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A digital computer simulation of a batch or semi-batch reactor

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A DIGITAL COMPUTER SIMULATION OF A BATCH OR SEMI-BATCH REACTOR

BY

ROBERT EDWARD VICZOREK

A THESIS
PRESENTED IN PARTIAL FULFILLMENT OF
THE REQUIREMENTS FOR THE DEGREE
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ABSTRACT

A digital computer simulation of a batch or semi-batch reaction was developed. The system consisted of a jacketed, agitated vessel equipped with a temperature controller modulating a control valve in the stream to the jacket. The reaction was liquid phase, and the jacket medium was liquid.

The program was written in a general form so as to be applicable to any liquid phase reaction with minimum modification.

A numerical technique was employed using initial values of the process variables in the first cycle of calculations for a time interval, and then using average values for further iterations. The simulation proceeded by time increments until the maximum desired reaction time was reached, or until the reaction rate dropped to the minimum desired conversion per time interval.

For the trial runs of the program, a reaction, the esterification of acetic acid with ethyl alcohol, and conditions were selected, along with other specifics such as equipment, instrumentation, and cooling medium. All the necessary data on these items were collected.

A series of simulations were performed for various controller settings. The reaction temperature was plotted against time with the controller settings as parameters to illustrate the effect of the settings on temperature control.

The results obtained agree in general with the behavior expected, with temperature control improving with increasing rate and integral setting and improving with increasing gain up to a certain point.

APPROVAL OF THESIS

A DIGITAL COMPUTER SIMULATION
OF A BATCH OR SEMI-BATCH REACTOR

BY

ROBERT EDWARD VICZOREK

FOR

DEPARTMENT OF CHEMICAL ENGINEERING

NEWARK COLLEGE OF ENGINEERING

BY

FACULTY COMMITTEE

APPROVED:

NEWARK, NEW JERSEY

JUNE, 1970

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1. To Dr. Saul I. Kreps for his help and direction during all phases of the thesis preparation.
2. To the members of the staff of the Department of Computer Science for their assistance during program debugging.
3. To my wife, Roseann, for the typing of this material.

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CHAPTER 1.

INTRODUCTION

The objective of the thesis was to prepare a digital computer simulation of a batch or semi-batch liquid phase chemical reaction utilizing a liquid heating or cooling medium. The reaction takes place in a jacketed, agitated vessel equipped with a three-mode temperature controller and temperature control valve on the heat transfer medium to the jacket.

The computer program was written in a general form so as to be applicable to any liquid phase reaction with minimum modification.

The reactor simulation was developed in the following phases:

(1) definition of method
(2) detailed mathematical development
(3) computer program preparation
(4) selection of test process and data collection
(5) program debugging
(6) test running of program

The test running of the program consisted of simulations at various combinations of controller settings to investigate the effect of each controller mode on temperature control.

CHAPTER II.

METHOD OF SIMULATION

The selected reaction is simulated by a numerical technique involving calculations for the reaction and controller for a discrete time interval. The calculations are first performed using initial conditions. Average temperatures and concentrations for the time interval are then calculated and the reaction and controller calculations repeated using the average conditions. Several iterations of the calculations are performed to produce convergence.

Final conditions for a time interval are then used as the initial conditions for the succeeding interval. The simulation proceeds in this manner until a specified total time limit is reached or until the reaction conversion drops to a specified minimum value.

For a particular time interval, batch temperature is the variable selected for convergence. The simulation proceeds to the next time interval after the batch temperatures calculated in two successive iterations agree within specified limits or when a specified maximum number of iterations have been performed.

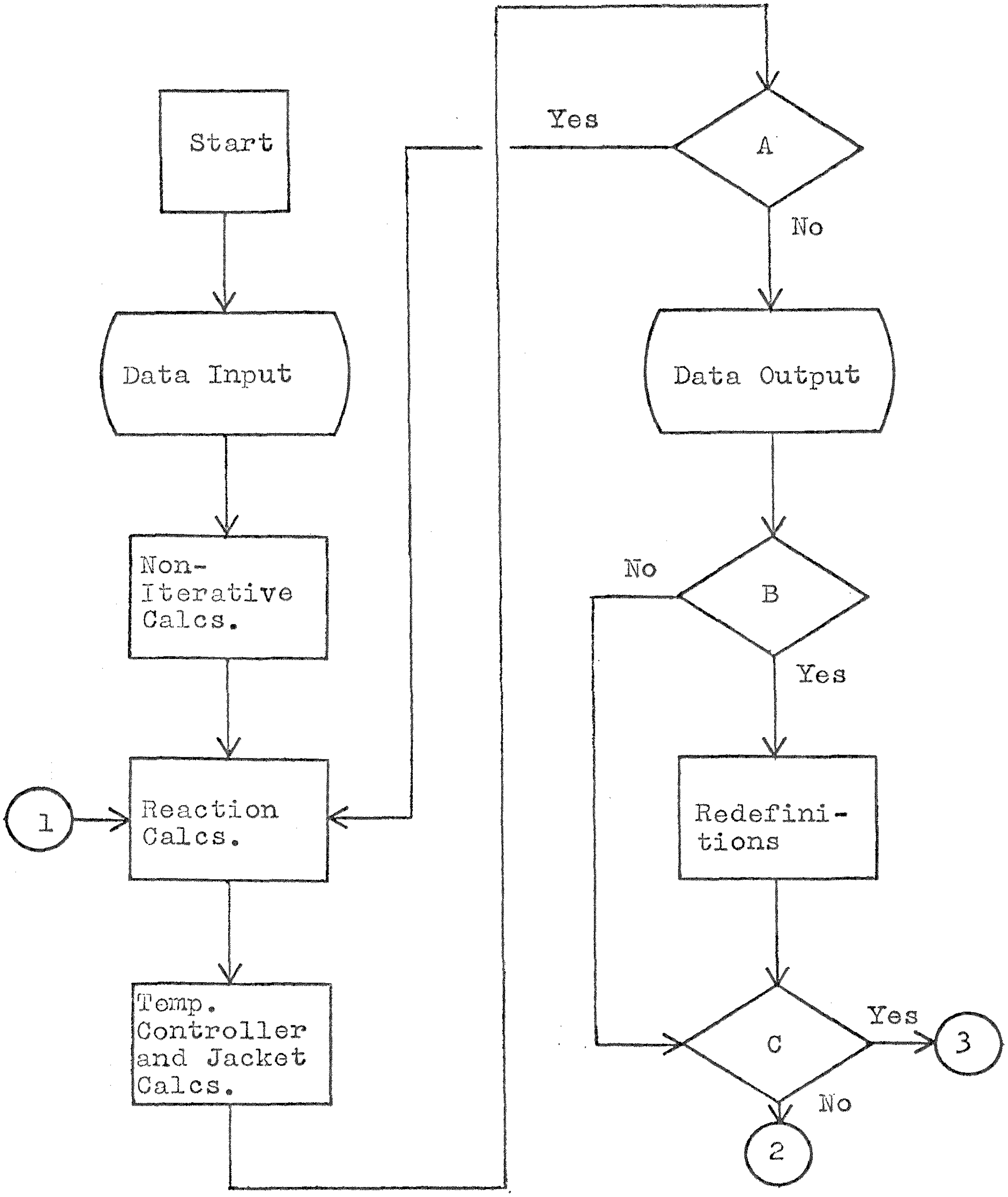
In the first portion of the simulation program one-time, or non-iterative, calculations are performed. The calculations in this section are associated with specific heats and densities for the materials involved. The general structure of the program is shown on Figure I, Overall Logic Diagram.

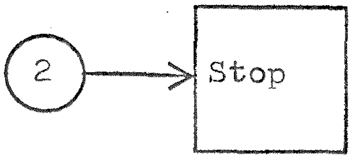
In the second section of the program, the calculations involving the reaction are performed. At reaction temperature, properties of the chemical components and reaction characteristics are determined. Batch volume and concentrations are calculated. Incremental mass changes for each component and the incremental heat evolved due to the reaction occurring during the time interval are computed. Finally, the change in batch temperature is determined taking into account the heat transferred to the jacket medium.

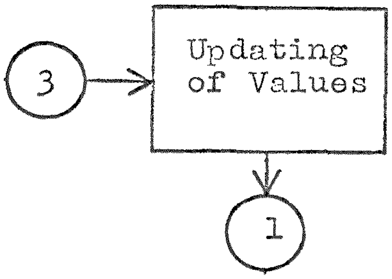
The third segment of the program includes calculations involving the vessel jacket and the temperature control system. The end-of-time-interval values for each component in the temperature control loop, from sensed temperature through pneumatic signal to the control valve, are determined. Also, the incremental temperature change

Figure I

Overall Logic Diagram







A - Tests for Additional Iterations

B - Tests for Changing Values or Conditions

C - Tests for Progression to Next Time Interval of the jacket medium is calculated through the performance of a heat balance on the jacket and its contents.

The final segment of the program consists of tests to determine if further iterations within the same time interval are required, if the program should proceed to the next interval, or if the program should be terminated. For certain variables whose values are to be changed at particular times in the program, tests are performed and values redefined where required. Also, the activation of the temperature controller is performed, if necessary, in this segment. Finally, the output of data is performed when desired.

The above general method is described in greater detail in the following material. The method is original with no reference having been made to other work.

CHAPTER III.

MATHEMATICAL DETAILS

A detailed logic diagram contained in Appendix B should be used as an aid in following the organization of the following calculations.

Non-Iterative Calculations

Watson liquid-phase expansion factor. In the first section of the program the initial item calculated is the Watson liquid-phase expansion factor. This quantity is used in the determination of specific heats at various temperatures of the reactants and products by the method of Chow and Bright.[1] The expansion factor is calculated for each reaction component at the reference temperature for which specific heat data has been submitted. The following equation is used:

$$w_{i,1} = 0.1745 - 0.0838\ T_{i,1}/T_{i,4} \qquad (1)$$

All symbols and subscripts are explained in Appendix A, Tables I and II. In the case of double subscripts, the first refers to a material and the second to a temperature. This identification is used throughout the chapter.

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[1] Chow and Bright, Chemical Engineering Progress, vol. 49, 1953, p. 175.

The expansion factor is then calculated for each reaction component at the reference temperature for heat of reaction according to the following:

$$w_{i,5} = 0.1745 - 0.0838\ T_5/T_{i,4} \tag{2}$$

Specific heats. These two above calculated quantities are then used with the submitted specific heat data to calculate the specific heat of each component at the reference temperature for heat of reaction.

$$(c_p)_{i,5} = (c_p)_i\ (w_{i,1}/w_{i,5})^{2.8} \tag{3}$$

The last two relationships are again used to obtain specific heats of the reaction components at the reference temperature for the concentration equilibrium constant.

$$w_{i,6} = 0.1745 - 0.0838\ T_6/T_{i,4} \tag{4}$$

$$(c_p)_{i,6} = (c_p)_i\ (w_{i,1}/w_{i,6})^{2.8} \tag{5}$$

Finally, the same two relationships are again used to obtain the specific heat of reactant B at the constant temperature at which it is continuously added. Prior to these calculations, the temperature of reactant B, T_7, is converted to degrees Rankine so that correct units will be used. After the calculations, T_7 is reconverted to degrees Fahrenheit.

$$T_7 = T_7 + 459.60 \tag{6}$$

$$w_{2,7} = 0.1745 - 0.0838\ T_7/T_{2,4} \tag{7}$$

$$(c_p)_{2,7} = (c_p)_2\ (w_{2,1}/w_{2,7})^{2.8} \tag{8}$$

$$T_7 = T_7 - 459.60 \tag{9}$$

Density calculations. Following these one-time calculations of specific heats, non-repetitive calculations involving densities are performed. The method used to calculate liquid densities as a function of temperature is the surface-tension correlation (modified Goldhammer equation).[2] First, the vapor densities of the reaction components and the jacket medium at their boiling temperatures are determined.

$$\rho v_{i,3} = MW_i/(5.461 \times T_{i,3}) \tag{10}$$

The factor 5.461 is the gas constant having the units gal.atm./lb.mole°R. Next, the vapor densities at the reference temperature for which density data has been submitted are calculated.

$$\rho v_{i,2} = \exp\ ((5.0((T_{i,2}/T_{i,3}) - 1.0) + \log_{10}(\rho v_{i,3}))\ \log_e (10.0)) \tag{11}$$

The density constant ($\rho 1$) used in this method is then calculated for each material. This quantity is used

[2] Gold, P. I. and G. J. Ogle, "Estimating Thermophysical Properties of Liquids - Part 3", Chemical Engineering, vol. 25, November 18, 1968, p. 172.

later in the program for the calculation of the densities of the reaction materials at various temperatures.

$$\rho l_i = (\rho R_i - \rho v_{i,2})/(1.0 - T_{i,2}/T_{i,4})^{0.3} \qquad (12)$$

The last "one-time" density calculation performed is the determination of the density of reactant B at the constant temperature at which it is continuously added. The vapor density of reactant B at T_7 is determined and then the liquid density ($\rho 27$) calculated as follows:

$$\rho v_{2,7} = \exp\ ((5.0(((T_7 + 459.60)/T_{2,3}) - 1.0) + \log_{10}\ (\rho v_{2,3}))\ \log_e (10.0)) \qquad (13)$$

$$\rho 27 = \rho v_{2,7} + \rho l_2\ (1.0 - (T_7 + 459.60)/T_{2,4})^{0.3} \qquad (14)$$

Heat of reaction at equilibrium constant reference temperature. The next quantity calculated is the heat of reaction at the reference temperature for the equilibrium constant. To calculate this item, the reference heat of reaction submitted in the data is used with arithmetic average specific heats for reactants and products between the reference temperatures for heat of reaction and equilibrium constant. The specific heats at the two reference temperatures were previously obtained using Equations (3) and (5). The stoichiometric constants are those for the reaction being simulated:

$$a_1A + a_2B \rightleftharpoons a_3C + a_4D \qquad (15)$$

where A, B, C, and D represent the chemical reactants and products. The calculation is:

$$\begin{aligned}\Delta H_K = \Delta H_R + (&a_3((c_p)_{3,6} + (c_p)_{3,5})\cdot \\ &MW_3 + a_4\ ((c_p)_{4,6} + (c_p)_{4,5})\cdot \\ &MW_4 - a_1\ ((c_p)_{1,6} + (c_p)_{1,5})\cdot \\ &MW_1 - a_2\ ((c_p)_{2,6} + (c_p)_{2,5})\cdot \\ &MW_2)(T_6 - T_5)/2.0\end{aligned} \qquad (16)$$

Iterative Calculations - Reaction

Specific heats. The calculations in the second segment of the program, iterative calculations for the reaction, are begun by determining the Watson liquid-phase expansion factor and specific heat for each component at the varying reaction temperature. The reaction temperature, T_8, is converted to degrees Rankine in the first calculation.

$$w_i = 0.1745 - 0.0838\ (T_8 + 459.60)/T_{i,4} \qquad (17)$$

$$(c_p)_{i,8} = (c_p)_i \ (w_{i,1}/w_i)^{2.8} \qquad (18)$$

Heat of reaction. Next, the heat of reaction at reaction temperature is calculated using the reference heat of reaction and average specific heats as in Equation (16). This equation is not completely general and might require modification for use on a particular reaction.

$$\begin{aligned} \Delta H_0 = \Delta H_R + (a_3((c_p)_{3,8} + (c_p)_{3,5})\cdot \\ MW_3 + a_4\ ((c_p)_{4,8} + (c_p)_{4,5})\cdot \\ MW_4 - a_1\ ((c_p)_{1,8} + (c_p)_{1,5})\cdot \\ MW_1 - a_2\ ((c_p)_{2,8} + (c_p)_{2,5})\cdot \\ MW_2)\ (T_8 + 459.60 - T_5)/2.0 \end{aligned} \qquad (19)$$

Equilibrium constant. The equilibrium constant at reaction temperature is next determined by using the average of the heats of reaction at reaction temperature, Equation (19), and at the equilibrium constant reference temperature, Equation (16), in the following equation:

$$\begin{aligned} K = K_R \cdot \exp\ ((\ \Delta H_0 + \Delta H_K)\ (1.0/T_6 - \\ 1.0/(T_8 + 459.60))/2R) \end{aligned} \qquad (20)$$

The derivation of this relationship is described in Chapter IV - Mathematical Derivations.

Reaction rate constants. The forward reaction rate constant is calculated using the Arrhenius Equation, and is then used with the equilibrium constant calculated above to determine the reverse reaction rate constant.

$$k = A \cdot \exp\ (E/(R(T_8 + 459.60))) \tag{21}$$

$$k' = k/K \tag{22}$$

Densities. Density calculations for the chemical components at reaction temperature are next performed according to the surface tension correlation (modified Goldhammer equation).[3] Using the boiling point vapor densities obtained from Equation (10), the reaction temperature vapor densities are determined for each component.

$$\rho v_{i,8} = \exp\ ((5.0(((T_8 + 459.60)/T_{i,3}) - 1.0) + \log_{10}\ (\rho v_{i,3}))\log_e (10.0)) \tag{23}$$

The liquid densities are then computed.

$$\rho_i = \rho v_{i,8} + \rho l_i\ (1.0 - (T_8 + 459.60)/T_{i,4})^{0.3} \tag{24}$$

Volume. Using these densities, the batch volume is computed. The assumption of ideal mixing is made for this calculation.

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[3] Ibid.

$$V = M_1/\rho_1 + M_2/\rho_2 + M_3/\rho_3 + M_4/\rho_4 \qquad (25)$$

Concentrations. For the above volume, the concentration for each of the reactants and products is obtained.

$$C_i = M_i/(V \cdot MW_i) \qquad (26)$$

Concentration and mass changes. Using these concentrations, the kinetic calculation is performed to determine the change in concentration of component A for the selected time increment. The change in mass of all components is then computed utilizing their stoichiometric relationship.

$$\Delta C_1 = - \Delta t(k \cdot C_1^{n_1} \cdot C_2^{n_2} - k' \cdot C_3^{n_3} \cdot C_4^{n_4}) \qquad (27)$$

$$\Delta M_1 = \Delta C_1 \cdot MW_1 \cdot V \qquad (28)$$

$$\Delta M_2 = (a_2 \cdot MW_2 \cdot \Delta M_1/(a_1 \cdot MW_1)) + FB \cdot \rho_{27} \cdot \Delta t \qquad (29)$$

$$\Delta M_3 = -a_3 \cdot MW_3 \cdot \Delta M_1/a_1 \cdot MW_1 \qquad (30)$$

$$\Delta M_4 = -a_4 \cdot MW_4 \cdot \Delta M_1/a_1 \cdot MW_1 \qquad (31)$$

In the kinetics calculation, Equation (27), the exponent (n_i) for each concentration is the kinetic order for that component. Also, in Equation (29) the change in mass of component B is adjusted for the quantity of B added at flow rate FB during the time increment.

Masses. Following this point, calculations for values at the end of the time interval and for average values during the interval are performed. The end-of-interval masses and average masses are determined for each component.

$$MI_i = M'_i + \Delta M_i \qquad (32)$$

$$MA_i = M'_i + \Delta M_i/2.0 \qquad (33)$$

M'_i is defined as the mass value for each component at the beginning of the time interval.

Heat evolved. Next, using the heat of reaction, Equation (19); the incremental change in concentration of component A, Equation (27); and batch volume, Equation (25); the heat produced by the reaction occurring during the time interval is calculated.

$$\Delta H = \Delta H_0 \cdot \Delta C_1 \cdot V \qquad (34)$$

Surface area. The surface area available in the jacketed vessel for heat transfer is calculated.

$$S = AH + 0.535\,(V - VH)/D \qquad (35)$$

The derivation of the above equation, as well as the following energy balance, is explained in Chapter IV - Mathematical Derivations.

Batch temperature change. Using the quantities obtained in Equations (34) and (35), the incremental change in temperature of the reaction mass is determined by the performance of an energy balance on the system. The system is bounded by and includes the reactor wall, which is assumed to have an incremental temperature change of one-half that of the reaction mass. The energy input to the system is considered to be the heat produced by the reaction and the enthalpy with respect to reaction temperature of the quantity of reactant B added during the time interval. The energy output is the heat transferred through the reactor wall to the jacket medium. The energy accumulation is the increase in enthalpy of the chemical components and reactor wall.

$$\Delta T = (\Delta H - U \cdot S\,(T_8 - T_9)\,\Delta t + (T_7 - T_8)\,FB \cdot \rho\,27 \cdot \Delta t((c_p)_{2,7} + (c_p)_{2,8})/2.0)/(M_1\,(c_p)_{1,8} + M_2 \cdot (c_p)_{2,8} + M_3\,(c_p)_{3,8} + M_4\,(c_p)_{4,8} + M_6\,(c_p)_6/2.0) \qquad (36)$$

The average specific heat of reactant B between its addition temperature and reaction temperature is used in the computation. In addition, the specific heat of the reactor material, $(c_p)_6$, is assumed to be constant over the range of temperatures encountered. The overall heat transfer coefficient is also assumed to be constant because of the unchanging reactor properties (agitator speed, dimensions, material of construction), the relatively small variation in physical properties of the reaction mass over the temperature range encountered, and the small effect of the flow rate of the jacket medium. Because of the large cross-sectional area available for flow through the vessel jacket, velocities are relatively low over the entire range of flow rates.

<u>Batch temperatures</u>. The final calculations in this segment of the program dealing with the reaction are the determinations of final and average reaction temperature for the time interval.

$$T1_8 = T' + \Delta T \qquad (37)$$

$$T_A = T' + \Delta T/2.0 \qquad (38)$$

T' is defined as the reaction temperature at the beginning of the time interval.

Iterative Calculations - Jacket and Controls

Sensed temperature. The third segment of the simulation involves the calculations for the vessel jacket and temperature control loop. The temperature sensed by the measuring element at the end of the time interval is the first quantity calculated, taking into account the time lag associated with this item. The mathematical description of this element, as well as all other parts of the control loop are taken from Franks.[4] Modification of Franks' equations to suit this particular application are described in Chapter IV - Mathematical Derivations. All time delays associated with elements of the control loop are assumed to be first order.

$$Tl_{12} = (T_{12} + (T_A - T_{12}/2.0)\ \Delta t/\tau_1) \qquad (39)$$
$$/(1.0 + \Delta t/2.0\,\tau_1)$$

Error. After the reaction temperature has first reached the controller set point temperature, the following calculations are performed for the remaining components of the control loop. First, the error at the end of the time increment between measured temperature

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[4] Franks, R. G. E., Mathematical Modeling in Chemical Engineering. New York: John Wiley & Sons, Inc., 1966, pp. 260-266.

and controller set point is calculated.

$$EP_1 = T_{11} - T1_{12} \tag{40}$$

Controller rate section. Using this quantity, the error at the beginning of the interval (EP), a time integral (Int) whose updated value is calculated later in the program, Equation (66), and controller constants associated with the rate section of the instrument (α and τ_2), the error output of the rate section at the end of the time interval (EPO_1) is computed.

$$EPO_1 = (\alpha \cdot EP_1 + (\alpha / \tau_2)(Int + (EP + EP_1 - EPO)\ \Delta t/2.0))/(1.0 + \alpha \cdot \Delta t/2.0\,\tau_2) \tag{41}$$

Next, the time integral of the rate section output is updated to include the present increment. The average value of the rate section error output during the interval is used for the calculation.

$$Itr_1 = Itr + (EPO + EPO_1)\ \Delta t/2.0 \tag{42}$$

Controller pneumatic output. This integral is then used in the determination of the overall controller pneumatic output at the end of the time interval. The controller settings for the remaining two modes, integral and proportional, are also used in this calculation. The controller is defined as having a 3-15 psi output range with a 9 psi output at zero error.

$$PO_1 = 9.0 + K_c \cdot EPO_1 + K_c \cdot Itr_1/\tau_3 \qquad (43)$$

Signal to control valve. Taking into account the time lag associated with the controller, the output to the control valve at the end of the time interval is determined.

$$PC_1 = (PC + (PO_1 + PO - PC)\ \Delta t/2.0\tau_4) \qquad (44)$$

$$/(1.0 + \Delta t/2.0\tau_4)$$

Jacket medium flow rate. Finally, this pneumatic signal to the valve is used to determine the flow of heating or cooling medium through the control valve at the end of the time interval.

$$FCW_1 = (15.0 - PC_1) \cdot C_v \cdot \Delta P^{0.5}/12.0 \qquad (45)$$

The control valve is assumed to be linear and is air-to-close. The flow through the valve is assumed to be proportional to the square root of the pressure drop, which is constant. The average flow for the time interval is also computed.

$$FCW_A = (FCW + FCW_1)/2.0 \qquad (46)$$

Jacket medium temperature change. To determine the temperature change of the jacket medium, an energy balance is performed on the jacket contents. The system consists of the medium in the jacket plus the jacket itself, which is assumed to be in temperature equilibrium with the jacket medium. First the vapor and liquid densities of the jacket medium are calculated by the method used previously for reactants and products.

$$\begin{aligned} \rho v_{5,9} = {} & \exp ((5.0(((T_9 + 459.60)/T_{5,3}) \\ & - 1.0) + \log_{10} (\rho v_{5,3})) \log_e \\ & (10.0)) \end{aligned} \tag{47}$$

$$\begin{aligned} \rho 59 = {} & \rho v_{5,9} + \rho l_5 (1.0 - (T_9 + 459.60) \\ & /T_{5,4})^{0.3} \end{aligned} \tag{48}$$

The instantaneous mass of liquid in the jacket is next determined.

$$M_5 = VJ \cdot \rho 59 \tag{49}$$

The energy balance is then performed for the time increment. Energy input is the heat transferred from the reactor contents through the vessel wall and the enthalpy of the entering jacket medium with respect to the initial jacket medium temperature. Perfect mixing of the jacket contents is assumed. The energy accumulation is the increase in enthalpy of the jacket contents and jacket wall.

$$\Delta TJ = (U \cdot S(T_A - T_9) - FCW_A \cdot \rho 59 (T_9 - T_{10}) (c_p)_5) \Delta t/(M_5 (c_p)_5 + M_7 (c_p)_7) \tag{50}$$

The same constant overall heat transfer coefficient and surface area that were used previously in the energy balance on the reactor contents, Equation (36), are again used. Average reaction temperature, Equation (38), and average jacket medium flow rate, Equation (46), are also used in the calculation. The specific heats of both the jacket medium and jacket wall material are assumed to be constant, and heat loss through the insulated jacket wall is assumed to be negligible. The mathematical determination of Equation (50) is described in Chapter IV - Mathematical Derivations.

Jacket medium temperature. Using the change in temperature for jacket contents and the initial temperature, the average temperature for the time interval is determined.

$$TJ_A = TJ' + \Delta TJ/2.0 \tag{51}$$

TJ' is defined as the jacket temperature at the beginning of the time interval.

Tests and Redefinitions

Redefinitions for next iteration. For a time interval, all of the iterative calculations are first performed using initial values for reaction temperature, reactant and product masses, and jacket medium temperature in order to obtain end-of-interval values. Average values for the temperatures and masses are then used in subsequent iterations. Thus, before iterations after the first cycle of calculations, the following operations are performed.

$$T_8 = T_A \tag{52}$$

$$T_9 = TJ_A \tag{53}$$

$$M_i = MA_i \tag{54}$$

Redefinitions for next time interval. After reaction temperature convergence has been obtained or the maximum desired number of iterations have been performed, the calculations for the next time interval are made. Before proceeding to the next interval, the elapsed time is updated, and the initial values for this next interval are defined as the end values for the last interval.

$t = t + \Delta t$ (elapsed time) (55)

$T_8 = Tl_8$ (batch temperature) (56)

$M_i = Ml_i$ (component masses) (57)

$T_{12} = Tl_{12}$ (sensed temperature) (58)

$EP = EP_1$ (error) (59)

$EPO = EPO_1$ (rate section output) (60)

$Itr = Itr_1$ (integral of rate section output) (61)

$PO = PO_1$ (controller pneumatic output) (62)

$PC = PC_1$ (signal to control valve) (63)

$FCW = FCW_1$ (jacket medium flow rate) (64)

$T_9 = TJ' + \Delta TJ$ (jacket medium temperature) (65)

Also, the time integral used in Equation (41) is updated to include the last time increment.

$$Int = Int + (EP + EP_1 - EPO - EPO_1)\ \Delta t/2.0 \qquad (66)$$

Initial values for controller variables. When the reaction temperature reaches the controller set point temperature for the first time, the following are performed in order to set initial values for variables associated with the control loop. These operations are performed only this one time.

$$EP = T_{11} - T1_{12} \tag{67}$$

$$EPO = \alpha \cdot EP \tag{68}$$

$$PO = 9.0 + k_c \cdot EPO \tag{69}$$

$$PC = PO \tag{70}$$

$$FCW = (15.0 - PC)\ c_v \cdot \Delta P^{0.5}/12.0 \tag{71}$$

The reasoning behind Equations (68) through (70) is explained in Chapter IV - Mathematical Derivations.

CHAPTER IV.

MATHEMATICAL DERIVATIONS

All symbols used in the following derivations are defined in Appendix A, Table I.

I. Equation (20) - Chemical Equilibrium Constant.

$$R \ln K = \int (\Delta H/T_i^{2})\, dT$$ [1]

A known equilibrium constant, K_R, at reference temperature T_6 is used to obtain the equilibrium constant, K, at reaction temperature T_8. The integral is evaluated by using an average value of Δ H between T_6 and T_8.

$$R \ln (K_R/K) = -((\Delta H_0 + \Delta H_K)/2.0)$$
$$(1/T_6 - 1/T_8)$$

$$K_R/K = \exp(-((\Delta H_0 + \Delta H_k)/2.0R)$$
$$(1/T_6 - 1/T_8))$$

Converting T_8 to degrees Rankine and solving for K,

$$K = K_R \cdot \exp((\Delta H_0 + \Delta H_K)(1/T_6 - 1/(T_8 + 459.60))/2.0R) \qquad (20)$$

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[1] Smith, J. M. and H. C. Van Ness, Introduction to Chemical Engineering Thermodynamics. New York: McGraw-Hill Book Company, Inc., 1959, p. 411.

II. Equation (35) - Heat Transfer Surface Area

The heat transfer area is equal to the area of the bottom vessel head, which remains constant, plus the area on the straight side of the vessel, which varies with batch volume.

$$S = AH + AS$$

Since batch volume is known at a particular time, the straight-side component of area is calculated after correcting for the quantity of material in the lower head.

$$(V - VH) = \pi D^2 h/4$$

$$h = 4(V - VH)/\pi D^2$$

$$AS = \pi Dh$$

$$= 4(V - VH)/D$$

Since the units of volume are gallons, it is necessary to first convert to cubic feet in order to obtain the area in the desired units of square feet. Thus, the factor of 7.48 gallons/cubic foot is introduced.

$$AS = 4(V - VH)/D (7.48)$$

$$= 0.535(V - VH)/D$$

$$S = AH + 0.535(V - VH)/D \qquad (35)$$

III. Equation (36) - Incremental Batch Temperature Change

The derivation of Equation (36) consists of the performance of an energy balance on the reactor contents. The system is bounded by and includes the reactor wall.

Input - Output = Accumulation

The input is considered to be the heat produced by the reaction and the enthalpy with respect to reaction temperatureof the quantity of reactant B added.

$$\text{Input} = dH/dt + (T_7 - T_8)\ FB \cdot \rho 27 \cdot ((c_p)_{2,7} + (c_p)_{2,8})/2.0$$

The average specific heat of reactant B between addition and reaction temperatures is used.

The energy output is the heat transferred through the vessel wall to the jacket medium.

$$\text{Output} = U \cdot S\ (T_8 - T_9)$$

A constant overall heat transfer coefficient is assumed for the reasons stated in the Chapter on Mathematical Details.

The accumulation of energy is the change in enthalpy of the reactor contents plus the reactor material itself. The specific heat of the reactor material is assumed to be constant for the temperatures encountered, and its temperature change is assumed to be one-half that of the reaction mass.

$$\begin{aligned}\text{Acc.} = {} & (M_1\ (c_p)_{1,8} + M_2\ (c_p)_{2,8} + M_3 \cdot \\ & (c_p)_{3,8} + M_4\ (c_p)_{4,8} + M_6\ (c_p)_6 / \\ & 2.0)\ dT_8/dt\end{aligned}$$

Inserting all terms into the energy balance,

$$\begin{aligned}& dH/dt + (T_7 - T_8)\ FB \cdot \rho\ 27\ ((c_p)_{2,7} + \\ & (c_p)_{2,8})/2.0 - U \cdot S\ (T_8 - T_9) = (M_1\ (c_p)_{1,8} \\ & + M_2\ (c_p)_{2,8} + M_3\ (c_p)_{3,8} + M_4\ (c_p)_{4,8} + \\ & M_6\ (c_p)_6/2.0)\ dT_8/dt\end{aligned}$$

Substituting ΔT for dT_8, Δt for dt, and ΔH for dH, and rearranging to solve for ΔT, Equation (36) is obtained.

$$\begin{aligned}\Delta T = (& \Delta H + \Delta t\ (T_7 - T_8)\ FB \cdot \\ & \rho\ 27\ ((c_p)_{2,7} + (c_p)_{2,8})/2.0 \\ & - U \cdot S\ (T_8 - T_9)\ \Delta t)/\ (M_1 \cdot \\ & (c_p)_{1,8} + M_2\ (c_p)_{2,8} + M_3\ (c_p)_{3,8} \\ & + M_4\ (c_p)_{4,8} + M_6\ (c_p)_6/2.0)\end{aligned} \qquad (36)$$

IV. Equation (39) - Sensed Batch Temperature

In this derivation and in those following which involve values for variables at both the beginning and end of the time interval, the end-of-interval values have the number one attached, whereas the beginning-of-interval values have no numerical designation. In equations containing derivatives and integrals, the instantaneous and integrated values have no numerical designation.

$$dT_{12}/dt = (T_8 - T_{12})/\tau_1$$ [2]

Substituting incremental quantities for the differentials and using average temperatures for the time interval,

$$\Delta T_{12} = (T_A - (Tl_{12} + T_{12})/2.0)\ \Delta t/\tau_1$$

$$Tl_{12} - T_{12} = (T_A - Tl_{12}/2.0 - T_{12}/2.0) \cdot \Delta t/\tau_1$$

$$Tl_{12} + T_{12}\ (\Delta t/2.0\tau_1) = T_{12} + (T_A - T_{12}/2.0) \cdot \Delta t/\tau_1$$

$$Tl_{12} = (T_{12} + (T_A - T_{12}/2.0)\ \Delta t/\tau_1)/(1.0 + \Delta t/2.0\tau_1) \qquad (39)$$

---

[2] Franks, R. G. E., *Mathematical Modeling in Chemical Engineering*. New York: John Wiley & Sons, Inc., 1966, pp. 260-266.

V. Equation (41) - Error Output of Controller Rate Section

$$EPO = \alpha \cdot EP + (\alpha / \tau_2) \int_0^t (EP - EPO)\,dt$$ [3]

To solve for EPO_1 at time $t_1 = t + \Delta t$, let $Int = \int_0^t (EP - EPO)dt$, the value of which is updated after each time interval and which is available. The value of the integral up to time t_1 equals Int plus the average value for (EP - EPO) during the time interval times Δ t.

$$\int_0^{t_1} (EP - EPO)\,dt = Int + (EP_1 - EPO_1 + EP - EPO) \cdot \Delta t/2.0$$

$$EPO_1 = \alpha \cdot EP_1 + (\alpha / \tau_2)(Int + (EP_1 - EPO_1 + EP - EPO)\ \Delta t/2.0)$$

$$EPO_1 + EPO_1\ (\alpha \cdot \Delta t/2.0\, \tau_2) = \alpha \cdot EP_1 + (\alpha / \tau_2)(Int + (EP_1 + EP - EPO) \cdot \Delta t/2.0)$$

$$EPO_1 = (\alpha \cdot EP_1 + (\alpha / \tau_2)\ (Int + (EP_1 + EP - EPO)\ \Delta t/2.0))/(1.0 + \alpha \cdot \Delta t/2.0\, \tau_2) \qquad (41)$$

---

[3] Ibid.

VI. Equation (43) - Controller Pneumatic Output

$$PO = k_c \cdot EPO + (k_c/\tau_3) \int_0^t EPO\ dt$$ [4]

For time $t_1 = t + \Delta t$,

$$\int_0^{t_1} EPO\ dt = \int_0^t EPO\ dt + \int_t^{t_1} EPO\ dt$$

$$\int_0^{t_1} EPO\ dt = Itr_1$$

$$\int_0^t EPO\ dt = Itr$$

Itr is available from the calculations for all preceding time intervals. The average value of EPO during the time interval is used to evaluate the integral between t and t_1.

$$\int_t^{t_1} EPO\ dt = (EPO + EPO_1)\ \Delta t/2.0$$

$$Itr_1 = Itr + (EPO + EPO_1)\ \Delta t/2.0 \qquad (42)$$

$$PO_1 = k_c \cdot EPO_1 + (k_c/\tau_3)\ Itr_1$$

Since it is desired that the pneumatic output be at mid-point of the 3-15 psi range when there is no error, rather than at zero, the factor of 9.0 psi is added to the last equation.

$$PO_1 = 9.0 + k_c \cdot EPO_1 + k_c \cdot Itr_1/\tau_3 \qquad (43)$$

[4] Ibid.

VII. Equation (44) - Pneumatic Signal to Valve

$$dPC/dt = (PO - PC)/\tau_4$$ [5]

Substituting incremental quantities for differentials and using average values for the time interval,

$$\Delta PC = (PO_1 - PC_1 + PO - PC)\ \Delta t/2.0\tau_4$$

$$PC_1 - PC = (PO_1 - PC_1 + PO - PC)\ \Delta t/2.0\tau_4$$

$$PC_1 + PC_1\ (\Delta t/2.0\tau_4) = PC + (PO_1 + PO - PC)\ \Delta t/2.0\tau_4$$

$$PC_1 = (PC + (PO_1 + PO - PC)\ \Delta t/2.0\tau_4)/(1.0 + \Delta t/2.0\tau_4) \qquad (44)$$

VIII. Equation (45) - Flow Rate of Jacket Medium

$$FCW_1 = X \cdot c_v \cdot f(\Delta P)$$ [6]

X is the fractional opening of the valve. The valve is defined as being linear and air-to-close. The fractional opening is a function of the controller pneumatic output as follows:

$$X = (15.0 - PC_1)/12.0$$

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[5] Ibid.

[6] Ibid.

where PC_1 can vary from 3.0 to 15.0.

The supply and return pressures of the available jacket medium are assumed to be fixed, and therefore, the pressure drop across the valve is constant. The flow rate through the valve is assumed to be proportional to the square root of this pressure drop.

$$f(\Delta P) = \Delta P^{0.5}$$

$$FCW_1 = (15.0 - PC_1) \cdot c_v \cdot \Delta P^{0.5}/12.0 \qquad (45)$$

IX. Equation (50) - Incremental Temperature Change of Jacket Medium

An energy balance is performed on the jacket contents. The system consists of the medium in the jacket and the jacket wall, which is assumed to be in temperature equilibrium with the jacket medium. Heat loss through the insulated jacket wall is assumed to be negligible. Energy input is considered to be the heat transferred through the reactor wall and the enthalpy of the entering jacket medium with respect to the jacket medium temperature.

$$\text{Input} = U \cdot S\,(T_A - T_9) + FCW_A \cdot \rho\,59 \cdot$$

$$(T_{10} - T_9) \cdot (c_p)_5$$

The specific heat of the jacket medium is assumed to be constant over the temperature range encountered.

Energy output is the enthalpy of the effluent jacket medium with respect to the jacket medium temperature. Because perfect mixing in the jacket is assumed, the temperature of the jacket effluent equals that of the jacket contents, and therefore the energy output is zero.

$$\text{Output} = FCW_A \cdot \rho 59 \ (c_p)_5 \ (T_9 - T_9) = 0$$

The accumulation of energy is the change in enthalpy of the jacket contents and jacket wall. Changes in specific heat of the wall material are assumed to be negligible.

$$\text{Acc.} = (M_5 \ (c_p)_5 + M_7 \ (c_p)_7) \ dT_9/dt$$

Combining all components of the balance and substituting incremental quantities for differentials,

$$U \cdot S \ (T_A - T_9) - FCW_A \cdot \rho 59 \ (T_9 - T_{10}) \ (c_p)_5 = (M_5 \ (c_p)_5 + M_7 \ (c_p)_7) \ \Delta TJ/ \Delta t$$

Solving for Δ TJ,

$$\Delta TJ = (U \cdot S (T_A - T_9) - FCW_A \cdot \rho 59 (T_9 - T_{10}) (c_p)_5) \Delta t / (M_5 (c_p)_5 + M_7 (c_p)_7) \qquad (50)$$

X. Equation (68) - Initial Error Output of Controller Rate Section

$$EPO = \alpha \cdot EP + (\alpha / \tau_2) \int_0^t (EP - EPO)\, dt$$ [7]

Since Equation (68) is used to calculate an initial value at time zero, the integral term is zero.

$$EPO = \alpha \cdot EP \qquad (68)$$

XI. Equation (69) - Initial Controller Pneumatic Output

$$PO = k_c \cdot EPO + (k_c / \tau_3) \int_0^t EPO\, dt$$ [8]

Since the calculation is performed at time zero, the integral term is zero. In addition, the factor of 9.0 psi is added to produce a mid-point output at zero error.

$$PO = 9.0 + k_c \cdot EPO \qquad (69)$$

[7] Ibid.

[8] Ibid.

XII. Equation (70) - Initial Pneumatic Signal to Valve

$$PC = PO \tag{70}$$

Since any difference between PC and PO is caused by time lags within the controller, at initial conditions before any elapsed time, the two should be equal.

CHAPTER V.

PROGRAMMING

The formulation of the computer program to perform the desired manipulation of the previously described mathematical relationships is discussed in this chapter. Reference should be made to the print out of the program in Appendix C and to the detailed logic diagram in Appendix B. An explanation of some of the operations within the program, which require elaboration, is contained below.

The entire program is written in Fortran IV for use on the RCA Spectra 70 computer. The Spectra 70 FORTRAN IV Reference Manual[1] was used as a reference for programming. The control statements used in the program are as prescribed in Interface.[2]

All of the mathematical relationships listed in the Chapter on Mathematical Details were converted to Fortran IV for use in the program, and Equation references are to Chapter III.

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[1] Spectra 70 FORTRAN IV Reference Manual, Radio Corporation of America, November, 1967.

[2] Interface, Number III, Newark, New Jersey: Newark College of Engineering Computing Center Newsletter, November, 1968, pp. 3-4.

Procedure for Retaining Initial Values

For a time interval, initial values of masses and temperatures are used for the first cycle of calculations. Average values for the time interval of these variables are then used in succeeding iterations. Therefore, after the calculation of Equation (31) in the first cycle of calculations, new primed variables; M_i', T', and TJ'; are given the initial values and retain them when the masses and temperatures in the equations are redefined to average values. At this point in the program, an arithmetic IF statement is performed to determine if the primed variables should be equated to the equation variables.

```
IF (ZMA (1) - ZM (1)) 20, 22, 22
```

The average mass for component 1 is defined as zero at the beginning of the time interval. Therefore, since the quantity is negative after the first cycle of calculations, the program proceeds to statement 20, and the primed variables are equated to the equation variables, which are initial values. Since later in the program the equation variables are set equal to the average values after the first cycle of calculations, the quantity in the arithmetic IF statement is zero, and the program proceeds directly to statement 22 for all iterative calculation cycles.

Limiting of Controller Output

After the calculation of the overall controller pneumatic output, Equation (43), a check is made using arithmetic IF statements to determine whether the output is within the capabilities of the instrument. If the calculated output is outside the 3 to 15 psi limits, it is corrected to the nearest limit.

```
     IF (P01 - 3.0) 26, 26, 27
27   IF (P01 - 15.0) 28, 28, 29
26   P01 = 3.0
     GO TO 28
29   P01 = 15.0
```

A similar procedure is performed after the calculation of the initial pneumatic signal to the control valve (Equation (70)).

Limiting of Jacket Medium Rate

After the calculation of the flow rate of jacket medium at the end of the time interval, Equation (45), the same type of checking and correcting is performed for the flow rate through the control valve. If the flow rate is outside the limits for the control valve, it is corrected to the nearest limit.

```
      IF (FCW1 - 0.0) 50, 50, 51
51    IF (FCW1 - CV * DP ** 0.5) 52, 52, 53
50    FCW1 = 0.0
      GO TO 52
53    FCW1 = CV * DP ** 0.5
```

Tests for Further Iterations

At the point in the program when all the process computations have been completed for a calculation cycle, tests are performed to determine if another iteration should be made for the same time interval or if the program should attempt to go on to the succeeding time interval. First, a test for convergence of end-of-interval reaction temperature is made by comparing the last calculated reaction temperature ($T1_8$) to $T1'$, which has previously been set equal to the reaction temperature determined in the previous iteration. Two arithmetic IF statements are used to determine if the two values agree within selected limits, plus or minus 0.001°F.

```
      IF (T18 - T1P - 0.001) 30, 31, 31
30    IF (T18 - T1P + 0.001) 31, 31, 32
```

If the two successive temperatures agree within the limits, the program will proceed to statement 32 and attempt to go on to the next time interval. However, if the two values do not agree, another test is performed to determine if the maximum desired number of iterations have been completed. First, the iteration index, M, is brought up to date and then compared to the maximum number in an arithmetic IF statement.

```
31    M = M + 1
      IF (M - 3) 34, 32, 32
```

If the number of iterations performed is equal to the maximum number, three, the program will attempt to proceed to the next interval. If the number of iterations is less than the maximum number, the program returns to statement 13 for another cycle of calculations after setting the equation values for reaction temperature, jacket medium temperature, and chemical component masses equal to their respective average values for the last iteration. If either test prevents another iteration in the same time interval, the program proceeds to statement 32 where total elapsed time is updated.

Procedure for Data Output

Since it is not desired to output data at the end of every time interval, an output index (NO) is updated and compared in an arithmetic IF statement to the number of desired intervals between data outputs.

```
NO = NO + 1
IF (NO - 4) 56, 55, 55
```

If the index equals four, a Write statement is executed after which the index is returned to zero. The variables whose values are written are: total elapsed time, reaction temperature, mass of the primary reactant (A), and flow rate of jacket medium. If the output index has not reached the value of four, the above two statements are skipped.

Test for Activating Temperature Controller

The procedure for determining whether the temperature controller should be brought into play is carried out as follows. Since the initial reaction temperature differs greatly from set point temperature, it is desired to keep the controller inactivated until the two temperatures are first equated. Otherwise, the integral mode of the controller accumulates large errors occurring over a significant period of time and prevents the controller from taking effect once set point is reached, and an error of opposite sign is incurred. The simulation is equivalent to a chemical operator monitoring the reaction temperature until it reaches the set point and then switching the controller to Automatic.

The total elapsed time is first compared to t^*.

```
56    IF (TL - TLS) 47, 45, 45
```

If t^* still has its initially assigned high value, the quantity is negative and a comparison is then made between sensed reaction temperature and set point temperature to determine whether the controller should be activated. Once reaction temperature reaches the set point, the controller is activated and t^* is redefined so that the quantity in the above arithmetic IF statement is zero or positive, and the test for controller activation is skipped after this time.

If the sensed reaction temperature has not previously reached controller set point, the two are compared.

```
47    IF (T112 - T (11)) 45, 46, 46
```

If the quantity is still negative, redefinition of t^* and a series of initial condition statements for the controller are skipped. However, if sensed reaction temperature has finally reached controller set point, t^* is equated to elapsed time at that point, following which Equations (67) through (71) are calculated to determine initial values of controller variables.

The initial values are required for the controller variables because the point at which sensed reaction temperature first reaches set point temperature is time zero for the controller, and the time-zero values are required for the calculation of the corresponding values at the end of the next time interval.

The same comparison of t and t^* as was performed in statement 56 is made before the calculations associated with the control loop are made (Equations (40) through (51)), and before the redefinition of controller variables is performed (Equations (59) through (64)). If the comparison indicates that the controller has not yet been activated, the calculation of the above equations is unnecessary, and therefore they are skipped.

Check for Termination of Reactant Addition

After the sequence of calculations involving controller activation, the next item checked is the addition time for the continuously added component B. If the total elapsed time has reached or exceeded the desired addition time for B, the flow rate of B is set to zero. Tests, which are described below, are then performed to determine whether the program should proceed to the next time interval or be terminated.

```
45   IF (TL - TLM1) 39, 40, 40
40   FB = 0.0
```

However, if the desired addition time has not been reached, statement 40 is skipped and the addition rate remains at its original value. The program then proceeds directly to the redefining of variables preparatory to advancing to the next time interval.

Tests for Simulation Termination

If the addition time for B has been reached and the flow rate set to zero, two tests are performed before proceeding to the next interval to decide if termination of the program is in order. First, the quantity of the primary reactant converted in the last time interval is compared to the minimum desired conversion. If the reaction rate has slowed to the point where the conversion during a time increment is less than that desired, the program terminates. Otherwise, the program proceeds to the next test which compares total elapsed time against the desired maximum running time for the reaction. If the elapsed time equals the maximum time, the program terminates. Otherwise, calculations for a new time interval are performed.

```
      IF (DM (1) + DMM) 38, 35, 35
38    IF (TL - TLM2) 39, 35, 35
```

If neither test stops the simulation, before proceeding to the next time interval, the iteration index and the average mass for component A are set to zero, and the initial values of variables are set equal to the corresponding end values for the preceding interval.

Having redefined all necessary variables, the program is returned by a GO TO statement to statement 13 for another overall sequence of calculations.

CHAPTER VI.

TEST PROCESS AND DATA

The reaction selected for simulation is the esterification of acetic acid with ethyl alcohol to produce ethyl acetate and water. The reaction takes place in a 500 gallon, single-jacketed, glass-lined reactor equipped with a temperature sensing element. The element is directly connected to a three-mode pneumatic temperature controller whose output modulates a pneumatic control valve. The control valve is located in the stream of cooling water to the jacket which absorbs the exothermic heat of reaction.

The reaction is semi-batch with 100% acetic acid being added over a prescribed period to an initial charge of ethanol.

For the selected reaction, the stoichiometric relationship is:

$$\underset{A}{CH_3CH_2OH(l)} + \underset{B}{CH_3COOH(l)} \underset{k'}{\overset{k}{\rightleftharpoons}} \underset{C}{CH_3COOCH_3(l)} + \underset{D}{H_2O(l)}$$

The reactants and products are assigned the identifying letters shown above.

The stoichiometric factor (a_i) for each component is one, and these values are submitted in the input data. All input data is listed in Table III of Appendix A, along with the source of information.

For each reaction component, the following data is submitted:

(1) specific heat and reference temperature
(2) density and reference temperature
(3) boiling temperature at one atmosphere
(4) critical temperature
(5) molecular weight
(6) initial mass

For the cooling water, examination of specific heat data in the Handbook of Chemistry and Physics[1] indicates a very small variation in the temperature range encountered, and therefore a single constant value for this item is submitted in the data. A density value with reference temperature, boiling temperature, and critical temperature are also submitted for cooling water.

The specific heat of the reactor and jacket steel is assumed to be constant, and a single constant value is

---

[1] Hodgman, C. D. (Editor-in-Chief), Handbook of Chemistry and Physics, Fortieth Edition. Cleveland, Ohio: Chemical Rubber Publishing Company, 1959, p. 2260.

submitted. The reactor wall is considered to be all steel because of the small mass percentage ($< 3\%$) of the glass lining.

Information on the vessel is taken from The Pfaudler Company literature.[2] The vessel is defined to be a 500 gallon, glass-lined, single jacketed, RA-series reactor. Items taken directly from the literature are vessel diameter, jacket volume, and volume of the bottom head. The surface area of the bottom head was determined by subtracting the calculated straight-side area from the total area given in the literature. Total weight for vessel plus jacket is listed in the Pfaudler information, and this weight was divided approximately between the vessel and jacket materials according to calculations based on vessel dimensions and specific gravities of the materials of construction. In addition, a Pfaudler suggested value of 50 Btu/hr. ft.^{2} ^{o}F. for the overall heat transfer coefficient for a new vessel is used.

The primary source for information on the reaction itself is example problems in Chemical Engineering Kinetics.[3]

[2] Pfaudler Bulletin 1040.

[3] Smith, J. M., Chemical Engineering Kinetics. New York: McGraw-Hill Book Company, Inc., 1956, p. 117.

The form of the kinetic equation and the order of the reaction, along with the equilibrium constant at a reference temperature, are taken from this source. Although the data in the problem is for a catalyzed reaction, it is felt that the information is sufficiently valid for the purposes of the trial computer simulation.

The value of the Arrhenius activation energy is taken from Shu-Lin, Shapiro, Linstead, and Newitt.[4] Using this value, along with the forward reaction rate constant and temperature taken from the above mentioned example problem, a value for the Arrhenius frequency factor was calculated and is submitted in the data.

The heat of reaction used as a reference in the simulation was calculated from heats of formation for the reactants and products given in Chemical Engineer's Handbook.[5] The reference temperature for the heat of reaction (536.6°R.) is that for which the heat of formation data was listed.

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[4] Shu-Lin P'eng, R. H. Shapiro, R. P. Linstead, and D. M. Newitt, Journal of the Chemical Society, 1938, pp. 784-791.

[5] Perry, R. H., C. H. Chilton, and S. D. Kirkpatrick, Chemical Engineer's Handbook, Fourth Edition. New York: McGraw-Hill Book Company, Inc., 1963, p. 3-134.

The temperature controller selected is a Taylor 124R Fulscope ® Recording Controller. Ranges for the gain, rate setting, and integral setting are taken from Taylor literature.[6] The value for the rate amplitude is selected from the range given in Mathematical Modeling in Chemical Engineering[7] for industrial controllers. The time lag of the temperature measuring element, which is located inside the baffle of the glass-lined vessel, is estimated from personal experience. The time lag associated with the controller itself is taken from the suggested approximate value of a few tenths of seconds in Franks.[8]

To determine a value for the maximum control valve capacity, an approximate hand calculation was performed to determine the maximum required heat transfer rate. The calculated valve capacity was used with the idea that it could be changed for future simulations if it proved to be inadequate. The control valve did not

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[6] Taylor Instrument Companies File 1-3A, Specification sheet 98291-S1, February, 1967.

[7] Franks, R. G. E., Mathematical Modeling in Chemical Engineering. New York: John Wiley & Sons, Inc., 1966, pp. 260-266.

[8] Ibid.

appear to be large enough that it would be velocity limited or have a significant time lag. The value for the pressure drop across the valve is taken from personal experience with available in-plant cooling water supply and discharge pressures. Variations of pressure drop through the jacket with flow were assumed to be negligible.

In addition to the reference temperatures for the equilibrium constant and for the heat of reaction mentioned above, values for the following temperatures are submitted in the data:

(1) temperature of reactant B - 70°F.
(2) initial reaction temperature - 70°F.
(3) initial jacket contents temperature - 70°F.
(4) jacket inlet temperature - 70°F.
(5) controller set point - 90°F.
(6) initial temperature sensed by element - 70°F.

The values for items (1), (2), and (4) above are selected to be a nominal ambient temperature. It is assumed that the initial temperature of the jacket contents, item (3), is equal to the jacket inlet temperature since no heat transfer has yet occurred. Also, it is assumed that the initial sensed temperature, item (6), is in equilibrium with and equal to the initial reaction temperature. The controller set point is arbitrarily selected at a value above the cooling water supply temperature.

Since the method of Chow and Bright[9] used for liquid density determinations is valid only for reduced temperatures below 0.65, all materials, for which this method is used, were checked to meet this criterion at the range of reaction temperatures to be encountered. Since the reaction is atmospheric, the other criterion that the pressure be less than ten atmospheres is also met.

Other miscellaneous variables whose values are submitted in the data are flow rate of reactant B (4.0 gal./min.), addition time for reactant B (60.0 min.), time increment (0.5 min.), total time limit for the reaction (480.0 min.), and minimum incremental conversion (0.10 lb.). In addition, the value with proper units for the gas constant (1.987 Btu/lb. mole °R.) is submitted.

[9] Chow and Bright, Chemical Engineering Progress, vol. 49, 1953, p. 175.

The flow rate and addition time for reactant B were selected to produce the addition of a molar quantity of B equal to that of reactant A originally charged. The values of the two variables which are involved in the termination of the simulation, maximum total time and minimum incremental conversion, were established at reasonable values after the initial trial computer runs. The value of the time increment used in the simulation was selected at as low a value as practical to attain good accuracy without resulting in unreasonably long computer runs.

The zero initial values were submitted for the following variables:

(1) elapsed time - 0.0 min.

(2) iteration index - 0

(3) output index - 0

(4) time integral of rate section output - 0.0 °F. min.

(5) time integral of the difference between error and rate section output - 0.0 °F. min.

(6) average mass of reactant A for time interval - 0.0 lb.

(7) reaction temperature at end of time interval - 0.0 °F.

Items (1) through (5) are obviously zero at the initiation of the program. Item (6) is set at zero so that the arithmetic IF statement in which it is used, as described in the Chapter on Programming, will produce the desired results during the first cycle of calculations. Item (7) is set at zero so that after $T1'$ is equated to it in the first cycle of calculations, the test for convergence of reaction temperature at the end of the cycle will produce another iteration.

CHAPTER VII.

DISCUSSION OF RESULTS

The primary objective of the thesis, the digital computer simulation of a temperature controlled semi-batch reaction, was accomplished. An output of information on mass of the primary reactant, reaction temperature, and flow of coolant to the jacket as a function of time was obtained.

In addition, simulations were performed at various controller settings in order to investigate the effect of these settings on control of reaction temperature. For each of the three controller modes, simulations were performed for four (4) different values, while the values for the other two settings were held constant. Results of the simulations are shown on Figures II, III, and IV where reaction temperature is plotted against time.

Referring to Figure II, the following results are observed for varying controller gain:

(1) Increasing gain results in decreased overshoot. Beyond a gain of approximately 6.0 psi/$^{\circ}$F., decreases in overshoot are not significant.

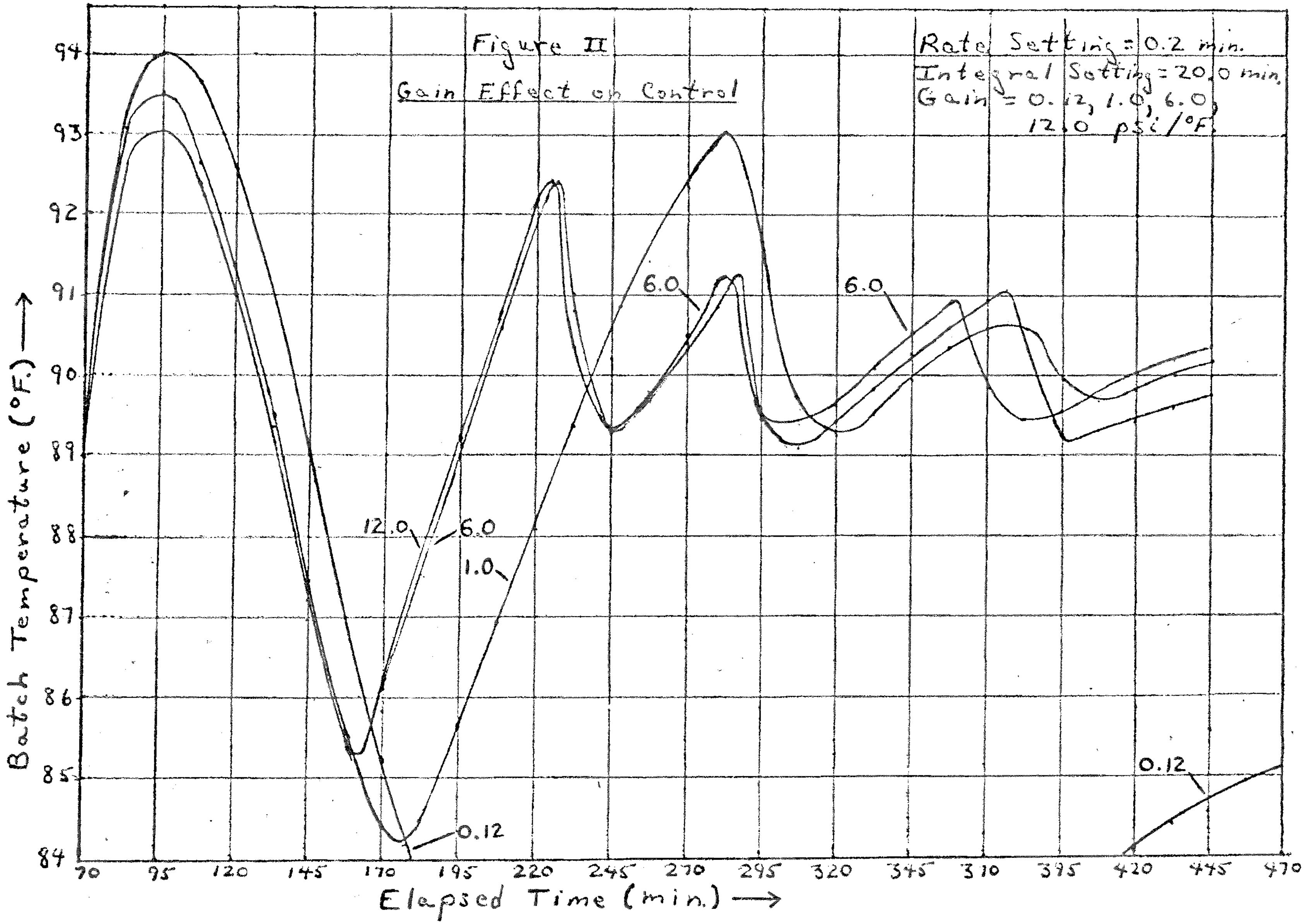


Figure II

Gain Effect on Control

(2) The decay ratio decreases with increasing gain up to a gain of about 6.0 psi/°F., and then increases slightly for higher values.

(3) The response time follows a pattern similar to that for the decay ratio. A gain of 6.0 psi/°F. produced the minimum response time to attain and maintain ± 1°F. of the set point.

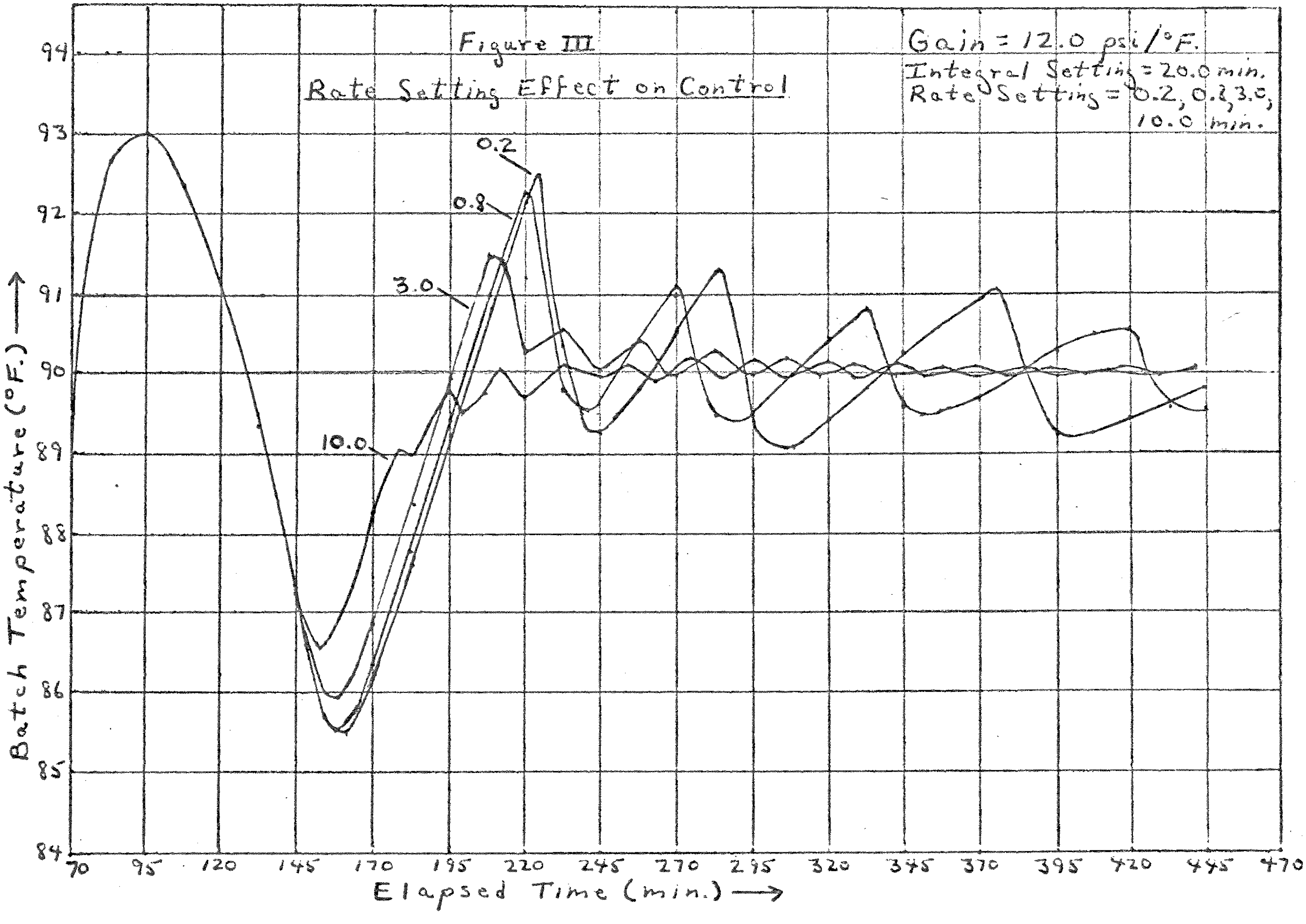
(4) The period of oscillation also decreases with increasing gain up to a gain of approximately 6.0 psi/°F. Higher values increase the period of oscillation.

The effects of varying the controller rate setting are illustrated on Figure III:

(1) No effect on initial overshoot is observed.

(2) Decay ratio decreases with increasing values of the rate setting. At the maximum value for τ_2 that was simulated, the unusual response prevented a meaningful evaluation of the decay ratio.

(3) Response time (± 1°F. of set point) decreases with increasing rate setting.



(4) The period of oscillation decreases with increasing rate setting. The decrease in period of oscillation is more pronounced at the lower rate settings and becomes less significant for the higher values.

The data plotted on Figure IV illustrate the effects of varying integral setting:

(1) No significant effect on initial overshoot is observed.

(2) Decay ratio decreases with increasing values of the integral setting. Also, the system appears to be unstable for the lower integral mode settings.

(3) The response time (± 1°F. of set point) decreases with increasing integral setting.

(4) The period of oscillation increases with increasing integral setting, becoming significantly greater at the high values.

The latest total time for a computer run on the Spectra 70 was one (1) minute and forty-six seconds.

The results of the simulations were generally in agreement with those expected from experience, with

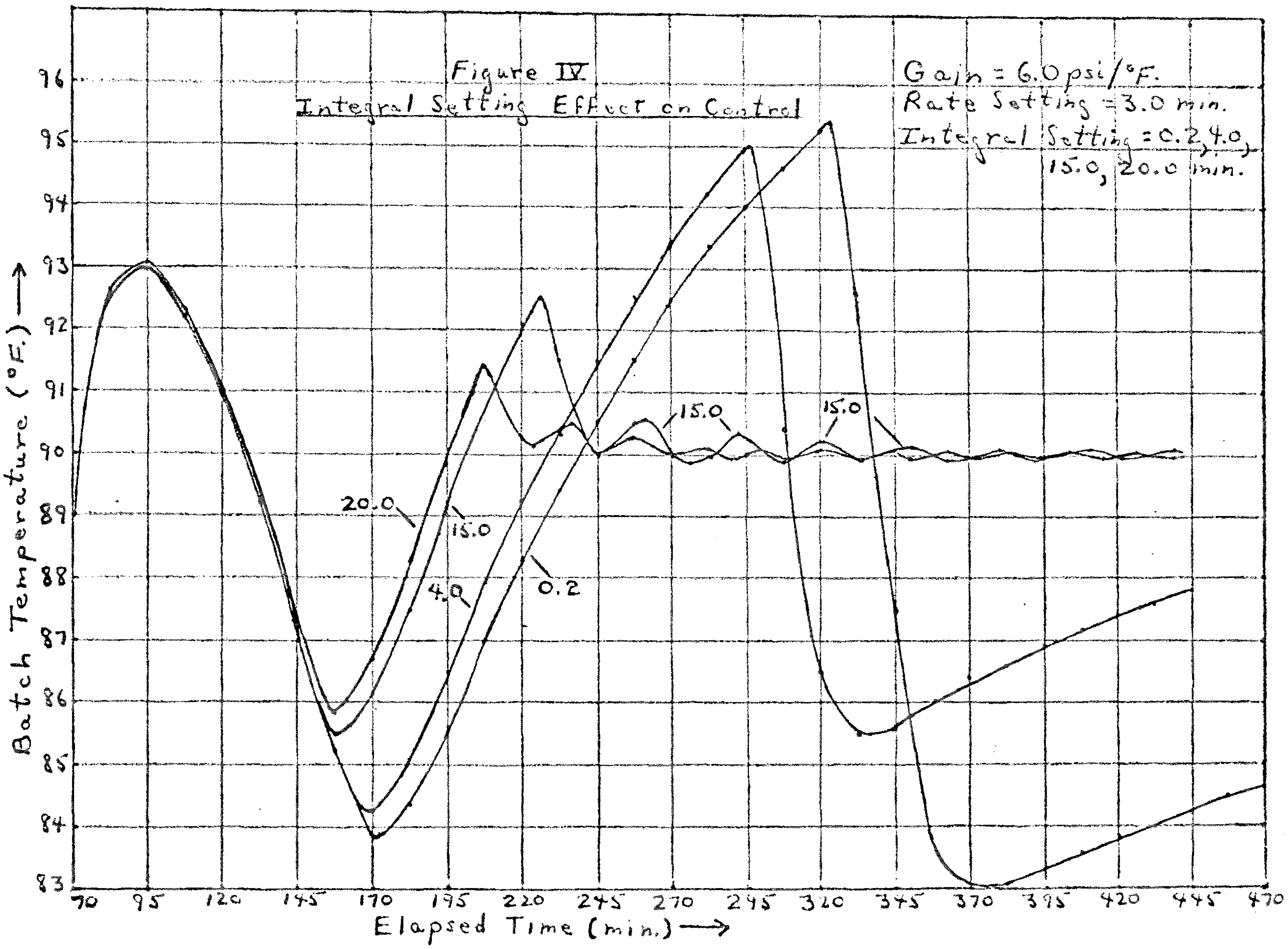


Figure IV

Integral Setting Effect on Control

nothing unusual being noted in the effect of varying controller settings or the progression of the reaction itself.

CHAPTER VIII.

CONCLUSIONS

It is concluded that the simulation is valid representation of the actual performance of a batch or semibatch reactor because of the general agreement of the results with those expected from experience.

Therefore, the program can serve as a useful tool in the investigation and optimization of reaction conditions and/or temperature controller settings for a variety of reactions of the type studied.

CHAPTER IX.

RECOMMENDATIONS

With the simulation program established, many possible uses for it and areas of investigation exist. Response of the system to a step change in controller set point for various controller settings is one possible area of investigation. Another is the experimentation with the chosen reaction at various temperatures. Also, simulations of other reactions could be tried.

Experimentation with the mechanics of the program itself is also a possibility. Items whose effect on output might be investigated are:

(1) temperature correction of the densities of reactants and products
(2) temperature correction of the specific heats of reactants and products
(3) temperature correction of equilibrium constant
(4) temperature correction of heat of reaction
(5) temperature correction of the reaction rates
(6) length of time increment
(7) number of calculation iterations

It is felt that Items (6) and (7) should be investigated to determine values which produce the desired convergence and accuracy. Of course, the required computer time would also be a consideration in the selection of the values for these two variables.

APPENDIX A

TABLES

TABLE I

NOMENCLATURE - GENERAL

The symbols are listed in the order in which they appear in the text.

	Item	Mathematical Symbol	Fortran Symbol	Units
1.	Watson liquid-phase expansion factor	w_i	W(I)	--
		$w_{i,j}$	WR(I,J)	--
2.	Temperature	T_j	T(J)	*
		$T_{i,j}$	TR(I,J)	*
3.	Specific heat	$(c_p)_i$	CPR(I)	Btu/lb. °F.
		$(c_p)_{i,j}$	CP(I,J)	Btu/lb. °F.
4.	Vapor density	$\rho v_{i,j}$	RV(I,J)	lb./gal.
5.	Molecular weight	MW_i	ZMW(I)	lb./lb. mole
6.	Density constant	$\rho 1_i$	R1(I)	lb./gal.
7.	Liquid density, reference	ρR_i	RR(I)	lb./gal.
8.	Liquid density at reaction temperature	ρ_i	RO(I)	lb./gal.
9.	Liquid density of reactant B at T_7	$\rho 27$	R27	lb./gal.

* Refer to Table II, Appendix A.

	Item	Mathematical Symbol	Fortran Symbol	Units
10.	Heat of reaction at T_6	ΔH_K	DHK	Btu/ lb. mole
11.	Heat of reaction, reference	ΔH_R	DHR	Btu/ lb. mole
12.	Stoichiometric constant	a_i	AL(I)	--
13.	Heat of reaction at reaction temperature	ΔH_0	DHZ	Btu/ lb. mole
14.	Equilibrium constant at reaction temperature	K	ZK	--
15.	Equilibrium constant, reference	K_R	ZKR	--
16.	Gas constant	R	R	Btu/ lb. mole °R.
17.	Forward reaction rate constant	k	ZKL	--
18.	Reverse reaction rate constant	k'	ZKP	--
19.	Arrhenius frequency factor	A	A	--
20.	Arrhenius activation energy	E	E	Btu/ lb. mole
21.	Batch Volume	V	V	gal.
22.	Mass	M_i	ZM(I)	lb.
23.	Concentration	C_i	C(I)	lb. mole/ gal.

	Item	Mathematical Symbol	Fortran Symbol	Units
24.	Incremental change in concentration	ΔC_i	DC(I)	lb. mole/ gal. min.
25.	Kinetic order of chemical component	n_i	N(I)	--
26.	Time	t	TL	min.
27.	Time increment	Δt	DTL	min.
28.	Incremental mass change	ΔM_i	DM(I)	lb.
29.	Addition rate of component B	FB	FB	gal./ min.
30.	Mass at end of time interval	Ml_i	ZMl(I)	lb.
31.	Average mass for time interval	MA_i	ZMA(I)	lb.
32.	Mass at beginning of time interval	M'_i	ZMP(I)	lb.
33.	Heat produced by incremental reaction	ΔH	DH	Btu/ min.
34.	Heat transfer surface	S	S	ft.^{2}
35.	Surface area of bottom head of vessel	AH	AH	ft.^{2}
36.	Volume of bottom head of vessel	VH	VH	gal.

	Item	Mathematical Symbol	Fortran Symbol	Units
37.	Inside diameter of vessel	D	D	ft.
38.	Incremental change in reaction temperature	ΔT	DT	°F.
39.	Overall heat transfer coefficient	U	U	Btu/min. ft.^{2} °F.
40.	Reaction temperature at end of time interval	$T1_8$	T18	°F.
41.	Average reaction temperature for time interval	T_A	TA	°F.
42.	Reaction temperature at start of time interval	T'	TP	°F.
43.	Temperature sensed by measuring element at end of time interval	$T1_{12}$	T112	°F.
44.	Time constant	τ_k	TAU(K)	min.
45.	Error at end of time interval	EP_1	EP1	°F.
46.	Output of controller rate section at end of time interval	EPO_1	EPO1	°F.
47.	Error at beginning of time interval	EP	EP	°F.

	Item	Mathematical Symbol	Fortran Symbol	Units
48.	Output of controller rate section at beginning of time interval	EPO	EPO	°F.
49.	Time integral of difference between error and rate section output	Int	ZINT	°F. min.
50.	Rate amplitude	α	ALP	--
51.	Time integral of rate section output at end of time interval	Itr_1	ZITR1	°F. min.
52.	Time integral of rate section output at beginning of time interval	Itr	ZITR	°F. min.
53.	Overall controller output at end of time interval	PO_1	PO1	$lb./in.^2$
54.	Overall controller output at beginning of time interval	PO	PO	$lb./in.^2$
55.	Controller gain setting	k_c	ZKC	psi/°F.
56.	Signal to control valve at end of time interval	PC_1	PC1	$lb./in.^2$
57.	Signal to control valve at beginning of time interval	PC	PC	$lb./in.^2$

	Item	Mathematical Symbol	Fortran Symbol	Units
58.	Flow rate of jacket medium at end of time interval	FCW_1	FCW1	gal./min.
59.	Flow rate of jacket medium at beginning of time interval	FCW	FCW	gal./min.
60.	Average flow rate of jacket medium for time interval	FCW_A	FCWA	gal./min.
61.	Maximum capacity of control valve	c_v	CV	gal./min.
62.	Pressure drop through control valve	ΔP	DP	lb./in.^{2}
63.	Liquid density of jacket medium	ρ 59	R59	lb./gal.
64.	Volume of jacket	VJ	VJ	gal.
65.	Incremental change in jacket medium temperature	ΔTJ	DTJ	°F.
66.	Average jacket medium temperature for time interval	TJ_A	TJA	°F.
67.	Jacket medium temperature at beginning of time interval	TJ'	TJP	°F.

	Item	Mathematical Symbol	Fortran Symbol	Units
68.	Time variable used in programmed test to determine if controller set point has yet been reached	t^*	TLS	min.
69.	Maximum reaction time	t_{m2}	TLM2	min.
70.	Reaction temperature at end of time interval	$T1'$	T1P	°F.
71.	Iteration index	M	M	--
72.	Output index	NO	NO	--
73.	Maximum addition time for reactant B	t_{m1}	TLM1	min.
74.	Minimum required change in mass of reactant A for time interval	ΔM_m	DMM	lb.

NOMENCLATURE FOR SYMBOLS USED ONLY IN CHAPTER IV - MATHEMATICAL DERIVATIONS

	Item	Mathematical Symbol	Fortran Symbol	Units
1.	Heat of reaction	ΔH		Btu/ lb. mole
2.	Surface area of straight side of reaction vessel	AS		$ft.^2$

	Item	Mathematical Symbol	Units
3.	Height of liquid above reactor tangent line	h	ft.
4.	Rate of heat evolution by reaction	dH/dt	Btu/min.
5.	Incremental change in sensed temperature over time interval	$\Delta\ T_{12}$	$^{o}F.$
6.	Time at end of interval	t_1	min.
7.	Incremental change in pneumatic signal over time interval	Δ PC	psi.
8.	Fractional opening of control valve	X	--

TABLE II

NOMENCLATURE - SUBSCRIPTS

	Item	Subscript Symbol	Fortran Symbol	Units
A.	Material subscript (general)	i	I	--
	1. Chemical reactant A	1	1	--
	2. Chemical reactant B	2	2	--
	3. Chemical product C	3	3	--
	4. Chemical product D	4	4	--
	5. Jacket medium	5	5	--
	6. Reactor material	6	6	--
	7. Jacket material	7	7	--
B.	Temperature subscript (general)	j	J	--
	1. Specific heat reference temperature	1	1	°R.
	2. Density reference temperature	2	2	°R.
	3. Boiling temperature	3	3	°R.

	Item	Subscript Symbol	Fortran Symbol	units
4.	Critical temperature	4	4	°R.
5.	Heat of reaction reference temperature	5	5	°R.
6.	Equilibrium constant reference temperature	6	6	°R.
7.	Temperature of continuously added reactant B	7	7	°F.
8.	Reaction temperature	8	8	°F.
9.	Effluent temperature of jacket medium	9	9	°F.
10.	Supply temperature of jacket medium	10	10	°F.
11.	Set point temperature of controller	11	11	°F.
12.	Temperature sensed by measuring element	12	12	°F.
C.	Time constant (general)	k	K	--
1.	Time lag-temperature measuring element	1	1	min.

	Item	Subscript Symbol	Fortran Symbol	Units
2.	Controller rate setting	2	2	min.
3.	Controller integral setting	3	3	min.
4.	Controller time lag	4	4	min.

TABLE III.

INPUT DATA

Variable	Value	Units	Reference
a_1	1.0	--	--
a_2	1.0	--	--
a_3	1.0	--	--
a_4	1.0	--	--
$T_{1,1}$	491.60	°R.	4
$T_{1,2}$	527.60	°R.	4
$T_{1,3}$	633.06	°R.	4
$T_{1,4}$	929.34	°R.	4
$T_{2,1}$	491.60	°R.	4
$T_{2,2}$	527.60	°R.	4
$T_{2,3}$	704.34	°R.	4
$T_{2,4}$	1070.64	°R.	4
$T_{3,1}$	527.60	°R.	4
$T_{3,2}$	527.60	°R.	4
$T_{3,3}$	630.59	°R.	4
$T_{3,4}$	941.94	°R.	4

Variable	Value	Units	Reference
$T_{4,1}$	608.60	°R.	4
$T_{4,2}$	527.60	°R.	4
$T_{4,3}$	671.72	°R.	4
$T_{4,4}$	1164.96	°R.	4
$T_{5,2}$	527.60	°R.	4
$T_{5,3}$	671.72	°R.	4
$T_{5,4}$	1164.96	°R.	4
$(c_p)_1$	0.535	Btu/lb. °F.	4
$(c_p)_2$	0.487	Btu/lb. °F.	4
$(c_p)_3$	0.459	Btu/lb. °F.	4
$(c_p)_4$	1.000	Btu/lb. °F.	4
$(c_p)_5$	1.000	Btu/lb. °F.	4
$(c_p)_6$	0.11	Btu/lb. °F.	6
$(c_p)_7$	0.11	Btu/lb. °F.	6
ρR_1	6.566	lb./gal.	4
ρR_2	8.730	lb./gal.	4
ρR_3	7.500	lb./gal.	4
ρR_4	8.322	lb./gal.	4
ρR_5	8.322	lb./gal.	4

Variable	Value	Units	Reference
MW_1	46.07	lb./lb. mole	4
MW_2	60.05	lb./lb. mole	4
MW_3	88.10	lb./lb. mole	4
MW_4	18.02	lb./lb. mole	4
M_1	1600.0	lb.	--
M_2	0.0	lb.	--
M_3	0.0	lb.	--
M_4	0.0	lb.	--
M_6	1750.0	lb.	7
M_7	920.0	lb.	7
D	4.8	ft.	7
AH	18.0	$ft.^2$	7
VH	80.0	gal.	7
VJ	50.0	gal.	7
U	0.85	Btu/min. $ft.^2$ $^{\circ}F.$	--
n_1	1	--	9
n_2	1	--	9
n_3	1	--	9
n_4	1	--	9

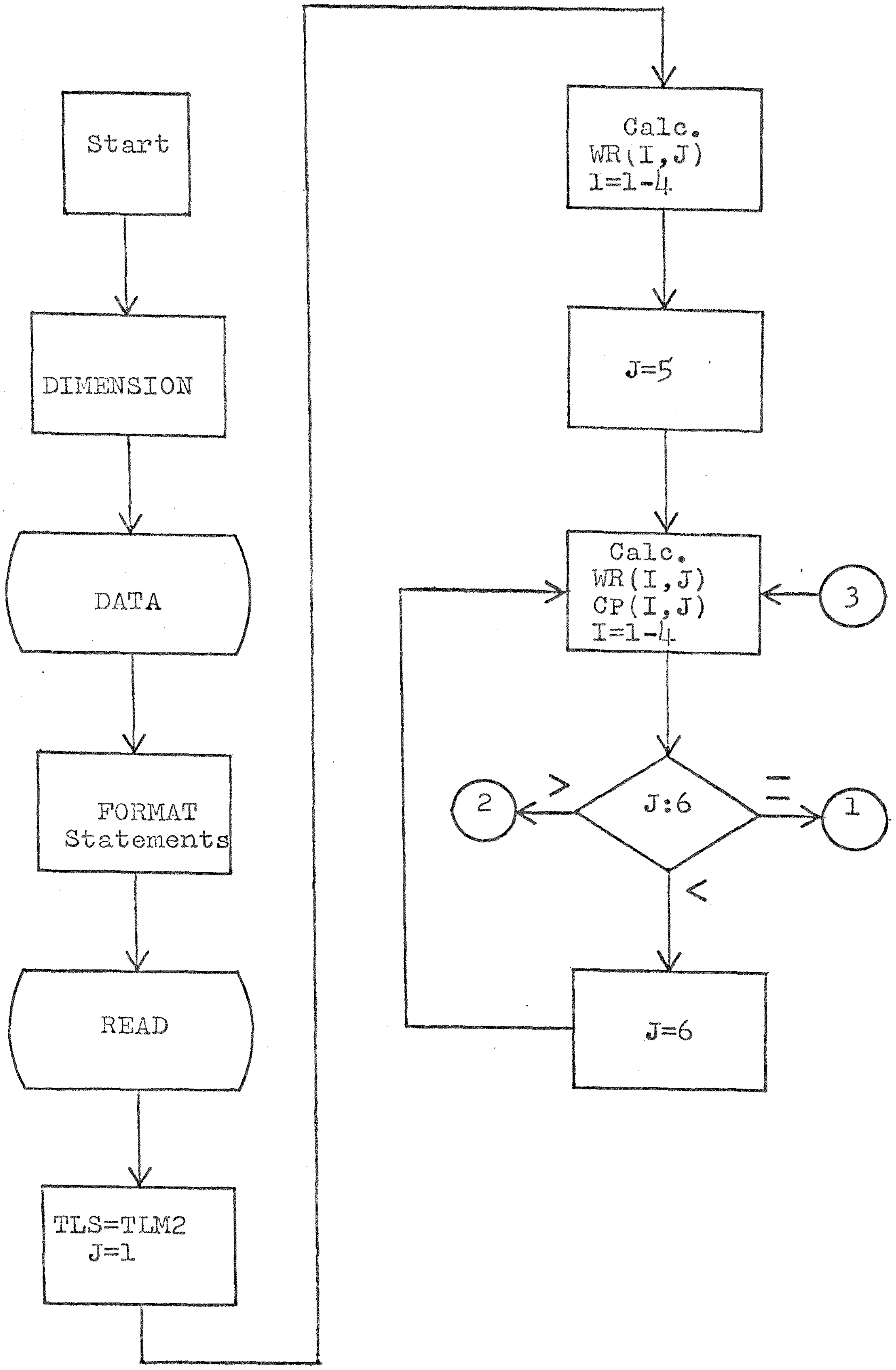
Variable	Value	Units	Reference
K_R	2.92	--	9
E	25,200.0	Btu/lb. mole	8
A	10.1×10^8	gal./min. lb. mole	--
ΔH_R	-8,110.0	Btu/lb. mole	6
k_c	0.12, 1.0, 6.0, 12.0	psi./°F.	12
τ_1	3.0	min.	--
τ_2	0.2, 0.8, 3.0, 10.0	min.	12
τ_3	0.2, 4.0, 15.0, 20.0	min.	12
τ_4	0.008	min.	2
α	5.0	min.	2
c_v	8.0	gal./min.	--
ΔP	40.0	psi.	--
T_5	536.6	°R.	6
T_6	536.6	°R.	9
T_7	70.0	°F.	--
T_8	70.0	°F.	--
T_9	70.0	°F.	--
T_{10}	70.0	°F.	--

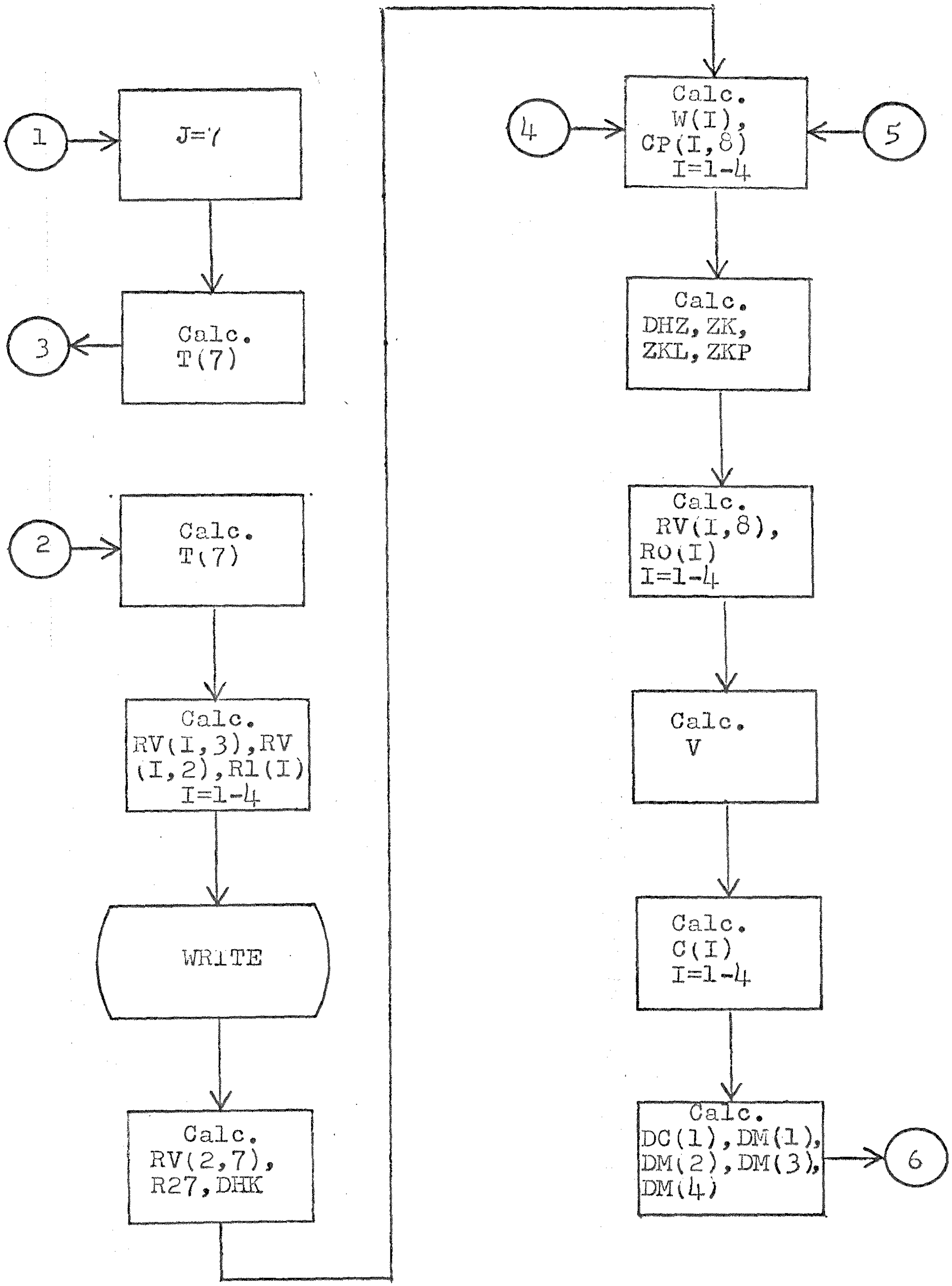
Variable	Value	Units	Reference
T_{11}	90.0	°F.	--
T_{12}	70.0	°F.	--
FB	4.0	gal./min.	--
t_{m1}	60.0	min.	--
Δt	0.5	min.	--
t_{m2}	480.0	min.	--
ΔM_m	0.10	lb.	--
R	1.987	Btu/lb. mole °R.	--
t	0.0	min.	--
M	0	--	--
NO	0	--	--
Itr	0.0	°F. min.	--
Int	0.0	°F. min.	--
MA_1	0.0	lb.	--
$T1_8$	0.0	°F.	--

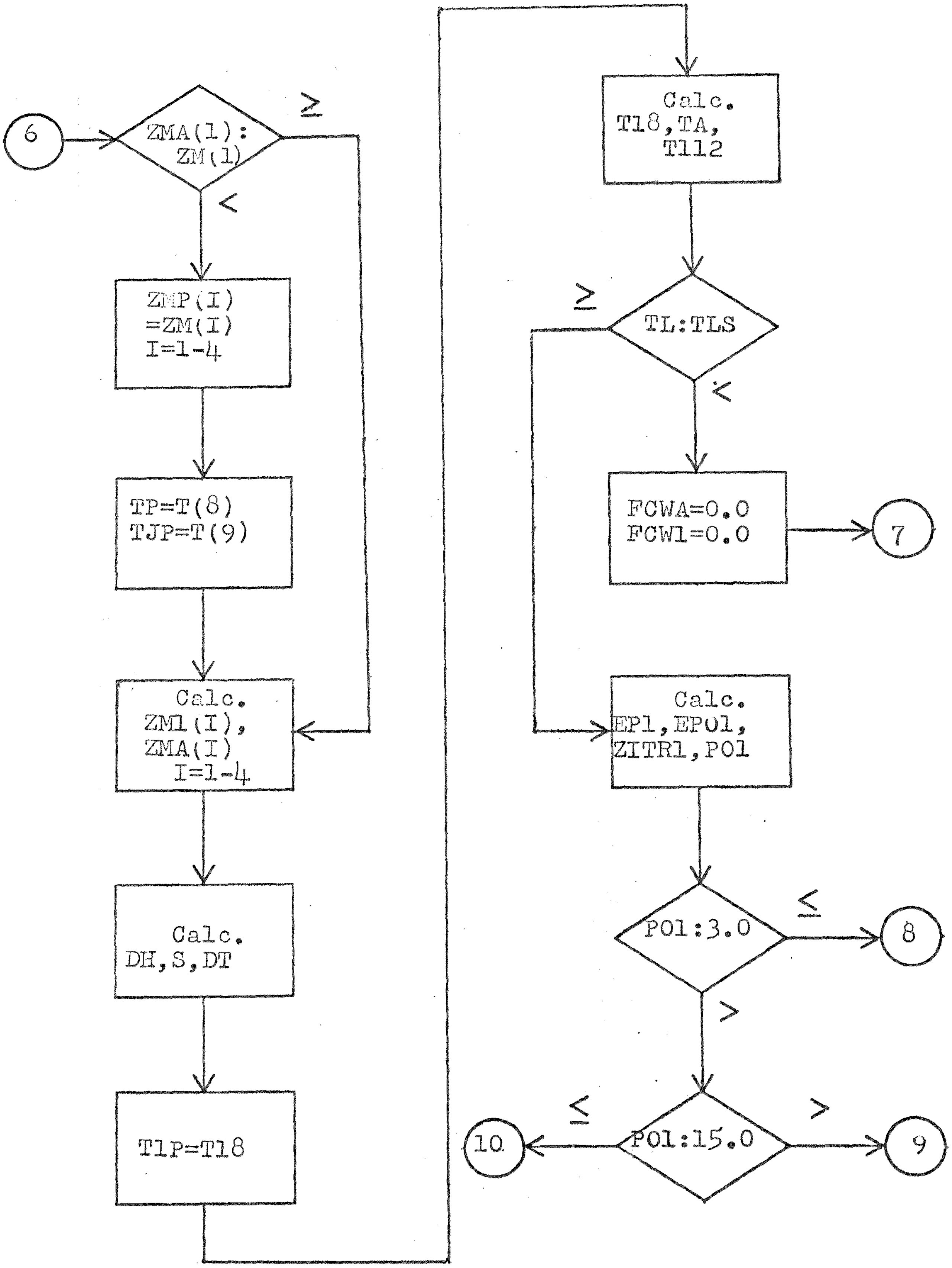
APPENDIX B

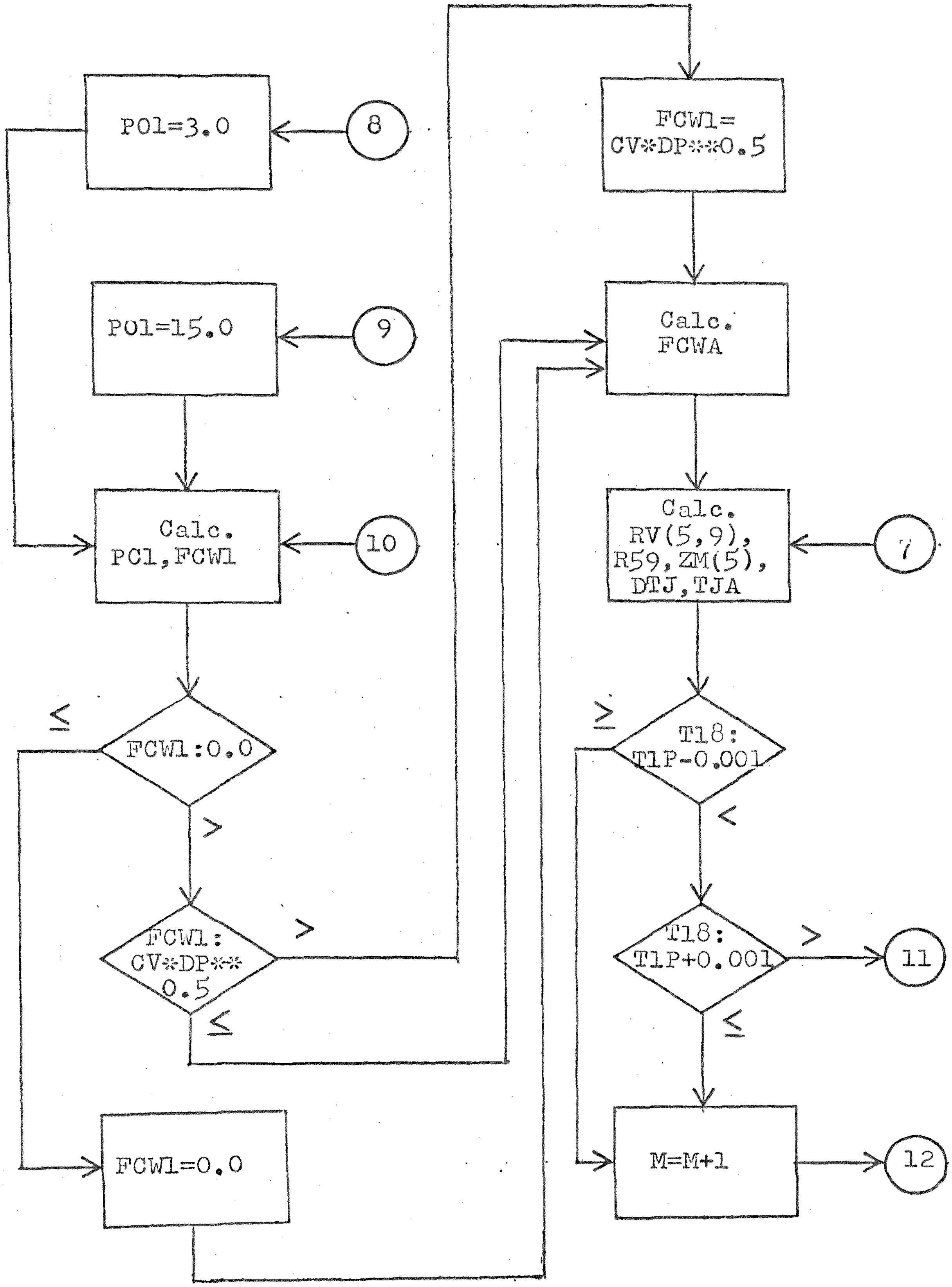
DETAILED LOGIC DIAGRAM

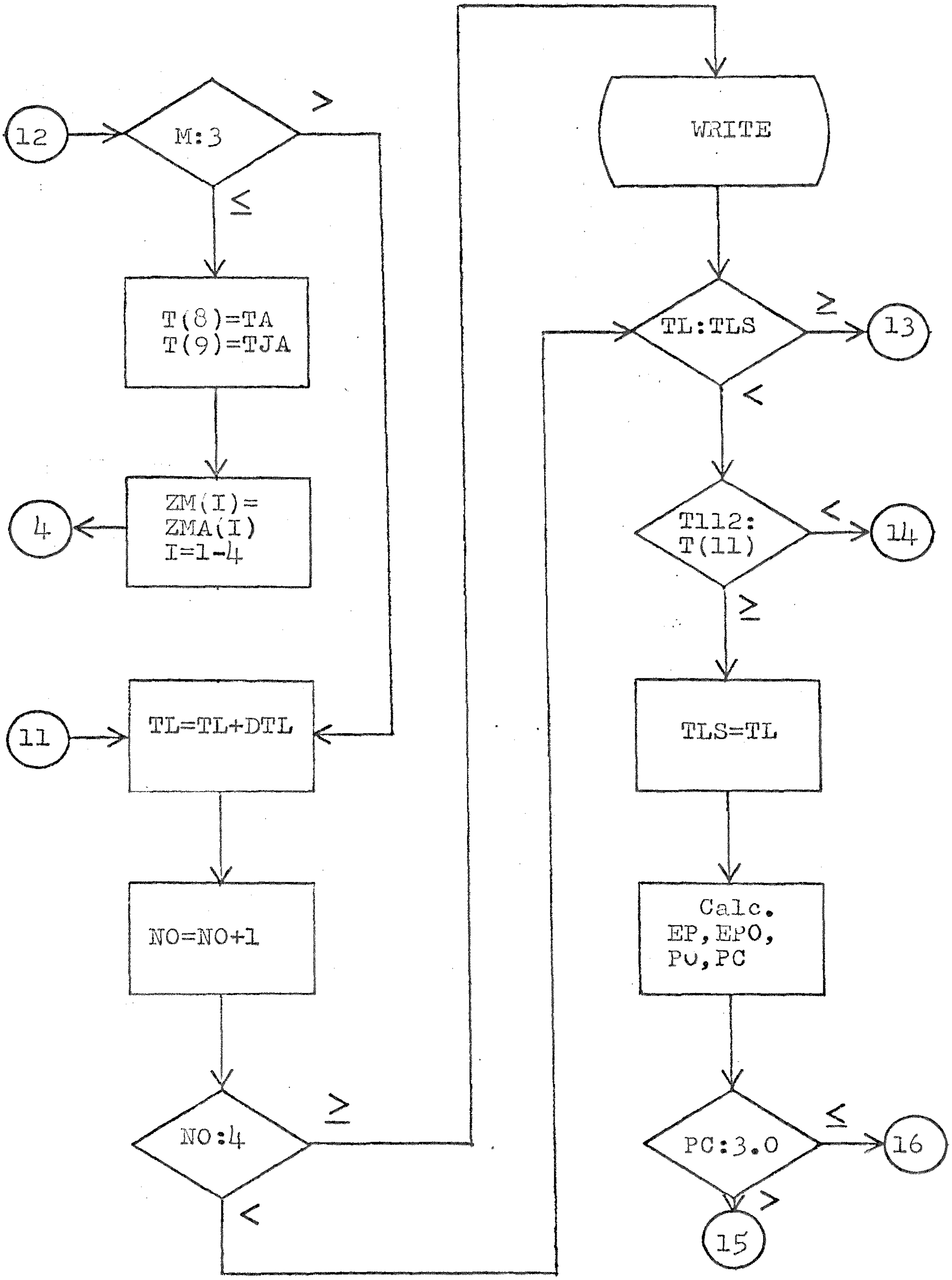
Figure V

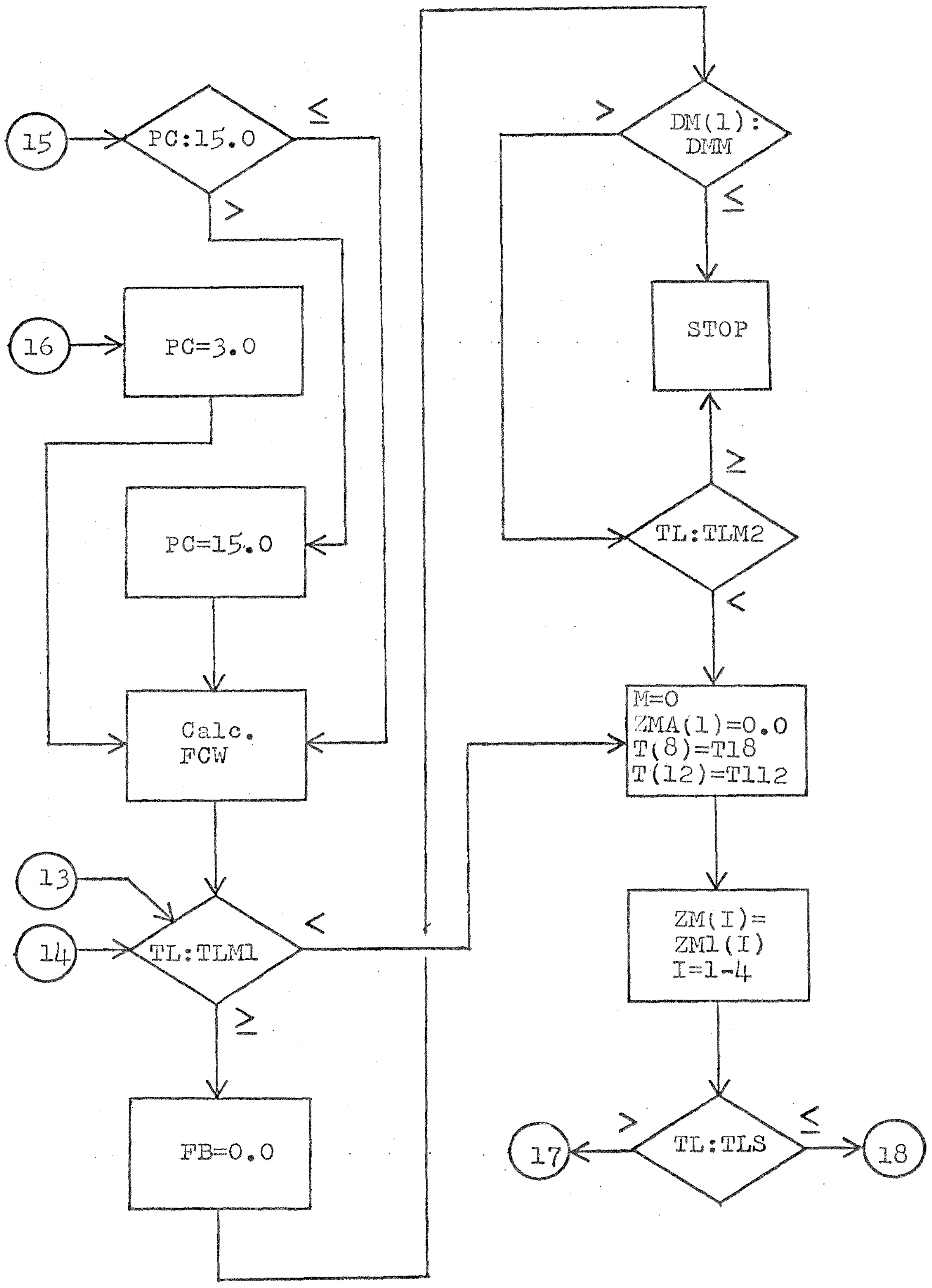

Start
DIMENSION
DATA
FORMAT Statements
READ
TLS=TLM2
J=1
Calc.
WR(I,J)
1=1-4
J=5
Calc.
WR(I,J)
CP(I,J)
I=1-4
3
J:6
>
2
=
1
<
J=6

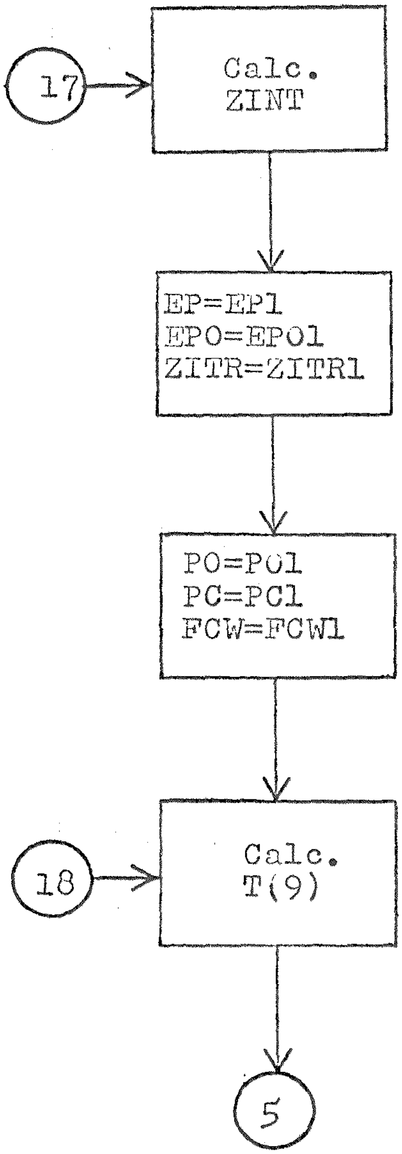

1
J=7
Calc.
T(7)
3
2
Calc.
T(7)
Calc.
RV(I,3),RV
(I,2),R1(I)
I=1-4
WRITE
Calc.
RV(2,7),
R27,DHK
4
Calc.
W(I),
CP(I,8)
I=1-4
5
Calc.
DHZ, ZK,
ZKL, ZKP
Calc.
RV(I,8),
RO(I)
I=1-4
Calc.
V
Calc.
C(I)
I=1-4
Calc.
DC(1),DM(1),
DM(2),DM(3),
DM(4)
6


6
ZMA(1):ZM(1)
≥
<
ZMP(I)=ZM(I) I=1-4
TP=T(8) TJP=T(9)
Calc. ZM1(I), ZMA(I) I=1-4
Calc. DH,S,DT
T1P=T18
Calc. T18,TA, T112
TL:TLS
≥
<
FCWA=0.0 FCW1=0.0
7
Calc. EP1,EP01, ZITR1,P01
P01:3.0
≤
8
>
P01:15.0
≤
>
10
9


P01=3.0
8
P01=15.0
9
Calc.
PC1,FCW1
10
≤
FCW1:0.0
>
FCW1:
CV*DP**
0.5
>
≤
FCW1=0.0
FCW1=
CV*DP**0.5
Calc.
FCWA
Calc.
RV(5,9),
R59,ZM(5),
DTJ,TJA
7
≥
T18:
T1P-0.001
<
T18:
T1P+0.001
>
11
≤
M=M+1
12


12
M:3
>
≤
T(8)=TA
T(9)=TJA
ZM(I)=
ZMA(I)
I=1-4
4
11
TL=TL+DTL
NO=NO+1
NO:4
≥
<
WRITE
TL:TLS
≥
13
<
T112:
T(11)
<
14
≥
TLS=TL
Calc.
EP,EPO,
PO,PC
PC:3.0
≤
16
>
15


15
PC:15.0
≤
>
16
PC=3.0
PC=15.0
Calc.
FCW
13
14
TL:TLM1
<
≥
FB=0.0
DM(1):
DMM
>
≤
STOP
≥
TL:TLM2
<
M=0
ZMA(1)=0.0
T(8)=T18
T(12)=T112
ZM(I)=
ZM1(I)
I=1-4
TL:TLS
>
≤
17
18


17
Calc.
ZINT
EP=EP1
EPO=EPO1
ZITR=ZITR1
PO=PO1
PC=PC1
FCW=FCW1
18
Calc.
T(9)
5

APPENDIX C

PROGRAM PRINTOUT

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```
// JOB CC??,SIMRTR,300,750,ROBERT VICZUREK
// PARAM MAP=NO
// FORTRAN     ROBERT VICZUREK
      PROGRAM SIMRTR
      DIMENSION TR(5,4),AL(4),B(4),ZM(7),T(12),RO(5),ZMW(4),TAU(4),
     1CPR(7),CP(4,8),DH(4),ZMA(4),VR(4,7),B(4),RV(5,9),RI(5),RP(5),
     2C(4),SC(4),ZMI(4),ZMP(4)
      DATA AL/4*1.0/,B/4*1/,TLR2,ZEP,DHR,TEM1,FR,U,VH,AP,D,DP,R,DTL,VJ,W,
     1TEM/480.0,2.02,-8110.0,60.0,4.0,0.35,80.0,18.0,4.8,40.0,1.987,0.5,
     250.0,0.0,1/,TL,T18,ZINT,ZITR/4*0.0/,ZMA(1)/0.0/,A,F/10.108,2.
     3E204/,EPS1,ZITR1,NO,DCI/0.0,0.0,0,0.0/
   10 FORMAT(6F10.3)
   18 FORMAT(' ',G10.5,2G12.7,4G12.5)
   24 FORMAT(4X,2HTL,10X,LNT,10X,2HN1,9X,5HERROR)
      READ(97,18)((TR(I,J),I=1,5),J=1,4),(CPR(I),I=1,7),(RP(I),I=1,5)
     1,(ZM(I),I=1,7),(T(J),J=1,12),(ZMW(I),I=1,4),(TAU(K),K=1,4),AMP,
     2RKC,CV
      TLS=TLR2
C     SECTION 1 NON-ITERATIVE CALCULATIONS
C     DATSP LIQUID PHASE EXPANSION FACTOR AT SPECIFIC HEAT REF. TEMP.
      J=1
      DO 5 I=1,4,1
    5 R(I,J)=0.1745-0.0838*TR(I,J)/TR(I,4)
C     SPECIFIC HEATS AT REFERENCE TEMPERATURES
      J=5
    7 DO 6 I=1,4,1
   10 R(I,J)=0.1745-0.0838*T(J)/TR(I,4)
    6 CP(I,J)=CPR(I)*(R(I,1)/R(I,J))**2.0
      IF(J-6)8,9,11
    8 J=6
      GO TO 7
    9 J=7
      T(7)=T(7)+459.60
      GO TO 7
   11 T(7)=T(7)-459.60
C     DENSITY CALCULATIONS
      DO 12 I=1,5,1
      RV(I,3)=ZMW(I)/(3.401*TR(I,3))
      RV(I,2)=EXP((5.0*(TR(I,2)/TR(I,3)-1.0)+ALOG10(RV(I,3)))*ALOG(10
     1.0))
   12 RI(I)=(RP(I)-RV(I,2))/(1.0-TR(I,2)/TR(I,4))**0.3
C     PRINT HEADINGS
   50 WRITE(99,24)
   17 RV(2,7)=EXP((5.0*((T(7)+459.60)/TR(2,3)-1.0)+ALOG10(RV(2,3)))
     1*ALOG(10.0))
      R27=RV(2,7)+RI(2)*(1.0-(T(7)+459.60)/TR(2,4))**0.3
C     HEAT OF REACTION AT EQUILIBRIUM CONSTANT REFERENCE TEMPERATURE
      DHR=DHR+(AL(3)*(CP(3,6)+CP(3,5))*ZMW(3)+AL(4)*(CP(4,6)+CP(4,5))
     1*ZMW(4)-AL(1)*(CP(1,6)+CP(1,5))*ZMW(1)-AL(2)*(CP(2,6)+CP(2,5))
     2*ZMW(2))*(T(6)-T(5))/2.0
C     SECTION 2 ITERATIVE CALCULATIONS FOR REACTION
```

95

```
C     SPECIFIC HEATS
   13 DO14I=1,4,1
      R(I)=0.1745-0.0838*(T(3)+459.60)/TR(I,4)
   14 CP(I,8)=CPP(I)*(RR(I,1)/R(I))**2.0
C     HEAT OF REACTION
      DHZ=DHP+(AL(3)*(CP(3,8)+CP(3,5))*ZMW(3)+AL(4)*(CP(4,8)+CP(4,5))
     1*ZMW(4)-AL(1)*(CP(1,8)+CP(1,5))*ZMW(1)-AL(2)*(CP(2,8)+CP(2,5))
     2*ZMW(2))*(T(8)-T(5)+459.60)/2.0
C     CHEMICAL EQUILIBRIUM CONSTANT
      ZK=ZKK*EXP((DHZ+DHK)*(1.0/T(6)-1.0/(T(3)+459.60)))/(2.0*R))
C     FORWARD REACTION RATE CONSTANT
      ZKL=A*EXP(-E/(R*(T(8)+459.60)))
C     REVERSE REACTION RATE CONSTANT
      ZKR=ZKL/ZK
C     DENSITIES
      DO15I=1,4,1
      PV(I,8)=EXP((5.0*((T(8)+459.60)/TR(I,3)-1.0)+ALOG10(PV(I,3)))
     1*ALOG(10.0))
   15 RO(I)=PV(I,8)+R1(I)*(1.0-(T(8)+459.60)/TR(I,4))**0.3
C     BATCH VOLUME
      V=ZM(1)/RO(1)+ZM(2)/RO(2)+ZM(3)/RO(3)+ZM(4)/RO(4)
C     CONCENTRATIONS
      DO16I=1,4,1
   16 C(I)=ZM(I)/(ZMW(I)*V)
C     KINETIC CALCULATION OF INCREMENTAL CONCENTRATION CHANGE
      DC(1)=-DTL*(ZKL*C(1)**N(1)*C(2)**N(2)-ZKR*C(3)**N(3)*C(4)**N(4))
C     INCREMENTAL MASS CHANGE
      DM(1)=DC(1)*ZMW(1)*V
      DM(2)=AL(2)*ZMW(2)*DM(1)/(AL(1)*ZMW(1))+FR*R27*DTL
      DM(3)=-AL(3)*ZMW(3)*DM(1)/(AL(1)*ZMW(1))
      DM(4)=-AL(4)*ZMW(4)*DM(1)/(AL(1)*ZMW(1))
C     TEST FOR DEFINING VALUES OF PRIMED VARIABLES
      IF(ZMA(1)-ZM(1))20,22,22
C     PRIMED VARIABLES EQUATED TO INITIAL VALUES
   20 DO21I=1,4,1
   21 ZMP(I)=ZM(I)
      TP=T(8)
      TJP=T(9)
C     END-OF-INTERVAL AND AVERAGE MASSES
   22 DO 23 I=1,4,1
      ZM1(I)=ZMP(I)+DM(I)
   23 ZMA(I)=ZMP(I)+DM(I)/2.0
C     HEAT EVOLVED
      H=DHZ*DC(1)*V
C     HEAT TRANSFER SURFACE
      S=AH+(V-VH)*0.535/D
C     REACTION TEMPERATURE CHANGE
      DT=(DH-U*S*(T(8)-T(9))*DTL+(T(7)-T(8))*FR*R27*DTL*(CP(2,7)+CP
     1(2,8))/2.0)/(ZM(1)*CP(1,8)+ZM(2)*CP(2,8)+ZM(3)*CP(3,8)+ZM(4)*CP
     2(4,8)+ZW(6)*CPR(6)/2.0)
      TIP=TI
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C     END-OF-INTERVAL AND AVERAGE REACTION TEMPERATURE
      T1R=TR+DT
      TA=TR+DT/2.0
C     SECTION 3 ITERATIVE CALCULATIONS FOR CONTROLLER AND JACKET
C     SENSED TEMPERATURE
      T112=(DTL*(TA-T(12)/2.0)/TAU(1)+T(12))/(1.0+DTL/(2.0*TAU(1)))
C     TEST TO DETERMINE IF CONTROLLER HAS BEEN ACTIVATED
      IF(TI-TLS)42,44,44
   42 FCWA=0.0
      FCW1=0.0
      GOTO43
C     ERROR
   44 ER1=T(11)-T112
C     ERROR OUTPUT OF CONTROLLER RATE SECTION
      ERO1=(ALP*(ER1+(ZINT+(ERP+ER1-ERO)*DTL/2.0)/TAU(2)))/(1.0+ALP*DTL
     1/(TAU(2)*2.0))
C     TIME INTEGRAL OF RATE SECTION ERROR OUTPUT
      ZITR1=ZITR+(ERO+ERO1)*DTL/2.0
C     OVERALL CONTROLLER PNEUMATIC OUTPUT
      PO1=9.0+ZKC*ERO1+ZKC*ZITR1/TAU(3)
C     TEST TO INSURE OUTPUT WITHIN INSTRUMENT CAPABILITY
      IF(PO1-3.0)26,26,27
   27 IF(PO1-15.0)28,28,29
   26 PO1=3.0
      GO TO 28
   29 PO1=15.0
C     PNEUMATIC SIGNAL TO CONTROL VALVE
   28 PC1=(DTL*(PO1+PO-PC)/(2.0*TAU(4))+PC)/(1.0+DTL/(2.0*TAU(4)))
C     FLOW RATE OF JACKET MEDIUM
      FCW1=(15.0-PC1)*CV*DP**0.5/12.0
C     TEST TO INSURE RATE WITHIN CAPABILITY OF VALVE
      IF(FCW1-0.0)50,50,51
   51 IF(FCW1-CV*DP**0.5)52,52,53
   50 FCW1=0.0
      GOTO52
   53 FCW1=CV*DP**0.5
C     AVERAGE FLOW RATE OF JACKET MEDIUM
   52 FCWA=(FCW+FCW1)/2.0
C     DENSITY OF MEDIUM IN JACKET
   43 PV(5,9)=EXP((5.0*((T(9)+459.69)/TR(5,5)-1.0)+ALOG10(PV(5,5)))
     1*ALOG(10.0))
      R59=PV(5,9)+R1(5)*(1.0-(T(9)+459.69)/TR(5,4))**0.3
C     MASS OF MEDIUM IN JACKET
      ZM(5)=VJ*R59
C     TEMPERATURE CHANGE OF JACKET MEDIUM
      DTJ=((UJ*S*(TA-T(9))-FCWA*R59*(T(9)-T(10))*CP(5))*DTL)/(ZM(5)*
     1CP(5)+ZM(7)*CPR(7))
C     AVERAGE TEMPERATURE OF JACKET MEDIUM
      TJA=TJR+DTJ/2.0
C     SECTION 4 TESTS AND REPETITIONS
C     TEST FOR CONVERGENCE
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      IF(TIB-TIP-0.001)30,31,31
   30 IF(TIB-TIP+0.001)31,31,32
C     UPDATE OF ITERATION INDEX
   31 N=N+1
C     TEST FOR FURTHER ITERATIONS
      IF(N-3)34,34,32
C     REDEFINITION OF VARIABLES FOR NEXT ITERATION
   34 T(7)=TA
      T(8)=TIA
      DO36I=1,4,1
   36 ZP(I)=ZA(I)
      GO TO 13
C     UPDATE OF ELAPSED TIME
   32 TL=TL+DTL
C     UPDATE OF OUTPUT INDEX
      NO=NO+1
C     TEST FOR DATA OUTPUT
      IF(NO-4)56,55,55
   55 WRITE(99,19)TL,TIB,ZP(1),FLOW
      NO=0
C     TEST TO DETERMINE IF CONTROLLER HAS BEEN ACTIVATED
   56 IF(TL-TLS)47,45,45
C     TEST TO DETERMINE IF CONTROLLER SHOULD BE ACTIVATED
   47 IF(TI12-T(11))45,46,46
   46 TLS=TL
C     INITIAL CONDITIONS FOR CONTROLLER VARIABLES
      EP=T(11)-TI12
      EPD=ALP*EP
      PU=9.0+ZKC*EPD
      PC=PU
C     TEST TO INSURE OUTPUT WITHIN INSTRUMENT CAPABILITY
      IF(PC-3.0)1,1,2
    2 IF(PC-15.0)3,3,4
    1 PC=3.0
      GO TO 3
    4 PC=15.0
    3 FLOW=(15.0-PC)*CV*DP**0.5/12.0
C     TEST FOR TERMINATION OF REACTANT ADDITION
   45 IF(TL-TL1)39,40,40
   40 FLOW=0.0
C     TEST FOR SIMULATION TERMINATION-MINIMUM CONVERSION
      IF(ZP(1)+ZMN)39,35,35
C     TEST FOR SIMULATION TERMINATION-MAXIMUM ELAPSED TIME
   39 IF(TL-TLM2)37,35,35
C     REDEFINITION OF VARIABLES FOR NEXT TIME INTERVAL
   37 N=0
      T(8)=TIB
      DO41I=1,4,1
   41 ZP(I)=ZA1(I)
      ZPA(1)=0.0
      T(12)=TI12
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                IF(TI-TL5)+5,43,49
          48    ZIN1=ZINT+(EP+EP1-EPR-EPR1)*DTL/2.0
                EP=EP1
                EPR=EPR1
                ZITR=ZITR1
                U=P1
                C=PC1
                CW=PC1
          49    T(?)=TJP+DTJ
                GO TO 13
          39    STOP
                END
        // EXEC
           491.60      491.60      527.60      508.60      508.60      527.60      527.60      527.60
           527.60      527.60      633.06      734.34      730.59      671.72      671.72      929.34
           1070.64     941.94      1164.94     1164.36     0.535       0.487       0.459       1.000
           1.000       0.11        0.11        6.565       8.730       7.500       8.322       8.322
           1600.00     0.00        0.00        0.00        0.00        1750.0      920.0       0.0
           0.0         0.0         0.0         536.6       536.6       70.0        70.0        70.0
           76.0        90.0        70.0        40.07       60.05       88.10       18.07       3.0
           3.0         15.0        0.002       5.0         6.0         8.0
        *EOF
ST
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