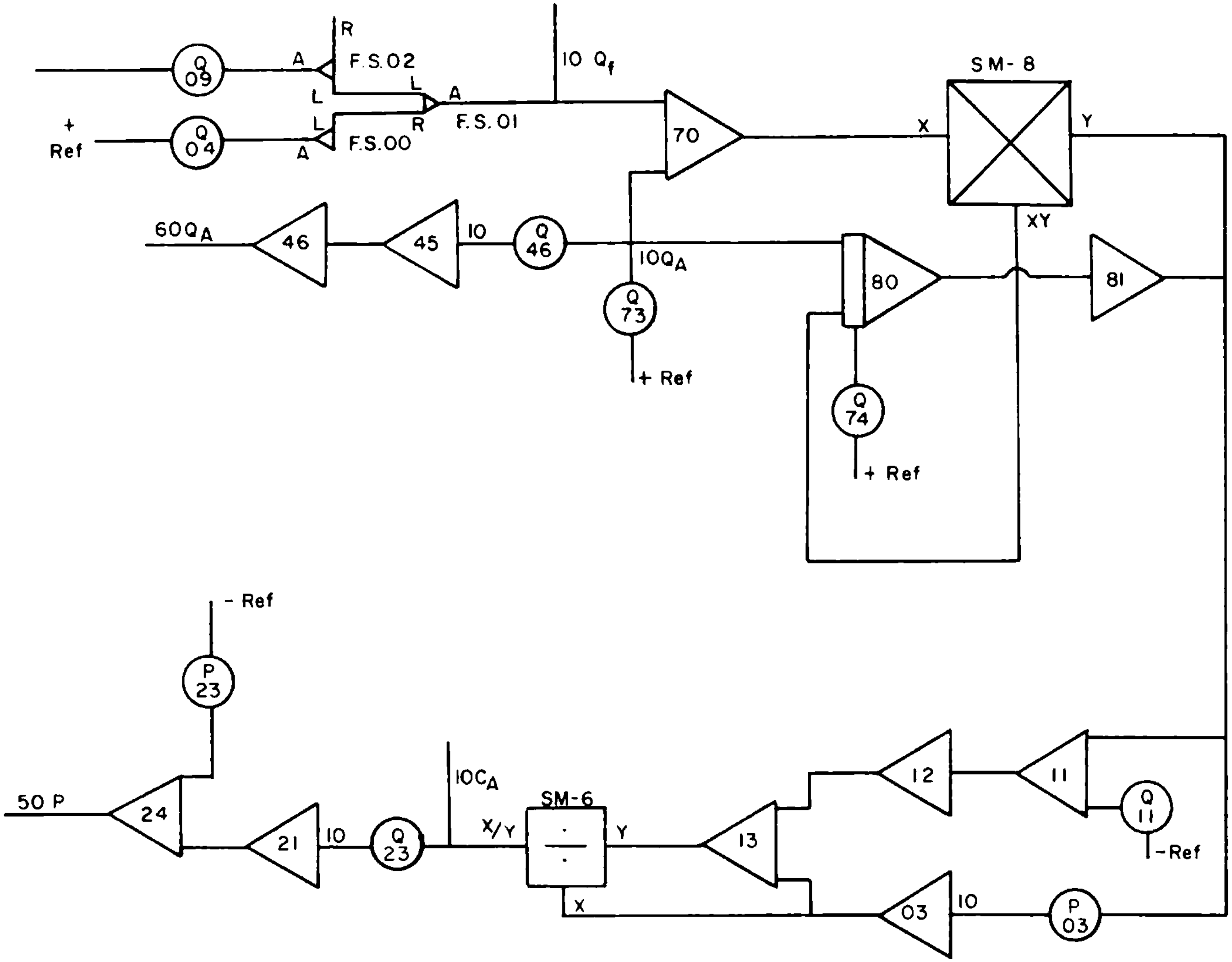

+ 100
Error
G
07
10
G
- 100
1
10KR
P
07
Q
07
P.B
100
R.R.
60 B
P
06
06
Controller
09
+ 100
Valve
Q
04

Figure 4

Figure 5. Material balance section of analog computer diagram.



R
A
F.S.02
L
L
A
10 Q_f
SM-8
+
Ref
L
R
F.S.01
X
Y
A
F.S.00
70
XY
$60Q_A$
46
45
10
$10Q_A$
80
81
+ Ref
+ Ref
- Ref
50 P
24
21
10
$10C_A$
SM-6
X/Y
Y
13
12
11
-Ref
X
03
10

Figure 5

Figure 6. Energy balance section of analog computer diagram.

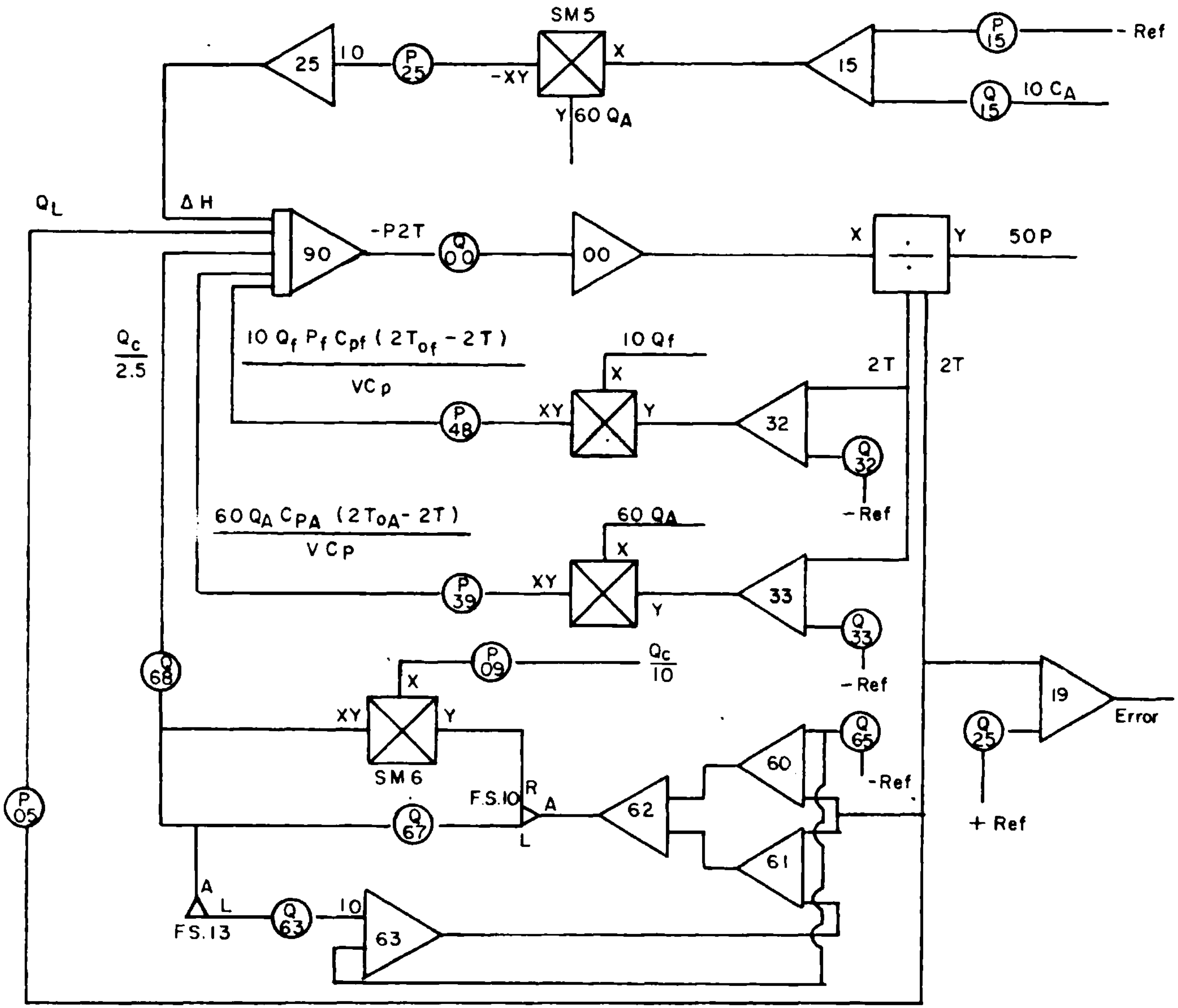

SM5
25
10
P 25
-XY
X
Y
60 Q_A
15
P 15
- Ref
Q 15
10 C_A
Q_L
ΔH
90
-P2T
Q 00
00
X
Y
50P
$\frac{Q_c}{2.5}$
$\frac{10\,Q_f\,P_f\,C_{pf}\,(2T_{of} - 2T)}{VC_p}$
10 Qf
2T
2T
P 48
XY
X
Y
32
Q 32
- Ref
$\frac{60\,Q_A\,C_{PA}\,(2T_{oA} - 2T)}{VC_p}$
60 Q_A
P 39
XY
X
Y
33
Q 33
- Ref
Q 68
P 09
$\frac{Q_c}{10}$
X
XY
Y
SM6
19
Error
Q 25
+ Ref
Q 65
- Ref
60
F.S.10
R
A
L
62
61
Q 67
P 05
A
L
FS.13
Q 63
10
63

Figure 6

Table 1. Important Potentiometer Assignments

Potentiometer	Parameter Represented
Q04	$10Q_F$, water flow rate, ml/min.
P06	$RR/60$, scaled reset rate
Q07	$PB/100$, proportional band
P07	$1/10K_R$, steady state reset gain
P25	T_{sp}, set point, ^oF
Q32	$2T_{oF}/100$, water temperature, ^oF
Q33	$2T_{oA}/100$, acid temperature
P40	$2T/100$, initial reactor temperature, ^oF
Q63	$0.5/Q_c$, cooling water flow rate, ml/min.
Q65	$2T_{cin}/100$, inlet cooling water temperature, ^oF
Q67	$UA/10$, cooling coil resistance cal/cm^2-^oC-min.
Q73	$10Q_A$, acid flow rate, ml/min.
Q74	$10C_{Ao}$, Initial reactor concentration, fraction

DESCRIPTION OF EQUIPMENT

In order to test the above equations on a physical system, it was necessary to construct a laboratory scale continuous stirred tank reactor. It was desirable to design and build the reactor to be as multi-purpose as possible so that the apparatus could be used for studying other reaction systems as well.

Certain information must be gathered before designing a process for carrying out a chemical reaction. The important factors to be considered are:

1. Corrosion problems
2. Heat effects associated with the reaction
3. Flow rates
4. Retention time in the reactor
5. Variables to be controlled
6. Selection of the measured variable.

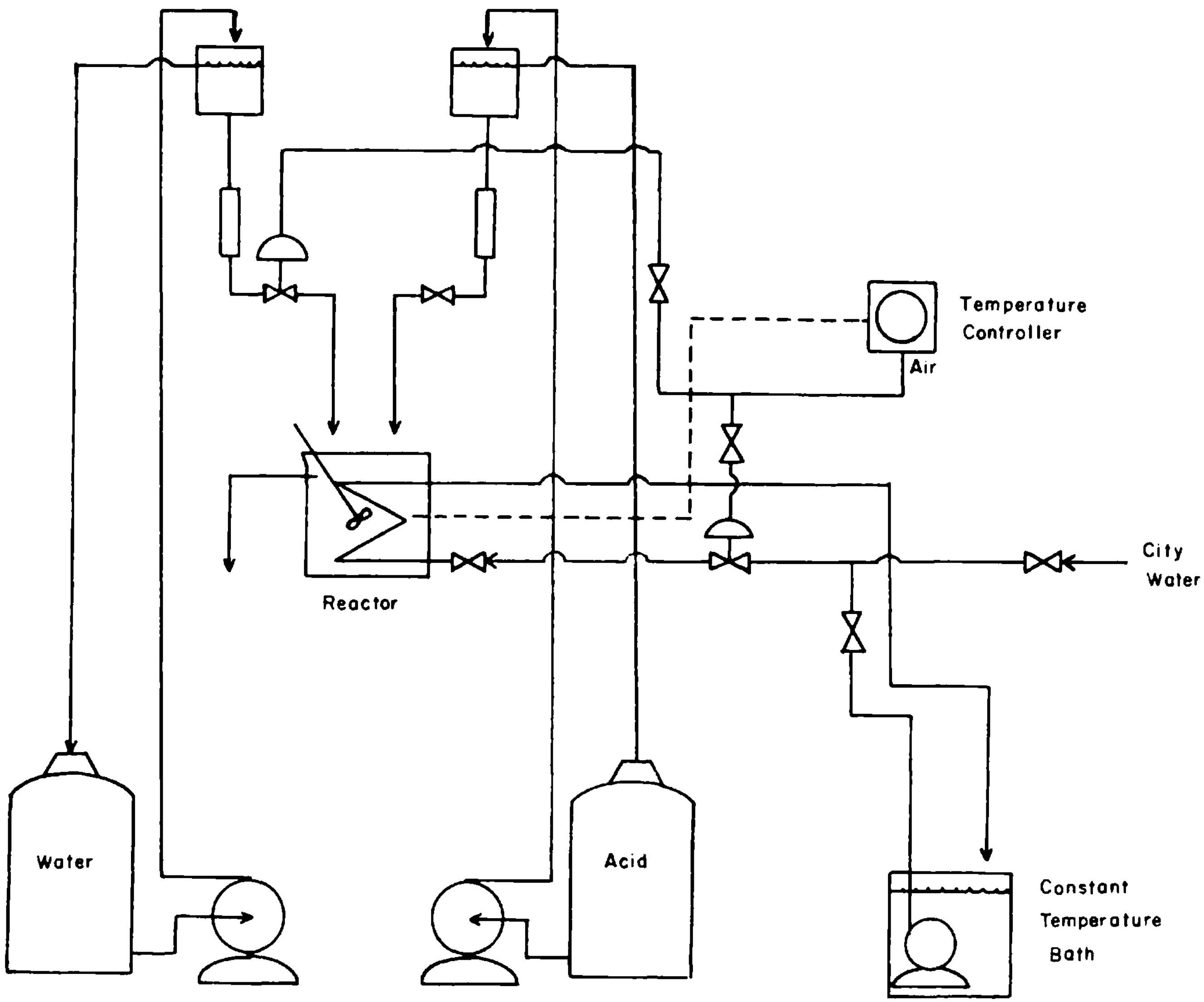
A system for general use should be able to handle as many combinations of the above situations as is possible. From the above list, the properties of a truly useful multi-purpose continuous stirred tank reactor can be outlined.

1. The reactor and associated accessories should be constructed of materials which are as chemically inert as possible.
2. Provisions should be made for supplying heat to and removing heat from the reactor.
3. It should be possible to supply reactants at any reasonable flow rates and these flow rates should be accurately measured.
4. It should be possible to change the volume of the reactor by controlling the level of the reaction mixture.
5. It should be possible to control the rate of heat removal or addition, and to control the flow rate of at least one reactant.
6. Measuring equipment, or at least space for measuring equipment, must be provided which can record continuously temperature, electrical conductivity, pH, etc. These instruments should also produce an output signal which could be fed to a controller.

The reactor which was used in this research was designed and built with the above qualities in mind. Figure 7 is a schematic flow diagram of the experimental reactor. The reactor itself was made from a 2-liter

Figure 7. Schematic flow diagram of experimental apparatus.

Figure 7


Temperature
Controller
Air
Reactor
City
Water
Water
Acid
Constant
Temperature
Bath

polyethylene beaker. An overflow pipe was inserted near the top to keep the volume of the reaction mixture constant. The effective reactor volume was exactly 2000 milliliters. A length of polyethylene tubing was connected to this outlet and directed the product of the reactor to the drain, or to a tank if it was desired to retain the product. To insure proper mixing of the reactants, a Lightnin Model F laboratory scale mixer was used. The mixer was clamped to an overhead support. A propeller shaft of 316 stainless steel extended downward from the power unit to within about 1/2 inch of the bottom of the reactor. A 1-inch diameter propeller was attached to the bottom of the shaft with a set screw.

To permit the addition or removal of heat from the reactor, a coil was installed. The coil was made from a 20-foot length of 316 stainless steel thin wall tubing by bending it around a section of 6-inch pipe. The coil has an outside area of 1200 square centimeters. Stainless steel bulkhead fittings connected the ends of the coil through the reactor wall to polyethylene tubing which carried the heat transfer medium. Provisions were made to use either tap water or water from a constant-temperature bath in the coil. The constant temperature bath which was contained in the apparatus was a Blue M "Magni-Whirl" unit which was fitted with both a heater and a small refrigeration unit. The bath will maintain approximately 2.5 gallons of water at temperatures from 0 to 100 degrees centigrade. A submersible pump was mounted in the bath to circulate the water to the coil.

It was possible to supply two reactants to the system. A pair of five gallon polyethylene carboys were located at the bottom of the apparatus to contain the reactants. Reactants were pumped from these carboys to constant head tanks mounted on an overhead support about seven feet above floor level. These tanks overflowed through 1/2-inch stainless steel tubing back to the carboys. The pumps were Eastern Electric Model D-11 centrifugals driven by General Electric 1/8 horse power motors. From the bottom of the constant head tanks the reactants were directed to the reactor. The stream on the left passed from the constant head tank through a Brooks Sho Rate 150 rotameter, and a Taylor Lin-E-Aire Model Number 400vm4220 automatic control valve. The valve permits water flow rates of from 0 to 510 milliliters per minute. The stream on the right passed through a similar rotameter and a Whitey

Micro-regulating manual valve. All piping of the reactant feed system was of 316 stainless steel tubing and Swagelok fittings, with the exception of the line from the bottom of the carboys to the pumps. These lines were of polyethylene tubing which is flexible and allows the carboys to be moved for filling.

Since it was decided that the temperature of the reaction mixture was to be the measured variable, a Minneapolis Honeywell Model Number 1s2p13ps-175-11p1 proportional-reset controller was installed on the apparatus. This device used a copper-constantan thermocouple for a sensing element and had proportional and reset control modes available over a range of -150 to +200 degrees Fahrenheit. The reactor temperature was recorded on a disc chart incorporated in the instrument. For use in future research, a Honeywell cam operated set point controller was also installed. Both units are supplied with 20 psi instrument air which was regulated and dried by a Taylor regulator and separator. The controller produced an air signal which operated the Taylor control valve mentioned above. The valve used was an air to close model. Either type of valve could have been used with the controller because it was possible to reverse the action of the controller by moving a link within the mechanism. The control action of this controller left much to be desired. Proportional band settings range only from 1 to 10 and there is no calibration on the reset control. The operating manual states that the reset screw should be turned until the system shows no offset. For future research a controller similar to a Speedomax H is recommended. All of the above equipment was mounted on a frame of welded 1-1/2 inch steel angle iron as can be seen in Figure 8. All electrical equipment was operated from a central switch panel located on the left front of the apparatus. The front of the top of the main frame box was covered with a hardboard table which could be used for writing or as space for additional measuring equipment. For this research, a Dynagraph type RS millivolt recorder was used to obtain accurate temperature time curves. The entire apparatus was mounted on casters to facilitate moving.

Figure 8. Equipment layout of experimental apparatus.

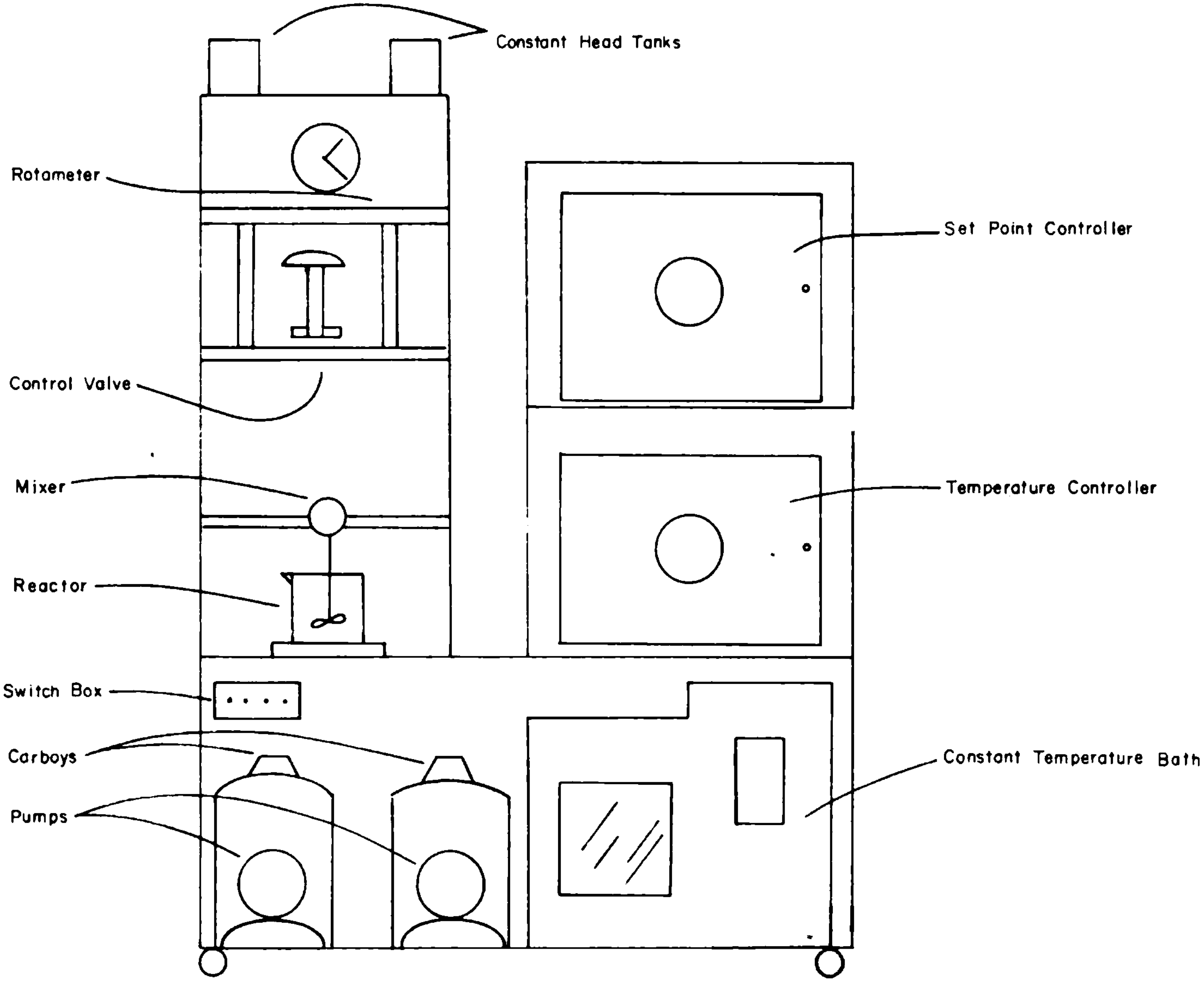

Constant Head Tanks
Rotameter
Set Point Controller
Control Valve
Mixer
Temperature Controller
Reactor
Switch Box
Carboys
Constant Temperature Bath
Pumps

Figure 8

PROCEDURE

Several pre-planned experimental runs were made using the experimental apparatus. The first set consisted of measuring the response to step changes in water flow rate, cooling water flow rate, and acid flow rate. The temperature in the reactor was the measured variable. Reactor temperature was measured by an iron-constantan thermocouple inserted in a length of 1/4-inch stainless steel tubing. The temperature-time curve was recorded on the Dynagraph with the sensitivity control set so that a temperature change of 3.33 degrees Fahrenheit caused a pen movement of 1 centimeter. The chart speed was set at 1 millimeter per second.

All variables were measured and recorded at the beginning and end of each run. These variables included flow rates of water and acid, the temperatures of the water and acid, the cooling water flow rate and temperature, the initial temperature in the reactor, and the initial concentration of acid in the reactor. The concentration was determined from the steady state value of the water to acid ratio in the previous run. If the reactor concentration was unknown, the contents were siphoned out and the reactor filled with a mixture of known concentration. With the reactor at steady-state conditions, step changes were made and the results recorded.

After the responses to the step inputs were determined, it was necessary to measure the heat transfer coefficient of the cooling coil, and the rate of heat loss from the surface of the reactor. The heat transfer coefficient was determined in the following manner. One carboy was filled with hot water, and the pump started to provide a continuous stream to the reactor. The cooling water rate was set and measured. When the temperature in the reactor reached steady state, the inlet and outlet temperature of the cooling water was measured. The cooling water rate was then changed, the system allowed to come to a new steady state, and the new temperatures measured. This process was repeated for a number of cooling water rates. From this data, using standard heat transfer equations, the heat transfer coefficients were calculated.

The rate of heat loss from the reactor was determined by filling the reactor with hot water, and, with no feed or cooling water turned on, recording the temperature-time curve on the Dynagraph. From this curve the heat losses were determined. Several sections of the curve were chosen and the slopes of these sections were measured to determine the rate of heat loss. The average temperature of the reactor was determined by taking the value of the temperature at the centers of the chosen portions of the curve for each time increment. Using the rate of heat loss and the average temperature difference between the reactor and the surroundings, the heat transfer coefficient was evaluated. This coefficient was found to be independent of temperature.

The basic differential equations describing the system were then time and magnitude scaled, and the process, control elements, and controller elements were simulated on the analog computer. After placing this program on the computer and adjusting the necessary potentiometers to represent the physical constants of the system, several runs were made simulating the operation of the experimental reactor. The same step changes were made on the simulated reactor as were made on the experimental reactor. These responses were plotted and compared to the results obtained from the experimental reactor. After the open loop responses of the computer simulation and the experimental reactor were compared, a circuit which simulates the action of a proportional-reset controller was added to the analog program. The control action was first placed on the water flow rate and second on the cooling water flow rate. Runs were made at various controller settings and set points to determine their effects on the control of the reactor. The controller which was included in the experimental apparatus was not fitted with a device for determining the numerical value of the reset rate. It was therefore impossible to compare the effects of changing the reset rate on the simulated controller with experimental data. In view of this, computer runs were made with the reset action removed. Corresponding runs were made on the experimental apparatus with various settings of proportional band. These results were then compared with the runs made using the computer model.

EXPERIMENTAL RESULTS

As was stated previously, the first objective of this research was to compare the response of the simulation to step changes with data taken from the experimental apparatus for the same step changes. Table 2 shows what step changes were made and the initial and final conditions. Figures 9 to 11 show a comparison between the temperature response predicted by the computer and the actual data taken from the experimental apparatus. Figure 9 shows the response to a change in water flow rate, figure 10 shows the response to a change in acid rate, and figure 11 gives the response to a change in cooling water rate. Refer to Table 2 for the conditions before and after the step changes were made. The solid lines on the figures show the predicted results and the points represent experimental data.

Figure 12 shows the effect of placing proportional and reset control on the flow rate of water. These curves were drawn by the computer and show no comparison with experimental data. Figures 13 through 17 show the effect of placing proportional plus reset control on the cooling water flow rate at different set points and controller settings. These curves are not compared with experimental data. Figure 18 shows a plot of U versus cooling water flow rate. Figure 19 shows a comparison between predicted and experimental results using proportional control only on the flow rate of water. In addition, figures 20 and 21 are phase plane plots, constructed by plotting temperature versus acid concentration. The first shows the response of the model to a step change in acid rate at three different cooling water rates. The second shows controlled response to a step change in acid rate. The different curves show the effect of using different initial conditions. These curves are useful in determining optimum start-up conditions, and the limitations of the system under specified conditions.

The time constants for the system were calculated for representative conditions. The time constant for the heat balance equation was about 2.4 minutes and the time constant for the material balance differential equation was about 3.6 minutes. This indicates that the temperature of the reaction mixture shows faster response than the concentration of acid, but that both systems respond slowly to set-point or load changes.

Table 2. Step Changes

	T-Reactor Temperature, °F	Moles Water / Mole Acid	Q_F-Water Flow Rate, ml/min.	Q_A-Acid Flow Rate, ml/min.	T_{oA} Acid Temperature, °F	T_{oF} Water Temperature, °F	Q_c Cooling Water Flow Rate, ml/min.	T_c Cooling Water Temperature, °F
1. Initial	103	50	510	30	80	80	180	80
Final	122	13.3	135	30	80	80	180	80
2. Initial	103	50	510	30	80	80	180	80
Final	119	25	510	60	80	80	180	80
3. Initial	103	50	510	30	80	80	180	80
Final	91	50	510	30	80	80	1160	80

Figure 9. Response to step change in water flow rate.

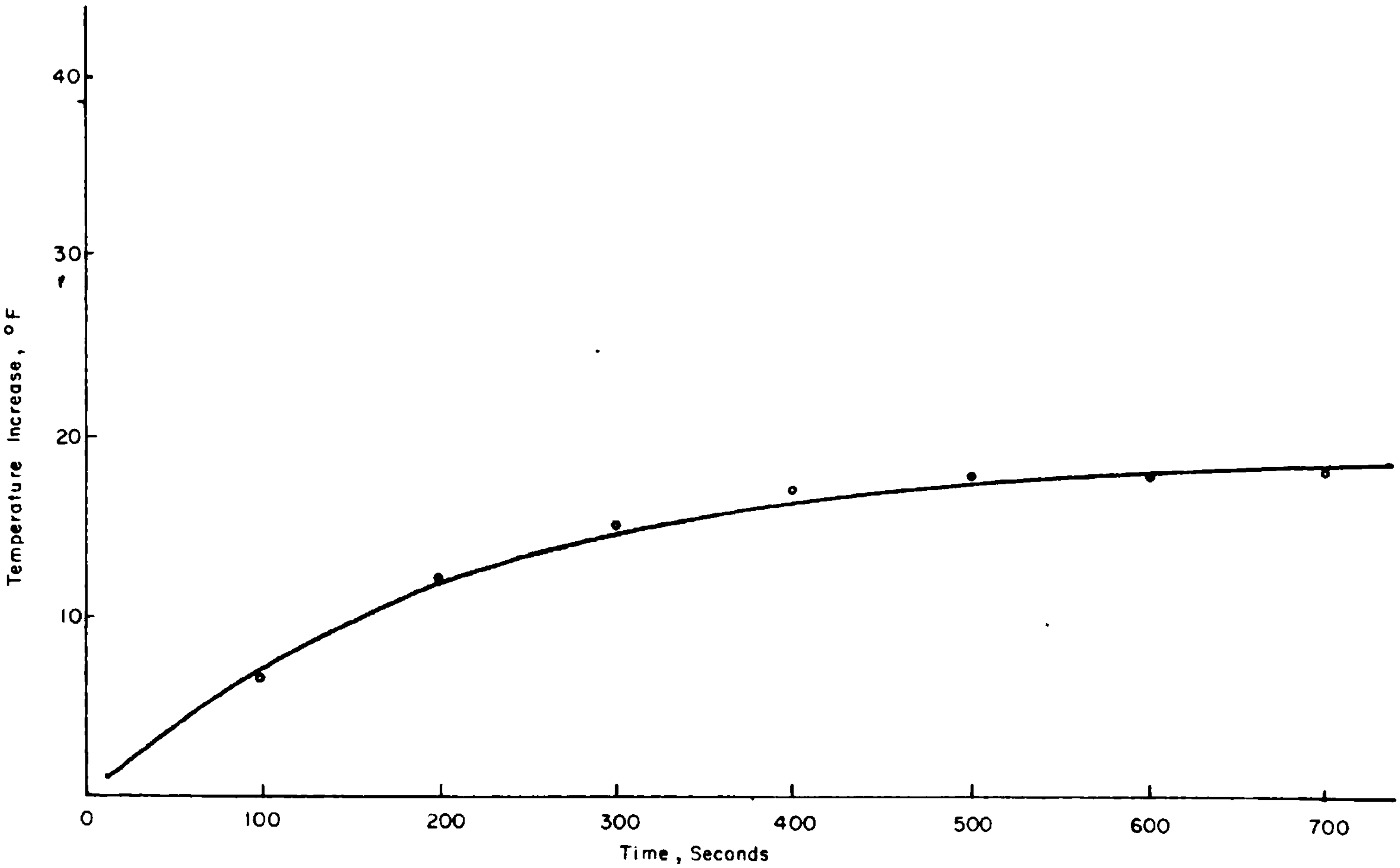
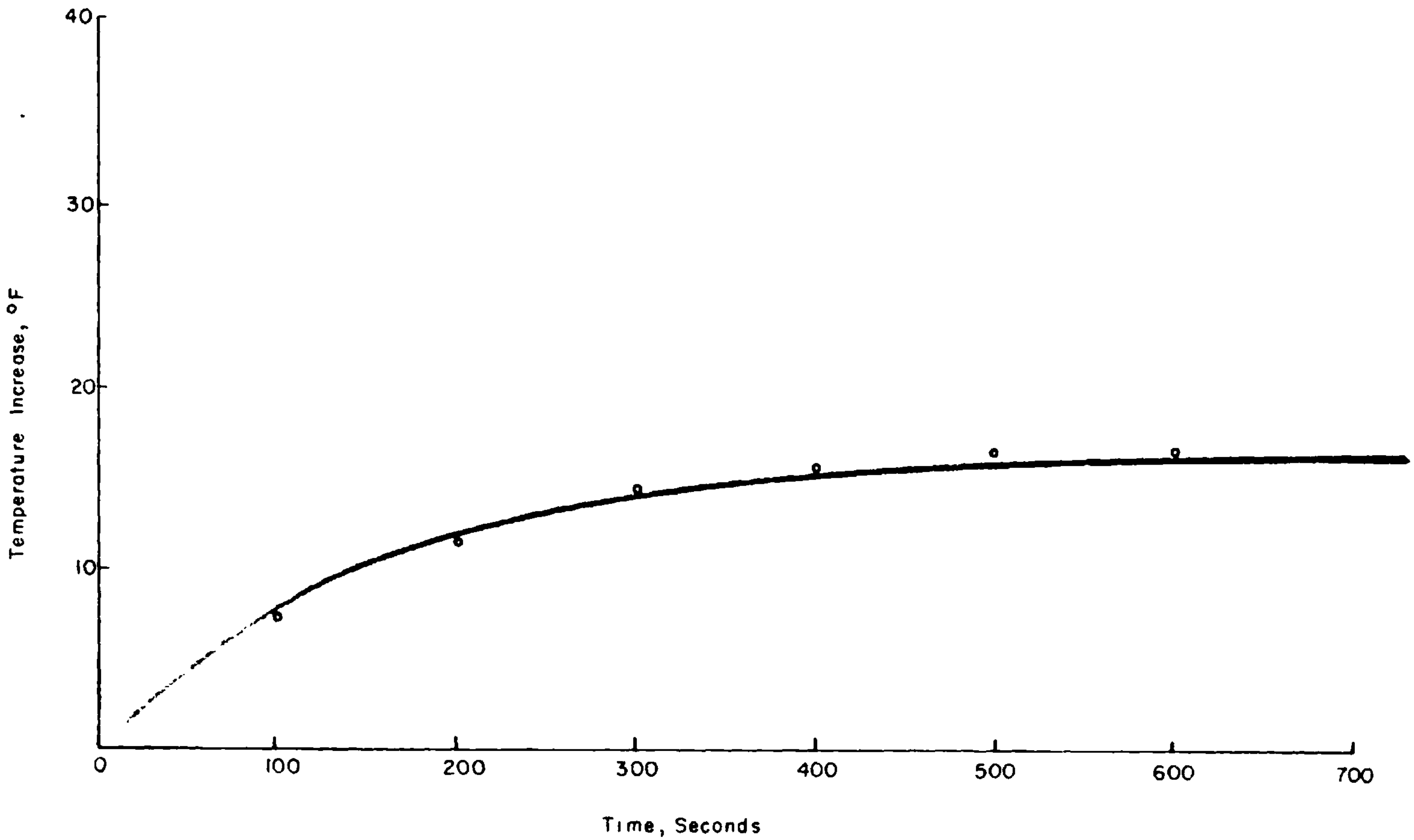

40
30
20
10
0
100
200
300
400
500
600
700
Temperature Increase, °F
Time, Seconds

Figure 9

Figure 10. Response of system to step change in acid flow rate.



40
30
20
10
Temperature Increase, °F
0
100
200
300
400
500
600
700
Time, Seconds

Figure 10

Figure 11. Response to step change in cooling water flow rate.

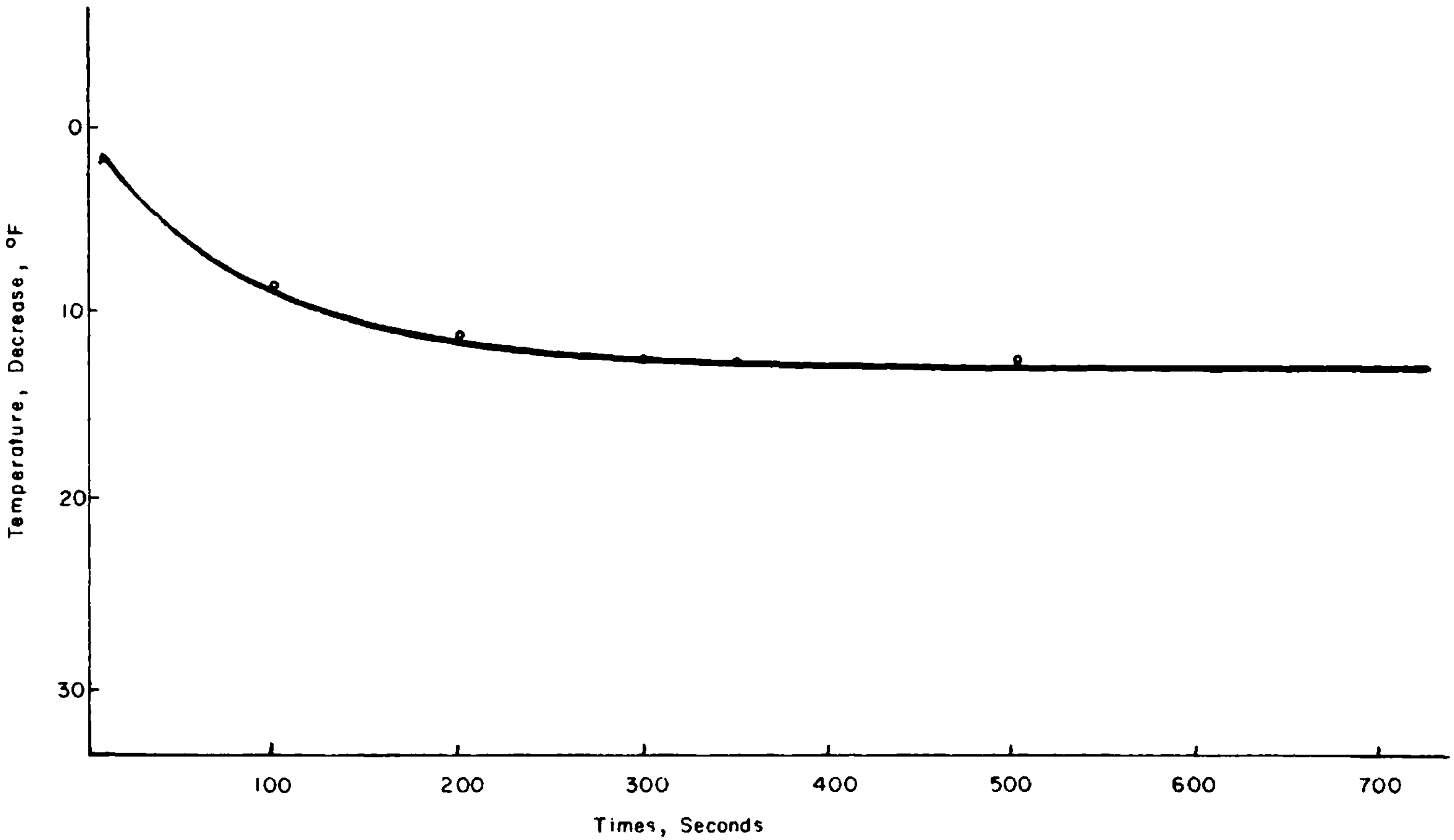
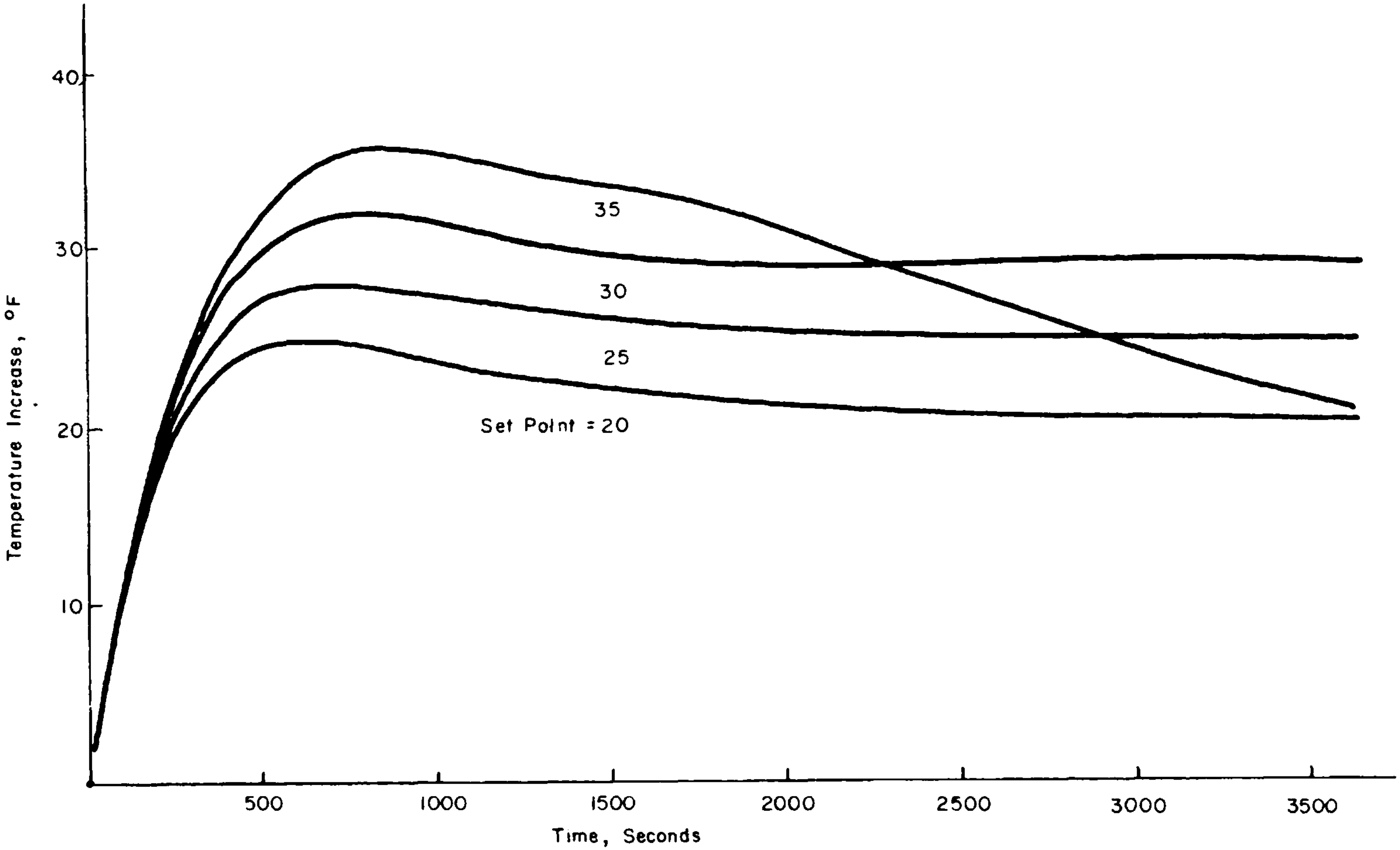

0
10
20
30
Temperature, Decrease, °F
100
200
300
400
500
600
700
Times, Seconds

Figure 11

Figure 12. Effect of placing proportional plus reset control on water flow rate at various set points.

Figure 12



Temperature Increase, °F
40
30
20
10
500
1000
1500
2000
2500
3000
3500
Time, Seconds
35
30
25
Set Point = 20

Figure 13. Effect of placing proportional plus reset control on cooling water flow rate at various set points.

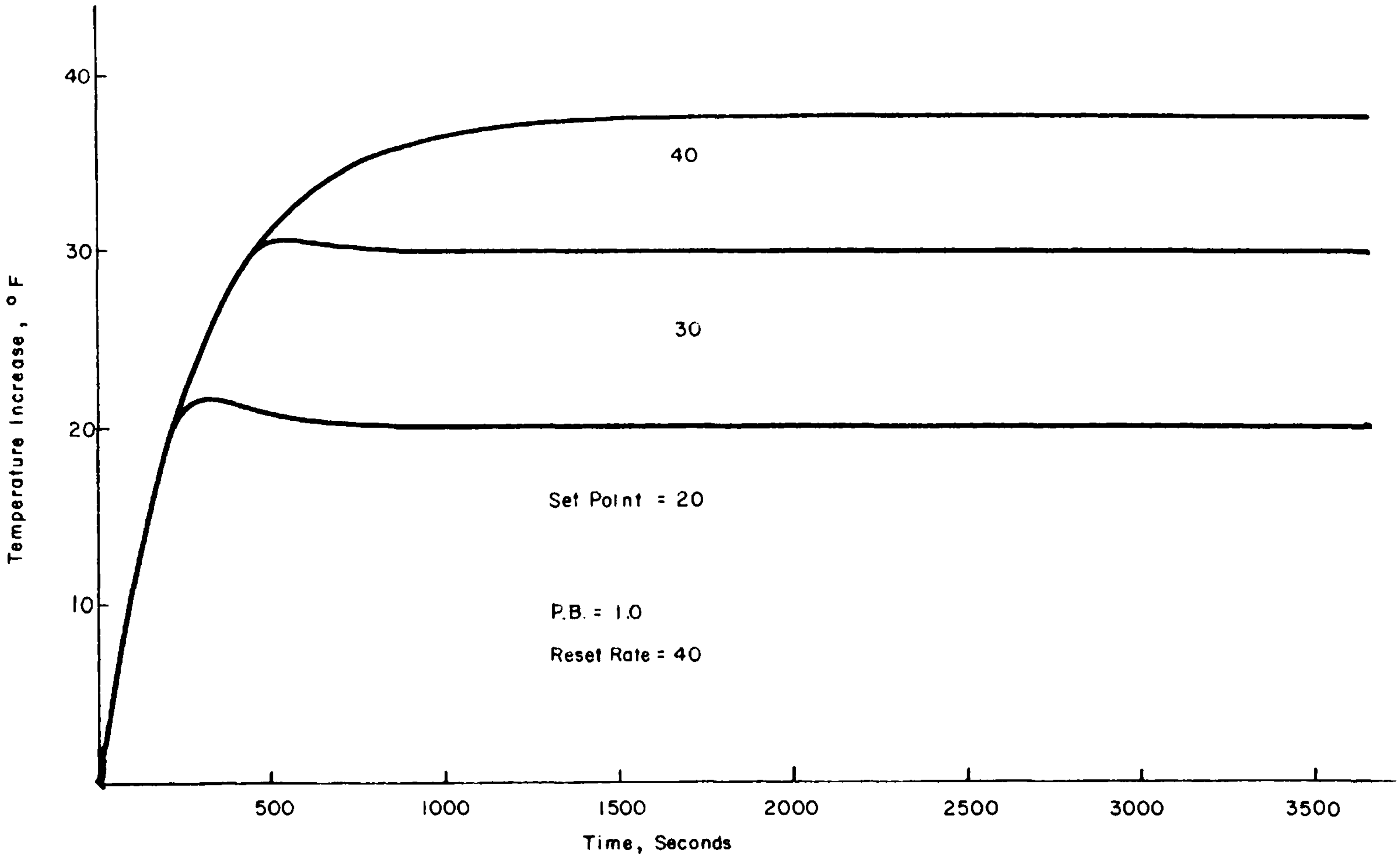

40
30
20
10
500
1000
1500
2000
2500
3000
3500
Time, Seconds
Temperature Increase, °F
40
30
Set Point = 20
P.B. = 1.0
Reset Rate = 40

Figure 13

Figure 14. Effect of placing proportional plus reset control on cooling water flow rate at different set points.

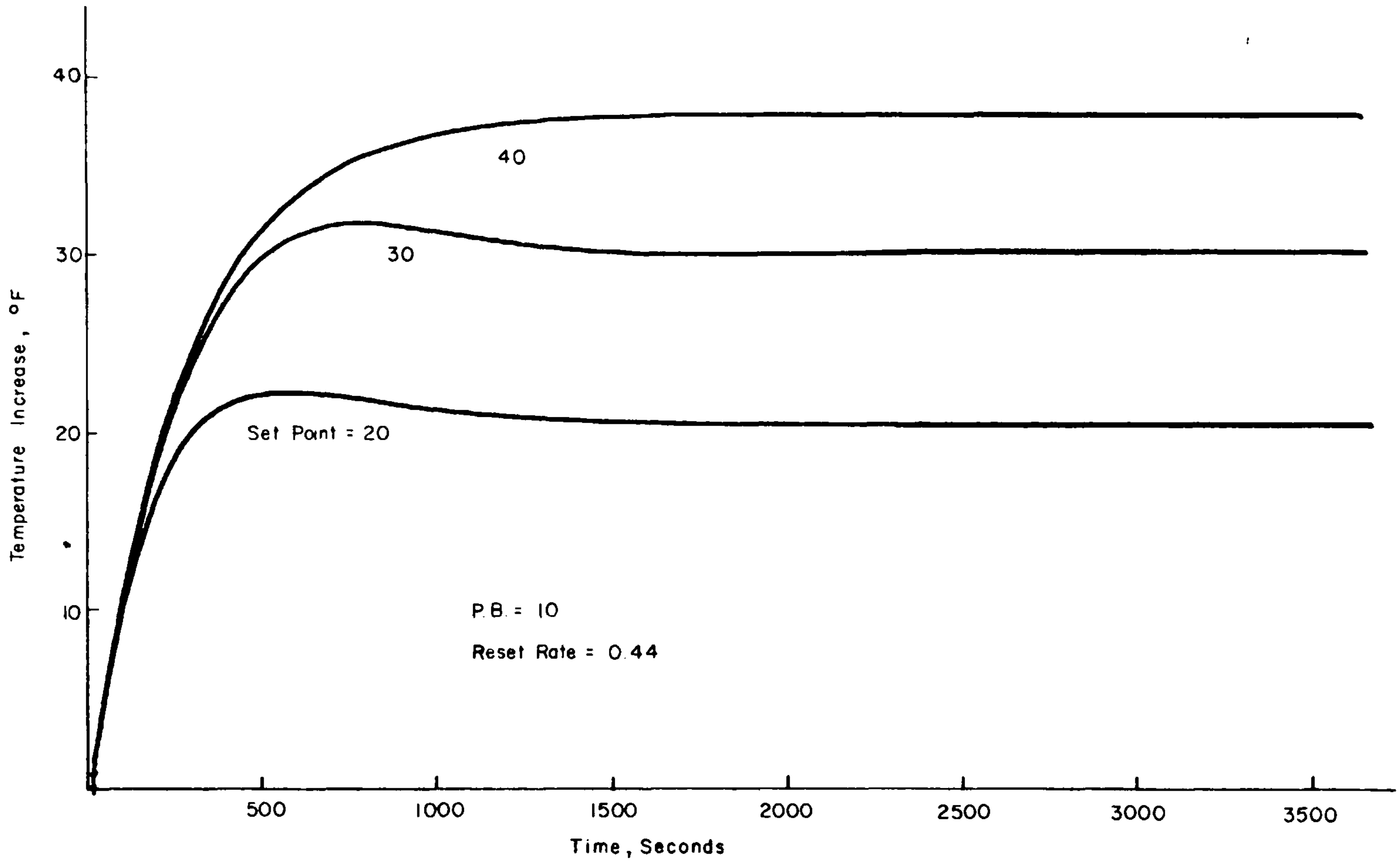
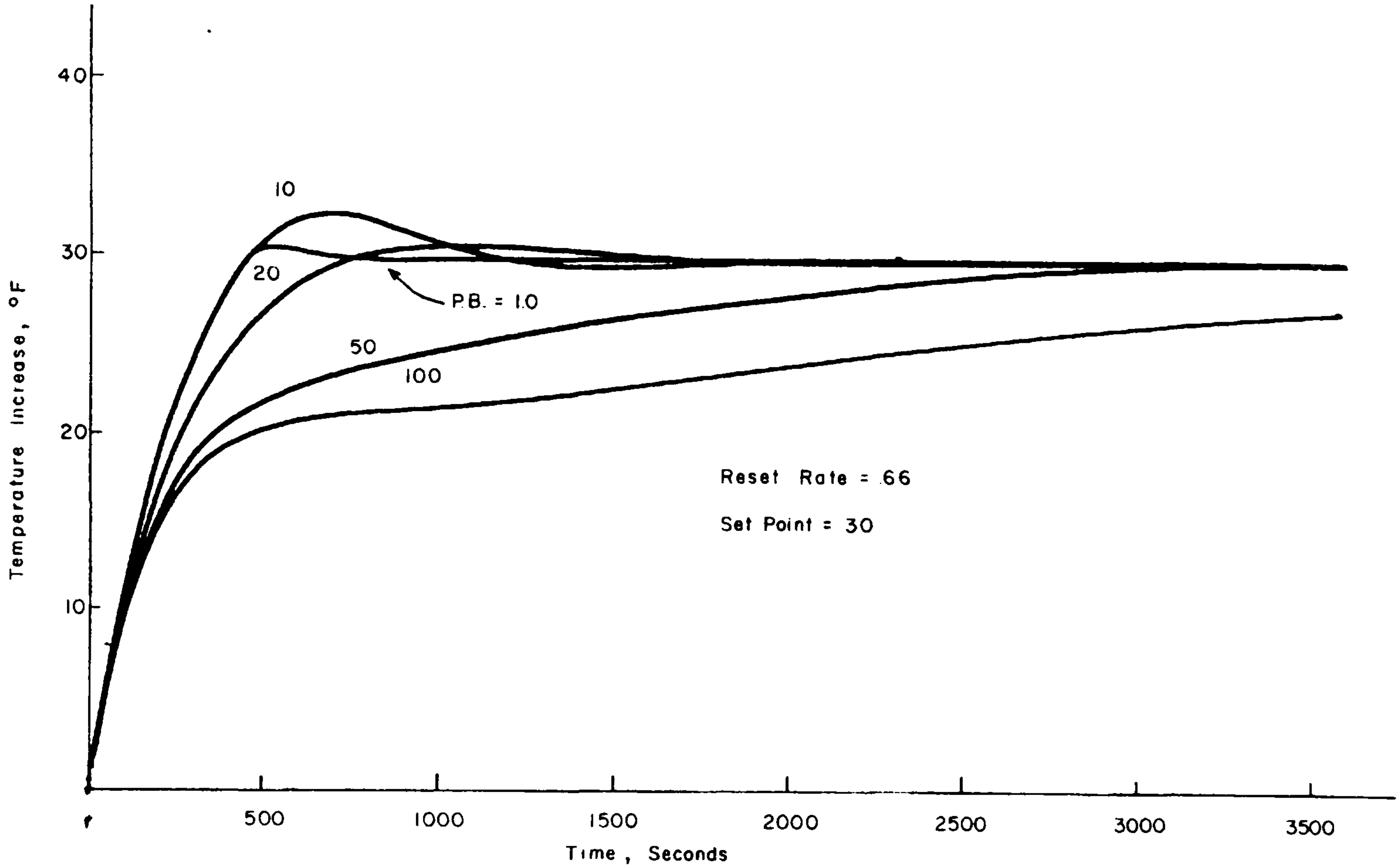

40
30
20
10
Temperature Increase, °F
500
1000
1500
2000
2500
3000
3500
Time, Seconds
40
30
Set Point = 20
P.B. = 10
Reset Rate = 0.44

Figure 14

Figure 15. Effect of placing proportional plus reset control on cooling water flow rate at different proportional band settings.

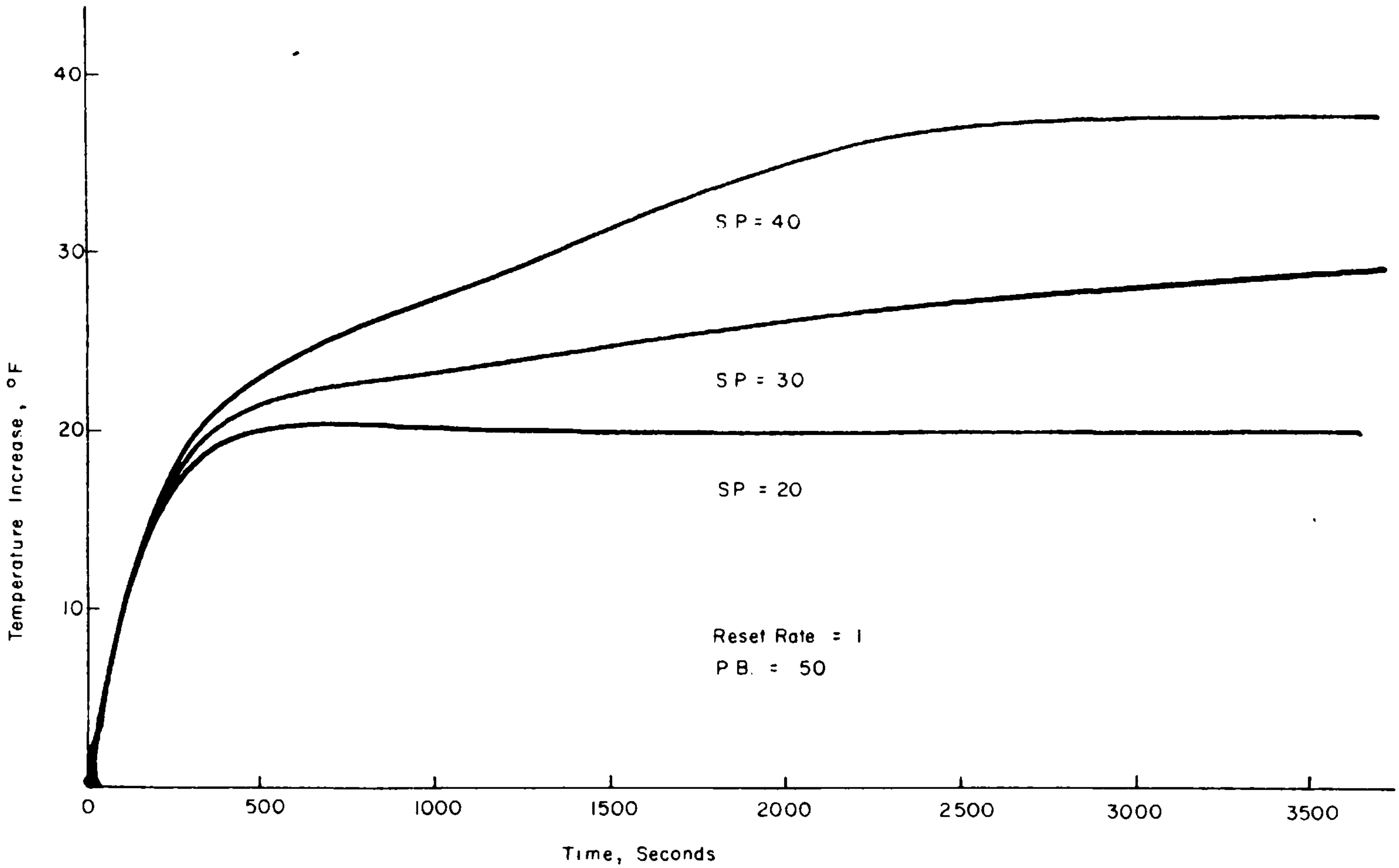


Temperature Increase, °F
40
30
20
10
10
20
P.B. = 1.0
50
100
Reset Rate = .66
Set Point = 30
500
1000
1500
2000
2500
3000
3500
Time, Seconds

Figure 15

Figure 16. Effect of placing proportional plus reset control on cooling water flow rate at different set points.

Figure 16



S P = 40
S P = 30
S P = 20
Reset Rate = 1
P B. = 50
Temperature Increase, °F
Time, Seconds
40
30
20
10
0
500
1000
1500
2000
2500
3000
3500

Figure 17. Effect of placing proportional plus reset control on cooling water flow rate at different set points.

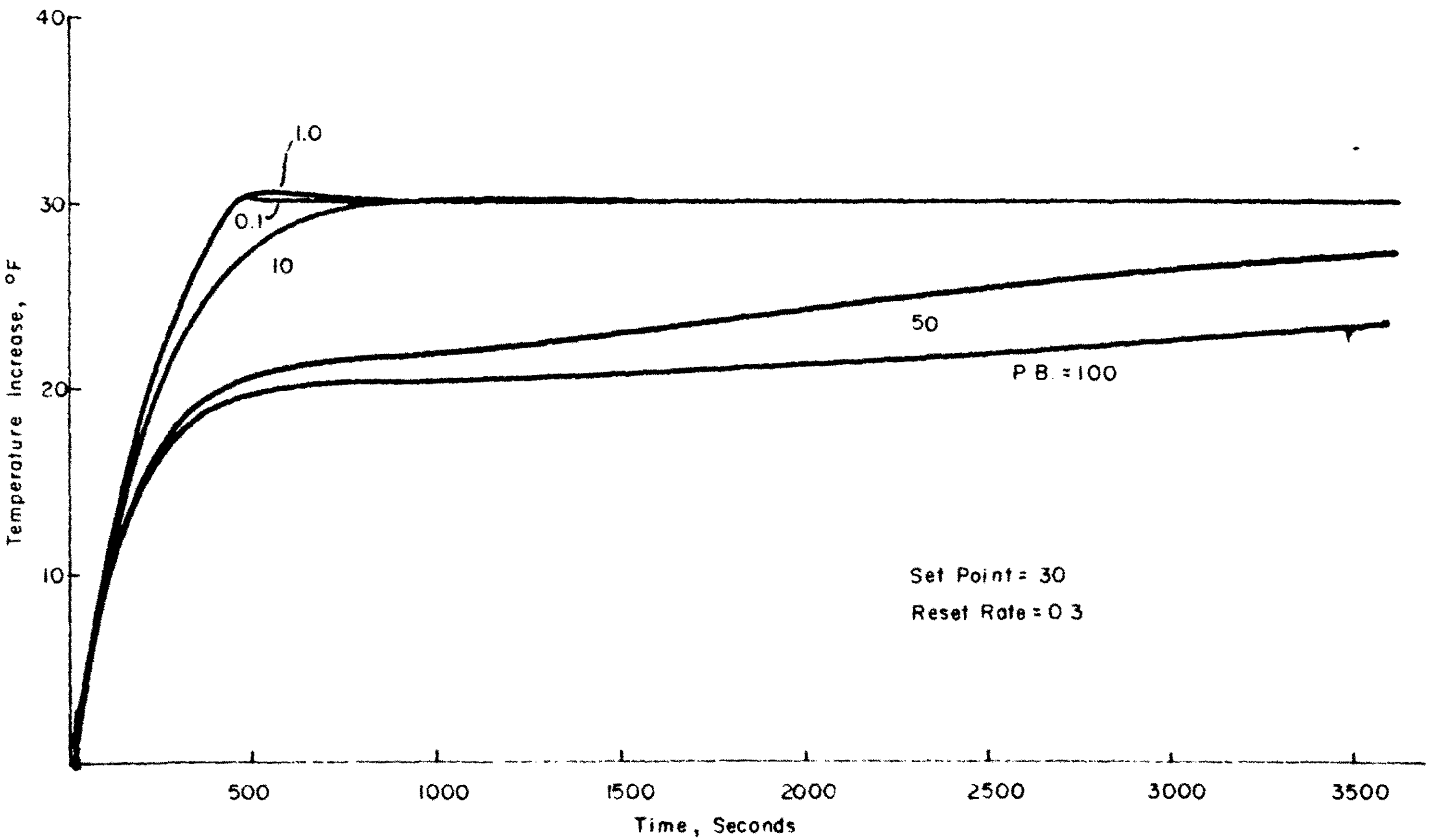

40
30
20
10
Temperature Increase, °F
500
1000
1500
2000
2500
3000
3500
Time, Seconds
1.0
0.1
10
50
P.B. = 100
Set Point = 30
Reset Rate = 0.3

Figure 17

Figure 18. Overall heat transfer coefficient versus cooling water flow rate.

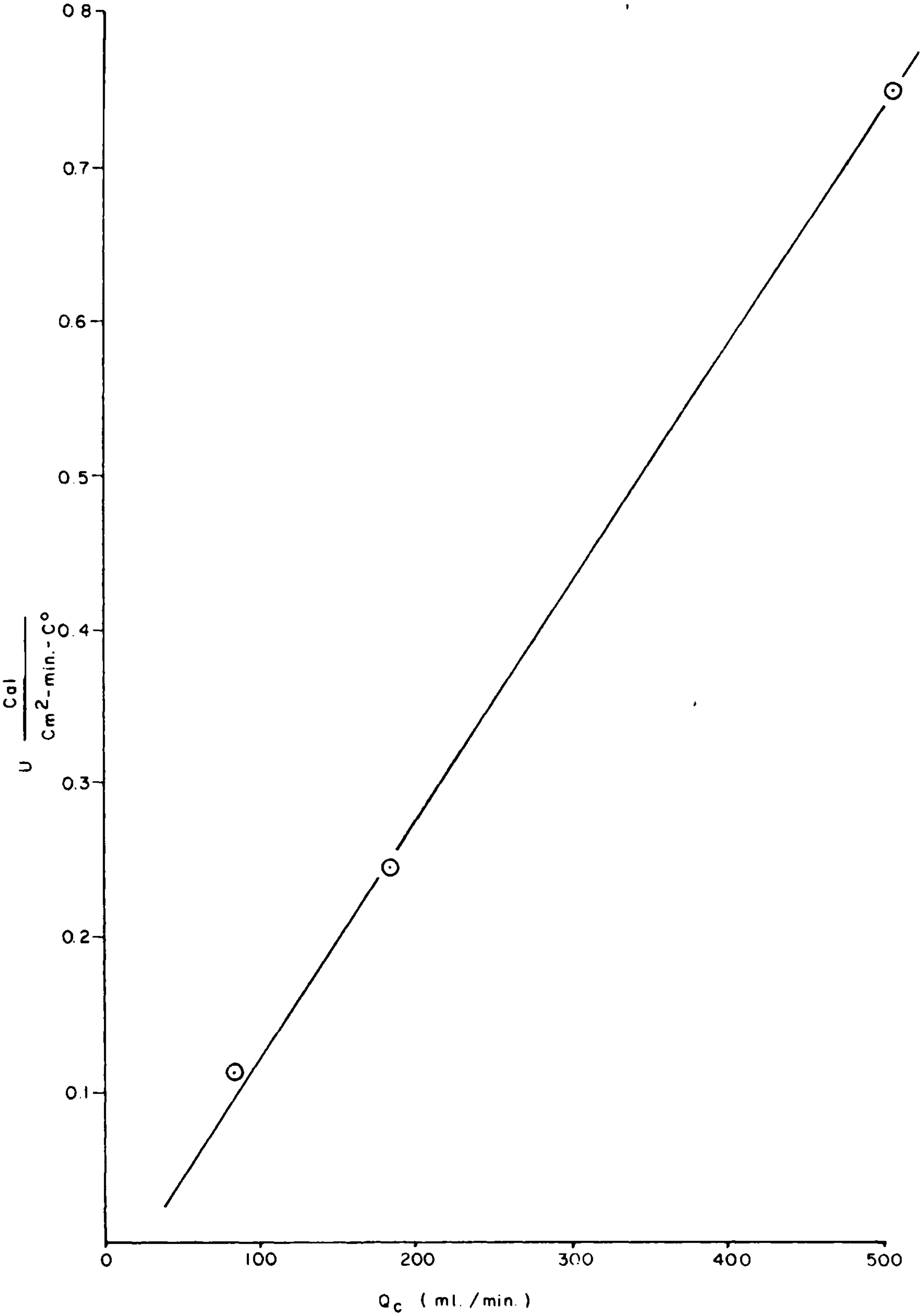
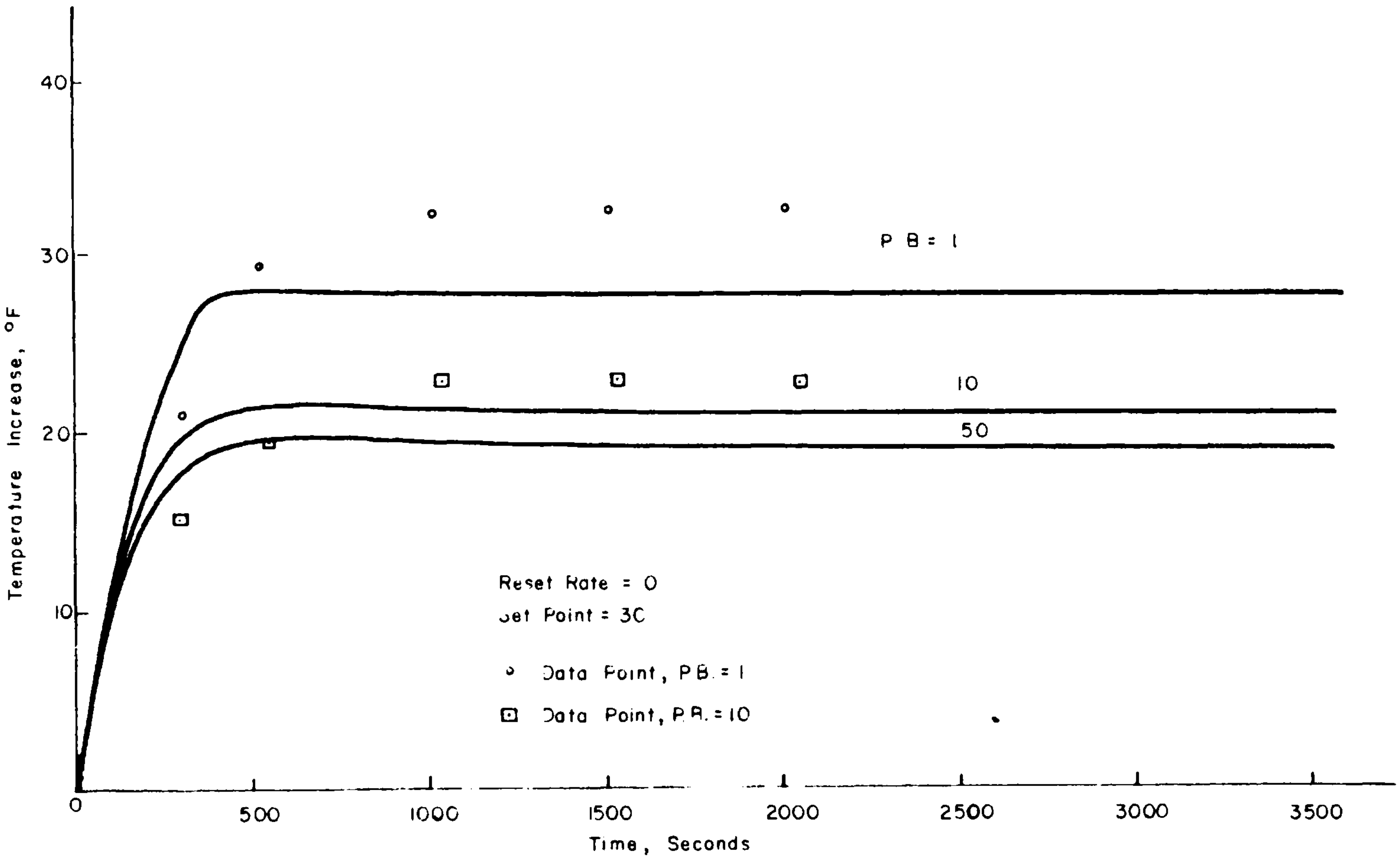

0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
100
200
300
400
500
U Cal/Cm²-min.-C°
Qc (ml./min.)

Figure 18

Figure 19. Comparison between experimental data and predicted results, proportional control only placed on cooling water flow rate.

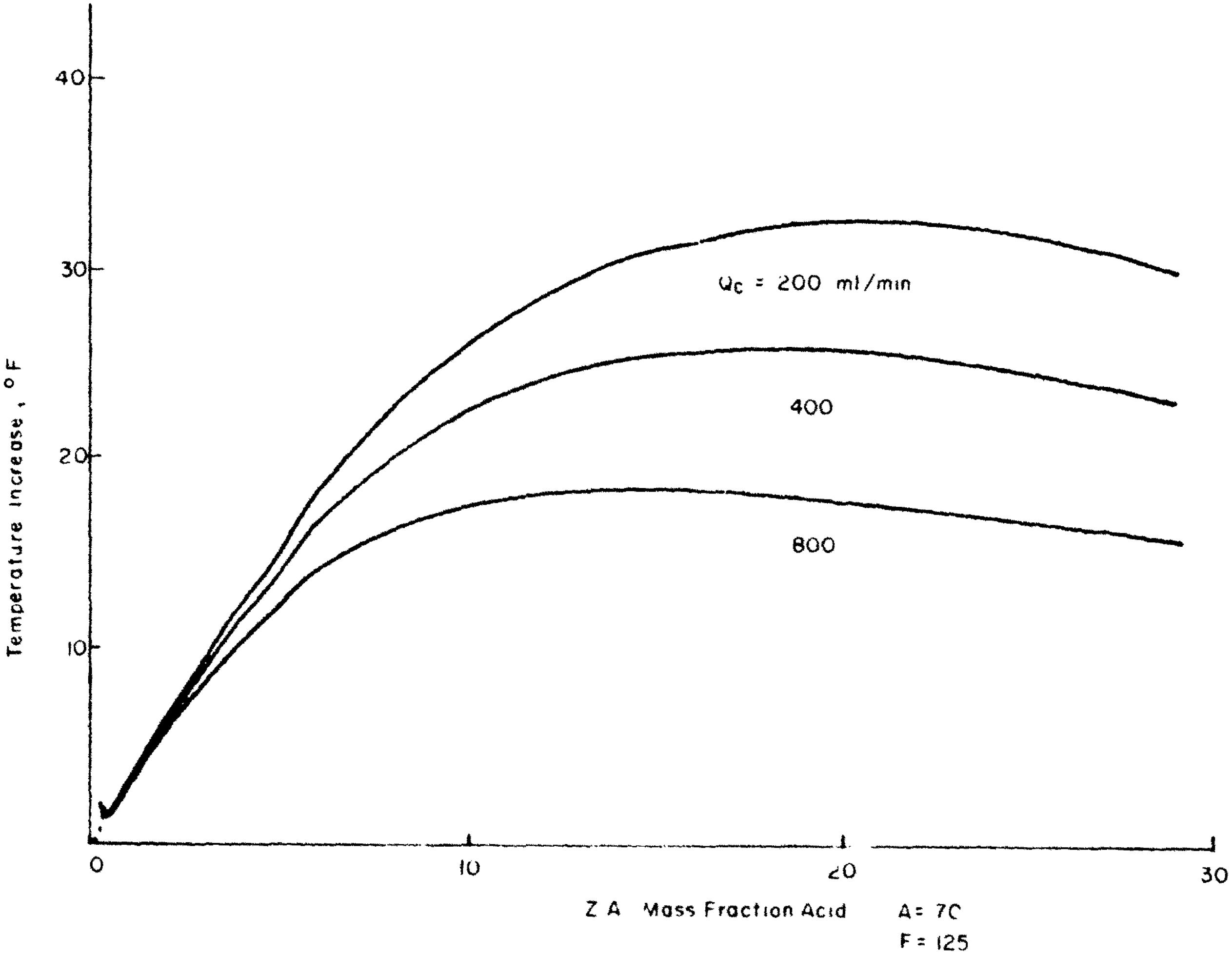
Figure 19



P B = 1
10
50
Reset Rate = 0
Set Point = 30
Data Point, P.B. = 1
Data Point, P.B. = 10
Temperature Increase, °F
Time, Seconds
0
10
20
30
40
500
1000
1500
2000
2500
3000
3500

Figure 20. Phase plane plot of mass fraction acid versus temperature increase at three different cooling water rates.

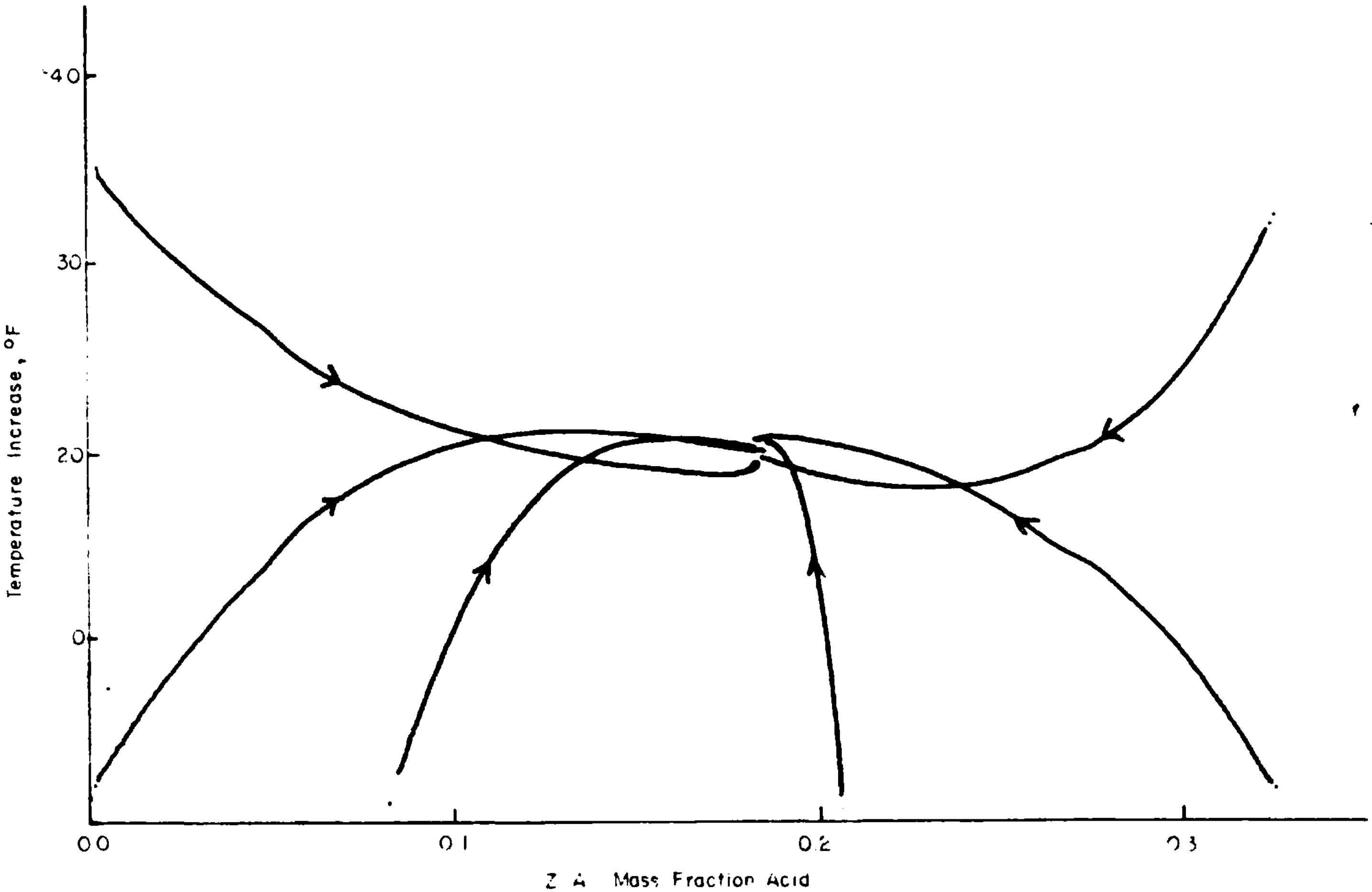
Figure 20



40
30
20
10
0
10
20
30
Temperature Increase , °F
Z A Mass Fraction Acid
A = 70
F = 125
Q_c = 200 ml/min
400
800

Figure 21. Phase plane plot of mass fraction acid versus temperature increase showing effect of varying initial conditions.

Figure 21



40
30
20
0
Temperature Increase, °F
0.0
0.1
0.2
0.3
Z A Mass Fraction Acid

DISCUSSION OF RESULTS

Earlier it was stated that the objective of this investigation was to test the process model and to determine certain information about the process, in particular:

1. Control of the process to obtain the desired results
2. Maintaining system stability
3. Determination of optimum start-up conditions.

First, it was necessary to determine if the model actually predicted the response of the system to step changes made on the experimental apparatus. Figures 9, 10, and 11 show that the model closely matched the responses of the actual system with a maximum error of 5 percent.

To determine whether or not the system could be controlled to produce the desired results (reaching a set steady state value of the temperature), the control action was first placed on the flow rate of water entering the reactor. This method worked well at moderate temperatures. As can be seen in figure 12, if a set point was chosen which was above the capabilities of the system, the valve would close, reducing the water rate, allowing the system to heat up. If the system did not reach the set point fast enough, the reactor would saturate with acid and there would be no further effects of adding acid to the system. The reactor temperature would then approach the temperature of the incoming cooling water. The maximum temperature which could be held was a function of the acid flow rate, and the cooling water rate. Due to this effect, it was concluded that controlling the flow rate of water to the reactor was not the best method of maintaining a set temperature in the reactor.

For all controlled runs, the concentration of acid in the reactor was not considered to be important; only the temperature of the reaction mixture was of interest.

The control action was then placed on the cooling water flow rate. Assuming that during the operation of the process, the acid and water streams are flowing at reasonable values (about half of maximum), figures 13 through 17 show that the process can be controlled within a sizeable range. The lower limit is approximately the temperature of the cooling water.

The upper limit of the control range is determined by the relative amounts of the acid and water being added to the reactor. With control action on the cooling water, there is a possibility of having offset if the set point is higher than the maximum obtainable temperature of the system. However, there would be far less offset in the high temperature portion of the range than with the control action placed on the water flow rate.

The next point in question was the determination of suitable controller settings. The process is inherently stable, having both upper and lower limits on the temperature. By examination of figures 13 to 17, it can be determined that a low proportional band setting (less than 10.0) makes the process come to the set point quickly, and that some reset action (reset rate about 1 repeat per minute) is necessary to eliminate offset. Since the process time constants were found to be large with respect to the control element time constants, the process should be fairly easy to control.

The third point to be considered was the determination of optimum start-up conditions. The phase plane plot shown in figure 21 indicates that the system will come to the set point quickly from any initial temperature and concentration with the control action placed on the cooling water flow rate. Therefore, the start-up conditions for this system are not critical. In more complicated reaction systems, however, phase plane plots indicate that if certain initial conditions of temperature and concentration are used, the process will not reach the set point (1). By constructing phase plane plots from an analog simulation, these undesirable initial conditions could be detected and avoided.

CONCLUSIONS

In order to maintain a fixed temperature by mixing sulfuric acid and water, it was concluded that the best results will be obtained by placing control action on the cooling water flow rate rather than on the flow rate of entering water.

It can be concluded also that the controller settings were not critical, and that suitable values were a proportional band setting of about 10 and a reset rate of approximately 1 repeat per minute. It was found that the start-up conditions were not critical. The system would come to the set point from any initial temperature and concentration.

It was found that the desired information concerning the control properties of the system could be determined best, even for a system as simple as the acid-water system, by an analog simulation.

RECOMMENDATIONS

This investigation provides the groundwork for much future research. The experimental apparatus constructed for this investigation was designed for use with a number of different reaction systems. The acid-water system was used only as a first approximation to a typical chemical reaction system. The techniques outlined in the previous section could easily be extended to investigate the effects of placing control action on different variables associated with a first or second order reaction system, with similar goals in mind. A representative first or second order system should be found and equipment located which would analyze continuously the concentration of some reaction component. With this equipment, an investigation could be carried out with concentration instead of temperature as the measured variable.

The proportional-reset controller used in this research should be replaced by a type which is more suitable for experimental work. A Speedomax H would be well suited for this purpose. The reaction vessel should be replaced by a larger unit fitted with a level controller to control the volume of the reaction mixture.

APPENDIX

Table 3. Kinetic Data for Hydrogen Peroxide Decomposition in Sodium Hydroxide

I. Temperature = 140F, NaOH concentration = 0.03 g moles/liter.

Time, Minutes	C/C_o	
0	1.0	
25	0.885	
110	0.420	k = 0.0053 $minutes^{-1}$

II. Temperature = 140F, NaOH concentration = 0.04 g moles/liter.

Time, Minutes	C/C_o	
0	1.0	
40	0.614	
70	0.396	
80	0.340	
105	0.234	k = 0.0064 $minutes^{-1}$

III. Temperature = 140F, NaOH concentration = 0.05 g moles/liter.

Time, Minutes	C/C_o	
0	1.0	
72	0.508	
84	0.480	
122	0.411	
130	0.380	k = 0.002 $minutes^{-1}$

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