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Calculation of the equilibrium composition of a reaction mixture inside a combustion chamber

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CALCULATION OF THE EQUILIBRIUM
COMPOSITION OF A REACTION
MIXTURE INSIDE A
COMBUSTION CHAMBER

by

WILLIAM D. STEELMAN

CALCULATION OF THE EQUILIBRIUM COMPOSITION OF A
REACTION MIXTURE INSIDE A COMBUSTION CHAMBER

by

William D. Steelman

A Research Report

Presented to the Graduate Faculty
of Lehigh University
in Candidacy for the Degree of
Master of Science

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1964

CERTIFICATE OF APPROVAL

This research report is accepted and approved
in partial fulfillment of the requirements for the
degree of Master of Science in Chemical Engineering.

July 13, 1964
(Date)

Morton S. Myler
(Professor in charge)

(Head of the Department)

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I wish to express my thanks to my advisor, Dr. Morton P. Moyle for his patience and advice, and to the computing staff of Lehigh University for their advice in writing the computer program. I also wish to thank my wife, Sara Ellen, for typing this report.

TABLE OF CONTENTS

	Page No.
Abstract.....	1
Introduction.....	2
Development of the Minimization of Free Energy Method..	9
Block Diagram.....	23
Program One.....	51
Program Two.....	59
Instructions for Submitting Program.....	72
Computer Print Out.....	83
Sample Calculations.....	87
Conclusion.....	99
Bibliography.....	100
List of Nomenclature.....	101

Abstract

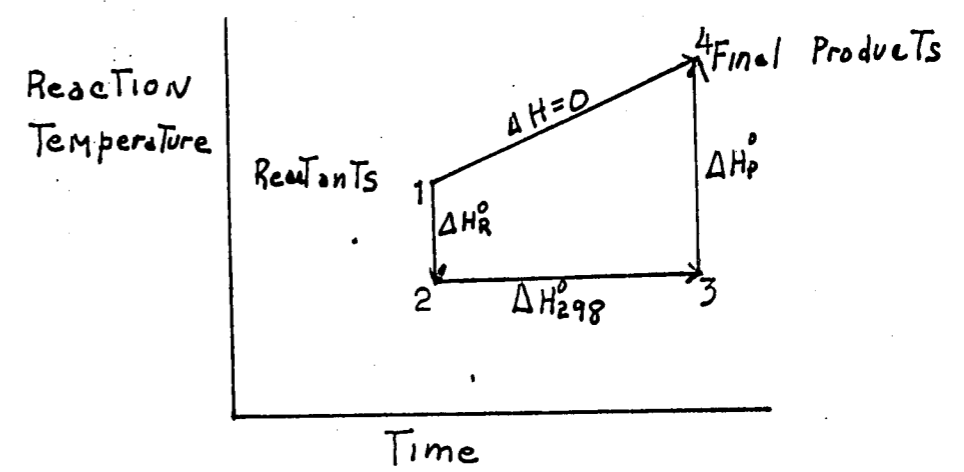
This report presents a computer program for calculating the equilibrium composition of a reaction mixture inside a combustion chamber. The program is designed to be run on any computer which has a fortran compiler and sufficient memory location. The minimization of free energy method was used in order to calculate the equilibrium composition in the chamber. A brief summary is given of the theory and basic equations used to develop the minimization of free energy method. A complete and detailed explanation of the program and the list of input data instructions necessary in order to use the program are also included. Sample calculations illustrating the use of the minimization of free energy are presented at the end of the report.

Introduction

There is a need for a computer program to calculate the performance parameters of a reaction mixture inside a combustion chamber because hand calculations are impossible to perform for complex propellants. Some of the more important rocket performance parameters which are of importance in evaluating a fuel are specific impulse, characteristic velocity, nozzle thrust coefficient, discharge coefficient and the total impulse. In order to calculate the various performance parameters the equilibrium composition and temperature inside the combustion chamber, and the equilibrium composition and temperature leaving the rocket nozzle must first be calculated.

In a rocket, the adiabatic combustion takes place at constant pressure and produces high-temperature exhaust gases which are expanded isentropically through a nozzle. The exhaust gases passing through the nozzle give a rocket its thrust. The equations for calculating the equilibrium composition inside a combustion chamber and leaving a rocket nozzle are similar, the main difference being that the reaction which occurs inside the chamber is a constant enthalpy process, and the expansion through the nozzle is a constant entropy process. This report presents a computer program for calculating the equilibrium composition and temperature of a reaction mixture inside the combustion chamber.

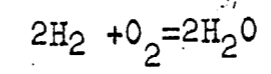
If no dissociation occurred in the combustion chamber the temperature would be given by the adiabatic flame temperature. The adiabatic flame temperature may be calculated from the following diagram and formula.



$$\Delta H=0 = \Delta H_R^0 + \Delta H_{298}^0 + \Delta H_P^0$$

$$= \Delta H_{298}^0 + \sum_{\text{Products}} (\eta \int c_p^0 dT) - \sum_{\text{Reactants}} (\eta \int c_p^0 dT)$$

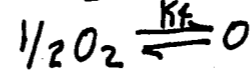
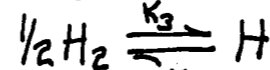
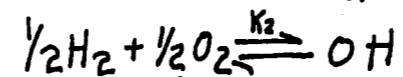
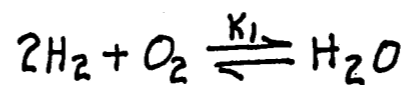
Consider a reaction involving two moles of H₂ and one mole of O₂ which goes to 100 % completion. If the H₂ and O₂ react in the following manner,



the reaction temperature can be calculated using the adiabatic flame temperature equation, and the equilibrium composition can be calculated using a material balance.

In actual practice, the hydrogen and oxygen will not combine to give two moles of water, but will give other products such as OH, O and H. In order to calculate the reaction products, a material balance must be maintained while simultaneously solving the following equations:

solving the following equations:



$$K_1 = \frac{[\text{H}_2\text{O}]}{[\text{H}_2]^2 [\text{O}_2]}$$

$$K_2 = \frac{[\text{OH}]}{[\text{H}_2]^{1/2} [\text{O}_2]^{1/2}}$$

$$K_3 = \frac{[\text{H}]}{[\text{H}_2]^{1/2}}$$

$$K_4 = \frac{[\text{O}]}{[\text{O}_2]^{1/2}}$$

Complex reaction mixtures require many more equations to describe the system, and a computer program is necessary to solve the trial and error equations.

Originally, thermodynamists theoretically calculated the performance of a few carbon-hydrogen-oxygen propellants by hand. However, the complexity of the calculation coupled with the lack of high temperature data limited their activity. As some rocket thermodynamists attempted to expand the scope of their work, short-cut methods of calculation were developed. However, these techniques invoked simplifying assumptions which introduced considerable error as the complexity of the propellants increased, particularly if condensed phases were formed as products of combustion.

In the early 1950's the first successful attempts were made to develop a program for calculation the performance of propellants. These attempts were at first limited to propellants composed of C, H, O, N, Cl, and F. Since then other programs have been written but neither new ingredient elements nor new products of combustion could be considered without re-writing the computer program.

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Further, the shortage of memory capacity in small and medium-sized digital computers has limited the complexity of the propellant system which could be evaluated. This program is neither limited by the number or type of elemental ingredients nor by the number or state of the products of combustion.

5

The two main methods of calculating the equilibrium composition inside a rocket chamber are the method of equilibrium constants (used above in the H_2 and O_2 example), and the minimization of free energy. In the first method, thermodynamic equilibrium constants are utilized to express the concentrations of other more abundant species. The solution is a trial-and-error one in which the chamber enthalpy balance and the nozzle entropy balance are conducted as assumed chamber and exit temperature, respectively. The second method, which was used in this report, is a more general one and is applicable to all equilibrium reactions. Instead of utilizing arbitrary equilibrium constants, solution is obtained by minimizing the free energy of the complex mixture of combustion products. The combustion and exhaust temperatures are obtained as part of the solution so that these quantities do not enter into the trial-and-error iteration. The accuracy of both methods is dependent only upon the accuracy of the basic thermodynamic data for the reactants and the products of combustion. While both methods are equally rigorous, it was felt the minimization of free energy method was more adaptable to a computer

2 45
solution; hence, the minimization method was the method chosen to calculate the chamber composition.

This completely general program reads in all the data used in the program in matrix form. Using this procedure the size and complexity of the reaction is only limited by the amount of memory location available in the computer. The program is neither limited by the number or type of elemental ingredients nor by the number or state of the combustion products. For all practical purposes, any propellant system for which thermodynamic data are available may be evaluated.

The program had to be written in two parts in order for it to be able to fit into the core space available in a GE 225 computer. The first program calculates the major products and orders them according to which products give the greatest reduction of free energy. The results of the first program are punched out on data cards which are then used as the input data for the second program. The second program re-introduces the minor species (all products existing in relatively small concentration which were not termed as major species in computer program one). Using an iterative process by which the free energy is continually reduced while simultaneously maintaining a mass balance until equilibrium is reached, the equilibrium composition in the combustion chamber is calculated.

The following assumptions were made in the minimization of free energy method:

- 2 6
- 7
1. Perfect Gas Law is obeyed.
 2. Dalton's Law applies.
 3. Molar enthalpies of all species and molar entropies of condensed phases are independent of pressure.
 4. Steady-State conditions exist during combustion and expansion.
 5. Combustion is adiabatic and occurs at constant pressure.
 6. Thermal and chemical equilibria exist in the combustion chamber.
 7. Isentropic, frictionless, one-dimensional flow occurs in the nozzle.
 8. Gases are insoluble in the condensed phase, and the condensed phases are immiscible.

The first four of these assumptions may be considered as justified by existing experimental evidence. The only questionable point appears to be the assumption of ideal behavior for the vapors of the metal oxides. However, the relatively small concentration of these vapors in the combustion products will tend to minimize the significance of any possible non-ideal behavior.

The assumption that the combustion is adiabatic and is followed by an isentropic expansion through a converging-diverging nozzle, represents the ideal limiting conditions of energy utilization and overall efficiency, and is approached experimentally in large rocket engines. In practice, the geometry of the rocket engine may affect the attainment of equilibrium. A short reaction chamber may not afford a sufficiently long residence

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2
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time for some chemical reactions to attain equilibrium. The one-dimensional flow approximation is an excellent one in short ducts of variable cross sectional area. Assumption 8 could introduce error, particularly for cases in which liquid metal oxides constitute a relatively large percentage of the total mass of combustion products.

Frequently the measured performance of rocket engines exceeds 95 % of the ideal, theoretical value. Furthermore, the accepted practice for designing rocket engines is to utilize ideal rocket performance parameters and modify these by empirical corrections.

The complete description of the program and how it operates is given in the computer print out sheets. A detailed description of the input variables needed in order to run the program is also given. The program has several intermediate print out statements. These intermediate print out statements are designed to help the programmer locate any errors that may have developed because of faulty input data or imperfections in the general program.

8
Since the calculational technique was completely rigorous, the accuracy of the calculations is limited only by the accuracy of the basic thermodynamic data used. Therefore, this report is submitted as a completely rigorous method for obtaining the equilibrium composition in a combustion chamber.

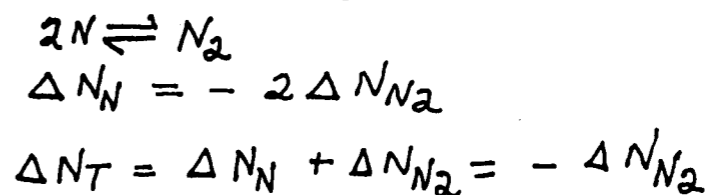
Development of Equation for The Minimization of Free Energy Method.

For any incremental change in the concentration of combustion products, there will be three contributions to the free energy of the mixture:

1. the free energy due to the formation of new products.
2. the free energy lost by the decrease in concentration of the reactants.
3. the free energy change due to the variation in the total number of gaseous moles.

The best way of understanding the free energy change is by way of example.

Consider the formation of Nitrogen gas from its atoms:



At a given temperature and concentration, the free energy of the mixture may be expressed as

$$F = N_N [H_N(T) - TS_N(T)] + RT N_N \ln \frac{N_N}{N_T}$$

$$+ N_{N_2} [H_{N_2}(T) - TS_{N_2}(T)] +$$

$$RT N_{N_2} \ln \frac{N_{N_2}}{N_T} + RT \ln \frac{P_T}{N_T}$$

The combustion in the reaction chamber is adiabatic (constant enthalpy reaction), therefore any change in the temperature of the mixture will cause a change in the temperature of the mixture. Over a short range, $C_p \Delta T \cong \Delta H$. Since the reaction in the chamber is a constant enthalpy process the change in enthalpy for the reaction is:

$$\Delta H = 0 = \Delta N_{N_2} [H_{N_2}(T) - 2H_N(T)] + \sum N_j C_{pj} \Delta T$$

$$\text{and } \Delta T = - \left[\frac{H_{N_2} - 2H_N}{\sum N_j C_{pj}} \right] \Delta N_{N_2}$$

$$\text{or } \Delta T = +K \Delta X$$

where

$$K = - \left[\frac{H_{N_2} - 2H_N}{\sum N_j C_{pj}} \right]$$

The coefficient K relates the change in temperature of the mixture to the change in concentration of an individual specie. The free energy change due to the formation of a new product, N_2 , and due to mixing is:

$$\Delta F = N_{N_2} [H_{N_2} - TS_{N_2}]_{T+\Delta T} + \Delta N_{N_2}$$

$$[H_{N_2} - TS_{N_2}]_{T+\Delta T} + R(T+\Delta T)$$

$$[(N_{N_2} - \Delta N_{N_2}) \ln(N_{N_2} + \Delta N_{N_2}) - N_{N_2} \ln N_{N_2}] + R \cdot \Delta T (N_{N_2} \ln N_{N_2})$$

The free energy change due to the decrease in concentration of the reactant, N, and due to mixing is:

$$(8) \quad \Delta F = N_N [H_N - TS_N]_{T+ΔT} - 2 \Delta N_{N_2} [H_N - TS_N]_{T+ΔT} + R(T+ΔT) [(N_N - 2\Delta N_{N_2}) \ln (N_N - 2\Delta N_{N_2}) - N_N \ln N_N] + R \cdot \Delta T (N_N \ln N_N)$$

The free energy change due to the variation in the total number of gaseous moles is:

$$(10) \quad \Delta F = R(T+ΔT)(N_T - \Delta N_{N_2}) \ln \frac{P_T}{N_T - \Delta N_{N_2}} - RT N_T \ln \frac{P_T}{N_T}$$

Equation (10) may be rewritten as:

$$(10.1) \quad \Delta F = R(T+ΔT)(N_T - \Delta N_{N_2}) \left[\ln \frac{P_T}{N_T} - \ln (-\Delta N_{N_2}) \right] - RT \ln \frac{P_T}{N_T}$$

which may be further expanded to give:

$$(10.2) \quad \Delta F = R(T+ΔT) \left[N_T \ln \frac{P_T}{N_T} - \Delta N_{N_2} \ln \frac{P_T}{N_T} - N_T \ln (-\Delta N_{N_2}) + \Delta N_{N_2} \ln (-\Delta N_{N_2}) \right] - RT N_T \ln \frac{P_T}{N_T}$$

$$(10.3) \quad \Delta F = -R(T+ΔT)(\Delta N_{N_2}) \ln \frac{P_T}{N_T} + R(T+ΔT) \left[-N_T \ln (-\Delta N_{N_2}) + \Delta N_{N_2} \ln (-\Delta N_{N_2}) \right]$$

By adding and subtracting $n_T \ln n_T$ to the term $R(T+ΔT) [-N_T \ln (-\Delta N_{N_2})]$

of the equation 10.3 we get,

$$(10.3) \quad \Delta F = -R(T+ΔT)(\Delta N_{N_2}) \ln \frac{P_T}{N_T} + R(T+ΔT) \left[N_T \ln N_T - (N_T - \Delta N_{N_2}) \ln (N_T - \Delta N_{N_2}) \right]$$

The equation on the past page are the functions of ΔT and ΔN . Since $\Delta T = K\Delta N$ the above equations may be reduced to a cubic function of ΔN . First, consider the ideal contribution to free energy. From the terms-

$$N_{N_2} [H_{N_2} - TS_{N_2}]_T^{T+\Delta T} - \Delta N_{N_2} [H_{N_2} - TS_{N_2}]_T^{T+\Delta T}$$

and

$$N_N [H_N - TS_N]_T^{T+\Delta T} - 2\Delta N_{N_2} [H_N - TS_N]_T^{T+\Delta T}$$

which come from equations (8) and (9) respectively, the following contributions to the free energy may be obtained:

at $T = \Delta T$,

$$(11) \quad N_N (-S_{O_N}) \Delta T + N_{N_2} (-S_{N_2}^0) \Delta T$$

and

$$(12) \quad -2\Delta N_{N_2} (-S_N^0) \Delta T + \Delta N_{N_2} (-S_{N_2}^0) \Delta T$$

equations (11) and (12) may be expressed in terms of one unknown by eliminating ΔT by means of equation (6),

$$\Delta T = +K\Delta X \quad \text{Equations (11) and (12) become}$$

$$(11A) \quad K(\Delta N_{N_2})(N_N)(-S_N^0) + K(\Delta N_{N_2})(-S_{N_2}^0)$$

$$(12A) \quad -2K(\Delta N_{N_2})^2(-S_N^0) + K(\Delta N_{N_2})^2(-S_{N_2}^0)$$

The enthalpy terms do not appear in either of the above equations because as ΔT approaches T , The enthalpy terms cancel.

at $T=T$,

using the definition $F=H-TS$

$$-2\Delta N_{N_2} (F_{N_2}^0) + \Delta N_{N_2} (F_{N_2}^0)$$

Next consider the entropy of mixing. The parabolic approximation

$$(14) \quad \Delta (X \ln X) \cong \Delta X \left[1 + \ln X + \frac{\Delta X}{X} \right]$$

will be used to calculate additional contributions to the change in free energy

The terms $R(T+\Delta T) [(N_{N_2} - \Delta N_{N_2}) \ln (N_{N_2} + \Delta N_{N_2}) - N_{N_2} \ln N_{N_2}] + R \cdot \Delta T (N_{N_2} \ln N_{N_2})$
and $R(T+\Delta T) [(N_N - 2\Delta N_{N_2}) \ln (N_N - 2\Delta N_{N_2}) - N_N \ln N_N] + R \cdot \Delta T (N_N \ln N_N)$

which come from the equations (8) and (9) respectively may be transformed by use of equation 14 into:

$$\begin{aligned} \Delta F \cong & R(T+\Delta T) (-2\Delta N_{N_2}) \left[1 + \ln N_N - \frac{2\Delta N_{N_2}}{N_N} \right] \\ & + R(N_N \ln N_N) \Delta T + R(T+\Delta T) \\ (15) & (\Delta N_{N_2}) \left[1 + \ln N_{N_2} + \frac{\Delta N_{N_2}}{N_{N_2}} \right] + \\ & R(N_{N_2} \ln N_{N_2}) \Delta T. \end{aligned}$$

The term

$$R(T + \Delta T)(-2\Delta NN_2) \left[1 + \ln NN - \frac{2\Delta NN_2}{NN} \right]$$

of equation 15 may be expanded to give:

$$RT(-2\Delta NN_2)(1 + \ln NN) \quad (15.1)$$

$$RT(-2\Delta NN_2) \left(\frac{-2\Delta NN_2}{NN} \right) \quad (15.2)$$

$$R \cdot \Delta T(-2\Delta NN_2)(1 + \ln(NN)) \quad (15.3)$$

$$R \cdot \Delta T(-2\Delta NN_2) \left(\frac{-2\Delta NN_2}{NN} \right) \quad (15.4)$$

The term

$$R(T + \Delta T)(\Delta NN_2) \left(1 + \ln NN_2 + \frac{\Delta NN_2}{NN_2} \right)$$

of equation 15 may be expanded to give:

$$RT(\Delta NN_2)(1 + \ln NN_2) \quad (15.5)$$

$$RT(\Delta NN_2) \left(\frac{\Delta NN_2}{NN_2} \right) \quad (15.6)$$

$$R \cdot \Delta T(\Delta NN_2)(1 + \ln NN_2) \quad (15.7)$$

$$R \cdot \Delta T(\Delta NN_2) \left(\frac{\Delta NN_2}{NN_2} \right) \quad (15.8)$$

The two terms

$$R(N_N \ln N_N) \Delta T \text{ and } R(N_{N_2} \ln N_{N_2}) \Delta T$$

from the equation 15 may be combined to give:

$$R(N_N \ln N_N) \Delta T + R(N_{N_2} \ln N_{N_2}) \Delta T$$

equation 15.9 may be reduced to an equation in one unknown by using equation 6 to eliminate ΔT

$$\begin{aligned} KR(\Delta N_{N_2}) (N_N \ln N_N) + KR(\Delta N_{N_2}) \\ (N_{N_2} \ln N_{N_2}) \end{aligned} \quad (15.10)$$

Terms 15.1 and 15.5 may be combined to give:

$$\begin{aligned} RT(-2 \Delta N_{N_2}) (1 + \ln N_N) + RT(\Delta N_{N_2}) \\ (1 + \ln N_{N_2}) \end{aligned} \quad (15.11)$$

Terms 15.2 and 15.6 may be combined to give:

$$\begin{aligned} RT(-2 \Delta N_{N_2}) \left(-\frac{2 \Delta N_{N_2}}{N_N} \right) + \\ RT(\Delta N_{N_2}) \left(\frac{\Delta N_{N_2}}{N_{N_2}} \right) \end{aligned} \quad (15.12)$$

Terms 15.3 and 15.7 may be combined to give:

$$R \cdot \Delta T (-2 \Delta N_N) (1 + \ln N_N) + R \cdot \Delta T (\Delta N_{N_2}) \\ (4 \ln N_{N_2}) \quad (15.13)$$

Terms 15.4 and 15.5 may be combined to give:

$$R \cdot \Delta T (-2 \Delta N_{N_2}) \left(-\frac{2 \Delta N_{N_2}}{N_N} \right) + R \cdot \Delta T \\ (\Delta N_{N_2}) \left(\frac{\Delta N_{N_2}}{N_{N_2}} \right) \quad (15.14)$$

The ΔT terms may be eliminated from equations 15.13 and 15.14 to give:

$$-2KR (\Delta N_N)^2 (1 + \ln N_N) + KR (\Delta N_{N_2})^2 \\ (1 + \ln (N_{N_2})) \quad (15.13a) \\ + 4KR \frac{(\Delta N_{N_2})^3}{N_N} + KR \frac{(\Delta N_{N_2})^3}{N_{N_2}} \quad (15.14a)$$

Finally, consider the effect of a change in the total moles of gas on the free energy. This contribution, equation 10.4, contains a term of the general form $-A(x \ln x)$ where $X = N_T$ and $X = -N_{N_2}$. Because of the minus sign, the same approximation used in the entropy of mixing contribution equation 14, will not apply here. The desired quadratic must satisfy the requirement

$$-A(x \ln x) = A(-x \ln x) \cong \text{quadratic in } \Delta X$$

The term

$$R(T + \Delta T) [N_T \ln N_T - (N_T - \Delta N_{N_2}) \\ \ln (N_T - \Delta N_{N_2})]$$

from equation 10.4 may be written as the following quadratic approximation:

$$R(T + \Delta T) \left[-(\ln N_T + 1) (\Delta N_T) + \frac{(N_{T_{MAX}} - N_T) T_{N_{T_{MAX}}} \ln \frac{N_T}{N_{T_{MAX}}} (\Delta N_{N_2})^2}{(N_{T_{MAX}} - N_T)^2} \right] \quad (17)$$

Equation 10.4 may now be written as:

$$\Delta F \leq -R(T + \Delta T) (\Delta N_{N_2}) \ln P_T + R \cdot \Delta T N_T \ln \frac{P_T}{N_T} + R(T + \Delta T) \left[-(\ln N_T + 1) (\Delta N_T) + \frac{(N_{T_{MAX}} - N_T) T_{N_{T_{MAX}}} \ln \frac{N_T}{N_{T_{MAX}}} (\Delta N_{N_2})^2}{(N_{T_{MAX}} - N_T)^2} \right] \quad (18)$$

Equation (18) may be broken up into the following free energy contributions:

$$-RT (\Delta N_{N_2}) \ln P_T \quad (18.1)$$

$$-R\Delta T (\Delta N_{N_2}) \ln P_T \quad (18.2)$$

The ΔT may be eliminated from equation 18.2 to give:

$$-KR (\Delta N_{N_2})^2 \ln P_T \quad (18.2A)$$

$$R \cdot \Delta T N_T \ln \frac{P_T}{N_T} \quad (18.3)$$

The ΔT may be eliminated from equation 18.3 to give:

$$KR (\Delta N_{N_2}) N_T \ln \frac{P_T}{N_T} \quad (18.3a)$$

$$\begin{aligned} -RT (\ln N_T + 1) \Delta N_T = \\ -RT (\ln N_T + 1) (\Delta N_{N_2}) \end{aligned} \quad (18.4)$$

$$-RAT (\ln N_T + 1) \Delta N_T \quad (18.5)$$

The ΔT may be eliminated from the equation 18.5 to give:

$$\begin{aligned} -KR (\Delta N_{N_2}) (\ln N_T + 1) \Delta N_T = \\ KR (\Delta N_{N_2})^2 (\ln N_T + 1) \end{aligned} \quad (18.5a)$$

$$\frac{RT (N_{Tmax} - N_T) + N_{Tmax} \ln \frac{N_T}{N_{Tmax}} (\Delta N_{N_2})^2}{(N_{Tmax} - N_T)^2} \quad (18.6)$$

$$R \cdot \Delta T \frac{(NT_{MAX} - NT) + NT_{MAX} \ln \frac{NT}{NT_{MAX}} (\Delta NN_2)^2}{(NT_{MAX} - NT)^2} \quad (18.7)$$

The ΔT may be eliminated from the equation (18.7) to give:

$$KR \frac{(NT_{MAX} - NT) + NT_{MAX} \ln \frac{NT}{NT_{MAX}} (\Delta NN_2)^3}{(NT_{MAX} - NT)^2} \quad (18.7a)$$

The equations developed thus far can be represented by the following formula

$$\Delta F \leq \sum_j [A_j \Delta x_j + B_j \Delta x_j^2 + C_j \Delta x_j^3] \quad (19)$$

The next step is to group all of the equations into sets

having ΔN_{N_2} , $(\Delta N_{N_2})^2$, and $(\Delta N_{N_2})^3$ as factors.

The following group of equations have (ΔN_{N_2}) as a factor, and are equal to A_j

$$K(N_N)(-S_N^0) + K(N_{N_2})(-S_{N_2}^0) \quad (11a)$$

$$KR(N_N \ln N_N) + KR(N_{N_2} \ln N_{N_2}) \quad (15.10)$$

$$-2(FN^0) + (FN_2^0) \quad (13)$$

$$-2RT(1 + \ln N_N) + RT(1 + \ln N_{N_2}) \quad (15.11)$$

$$-RT(\ln N_T + 1) \quad (18.4)$$

$$-RT \ln P_T \quad (18.1)$$

$$+ KRNT \ln \frac{P_T}{N_T} \quad (18.3a)$$

The next group of equations have $(\Delta N_{N_2})^2$ as a factor, and are equal to B_j

$$\frac{4RT}{N_N} + \frac{RT}{N_{N_2}} \quad (15.2)$$

$$-2K(-S_N^0) + K(-S_{N_2}^0) \quad (12a)$$

$$-2KR(1 + \ln N_N) + KR(1 + \ln N_{N_2}) \quad (15.13a)$$

$$-KR \ln P_T \quad (18.2a)$$

$$\frac{+RT(N_{TMAX} - N_T) + N_{TMAX} \ln \frac{N_T}{N_{TMAX}}}{(N_{TMAX} - N_T)^2} \quad (18.6)$$

The last group of equations have $(\Delta N_{N_2})^3$ as a factor, and are equal to 0.

$$\frac{4KR}{N_N} + \frac{KR}{N_{N_2}} \quad (15.14a)$$

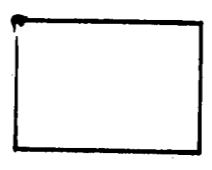
$$\frac{+KR(N_{TMAX} - N_T) + N_{TMAX} \ln \frac{N_T}{N_{TMAX}}}{(N_{TMAX} - N_T)^2} \quad (18.7a)$$

Now that the factors A_j , B_j , C_j , are known, the value of ΔX which minimizes ΔF may be found by differentiating equations 19 and setting the derivative equal to equation.

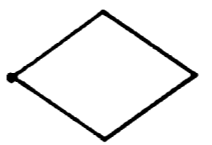
$$\Delta X = \frac{-B_j + \sqrt{(B_j)^2 - 3A_j C_j}}{3C_j}$$

Thus, a conservative approximation has been developed which can be solved directly to give ΔX . In order to maintain the mass balances, the concentration of any specie cannot become negative. At the same time, the concentration cannot exceed the maximum defined by the mass balances. These two restrictions serve as limits for the values of X found from the solution of the cubes. As equilibrium is approached, the approximate solution comes closer to and finally coincides with the rigorous evaluation of composition, temperature, and free energy.

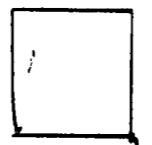
SYMBOLS USED IN BLOCK DIAGRAM



A rectangular box indicates any processing operation except a decision.



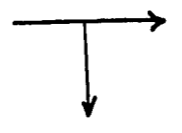
A diamond indicates a decision. The lines leaving the decision box are labeled with the decision result which causes each path to be followed.



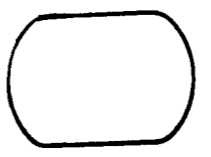
A square indicates a starting or stopping point of a program.



A small circle indicates a connection between two points in a block diagram.



Arrows indicate the direction of flow through the diagram.

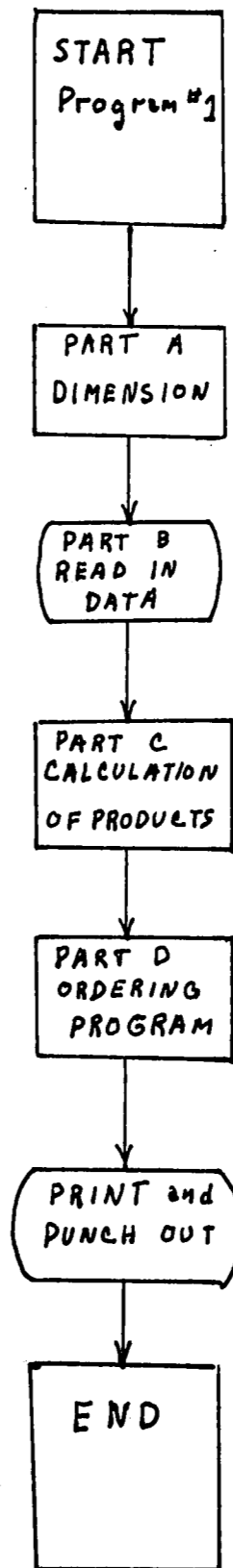


An oval box indicates an input or output operation.

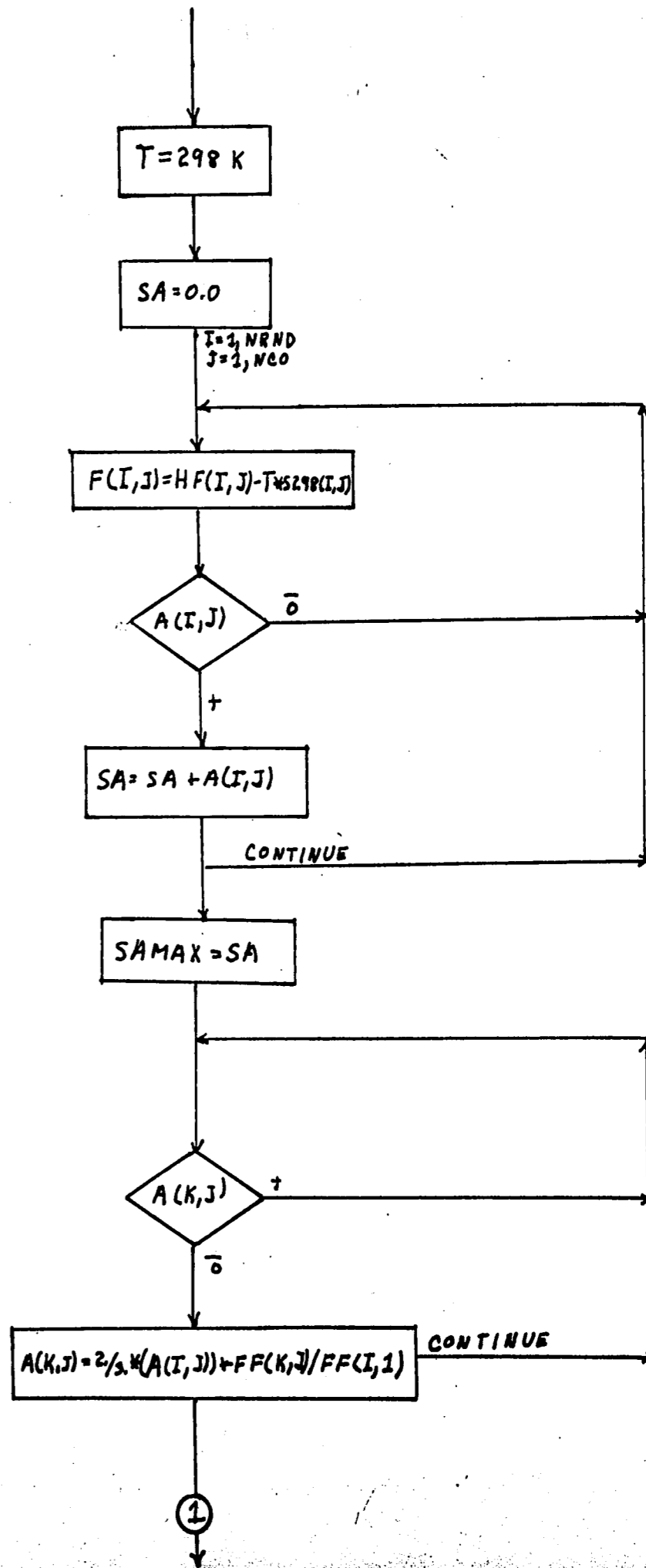
22

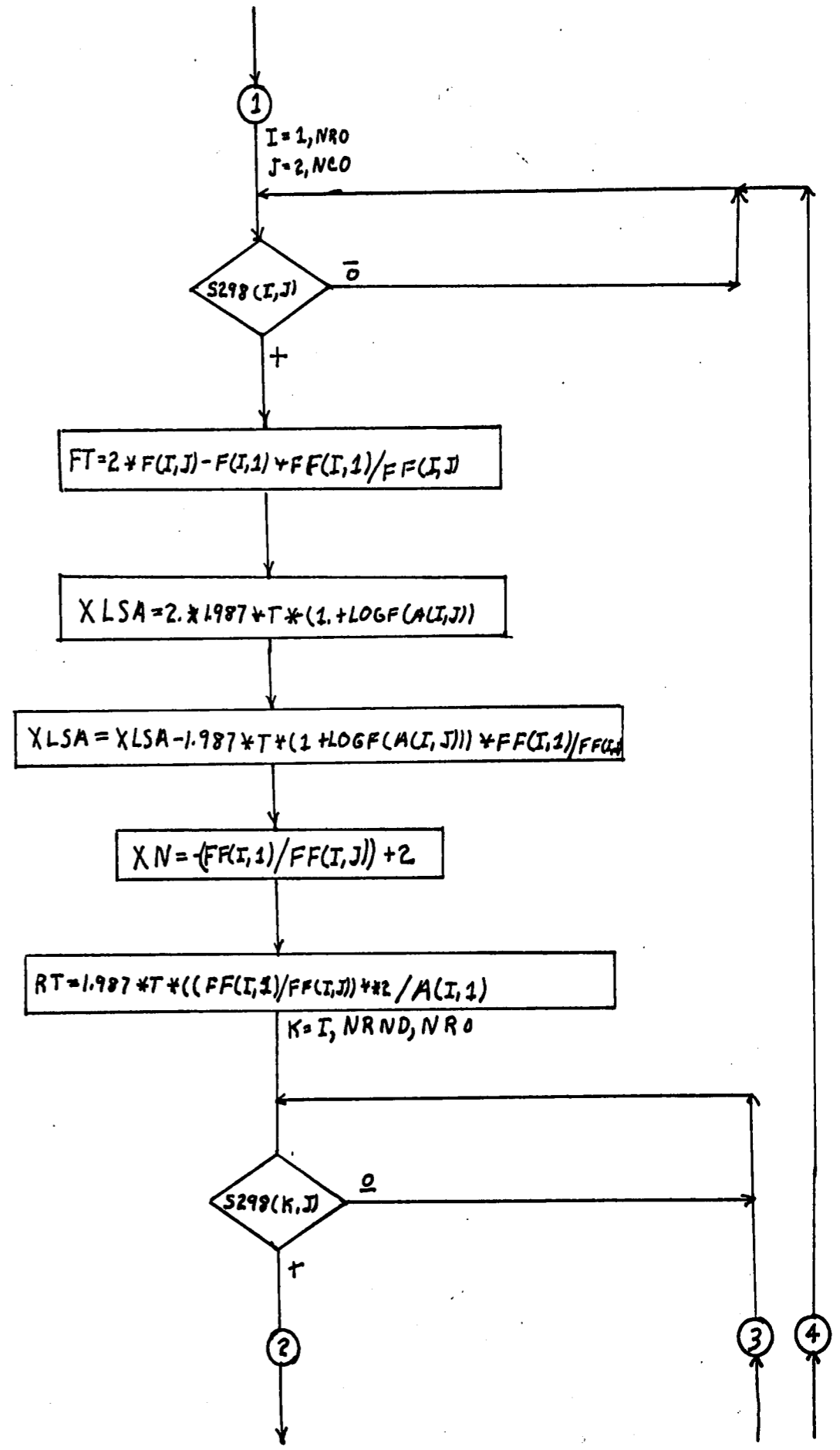
BLOCK DIAGRAM FOR THE MINIMIZATION OF FREE ENERGY

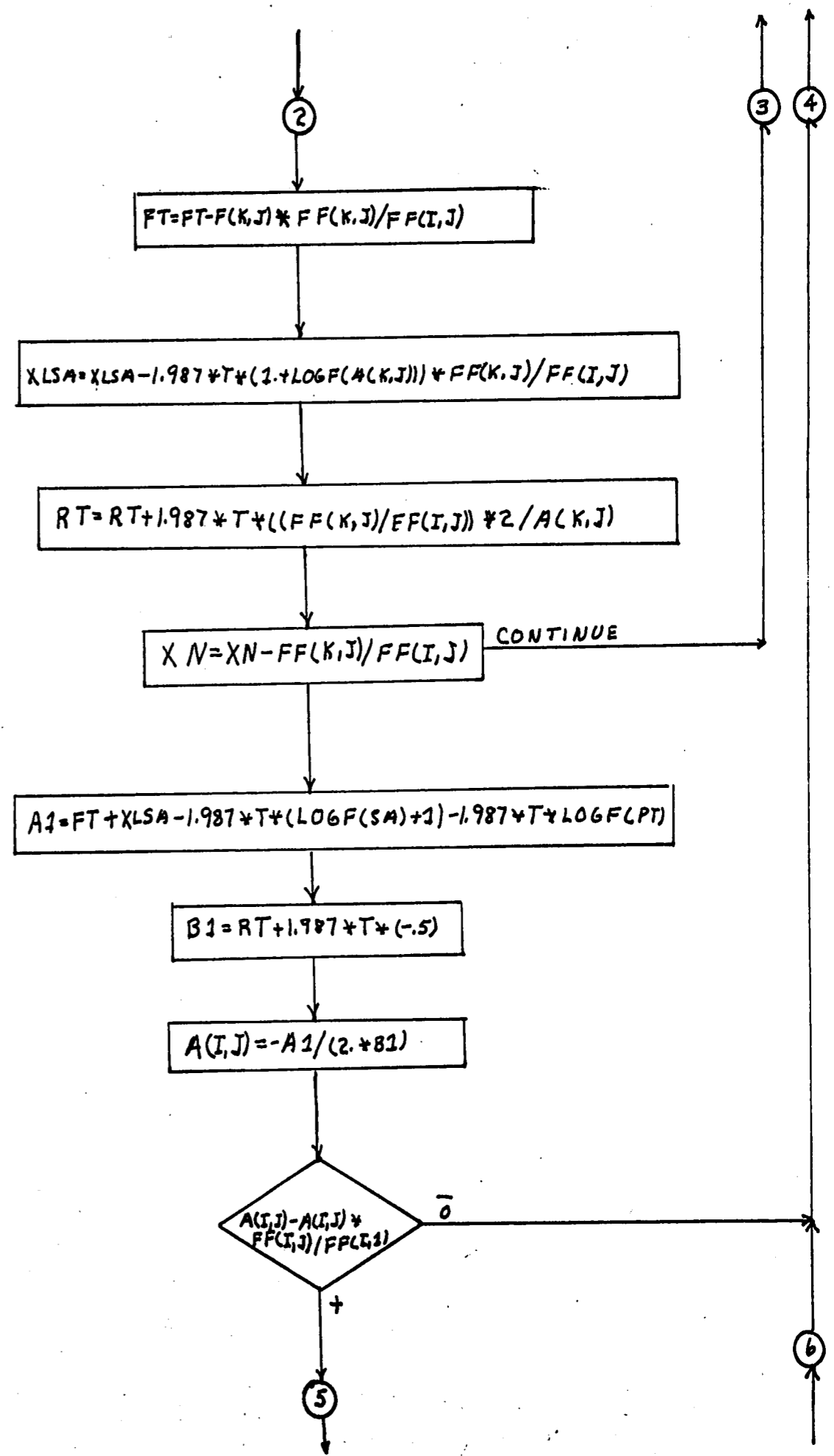
Program One

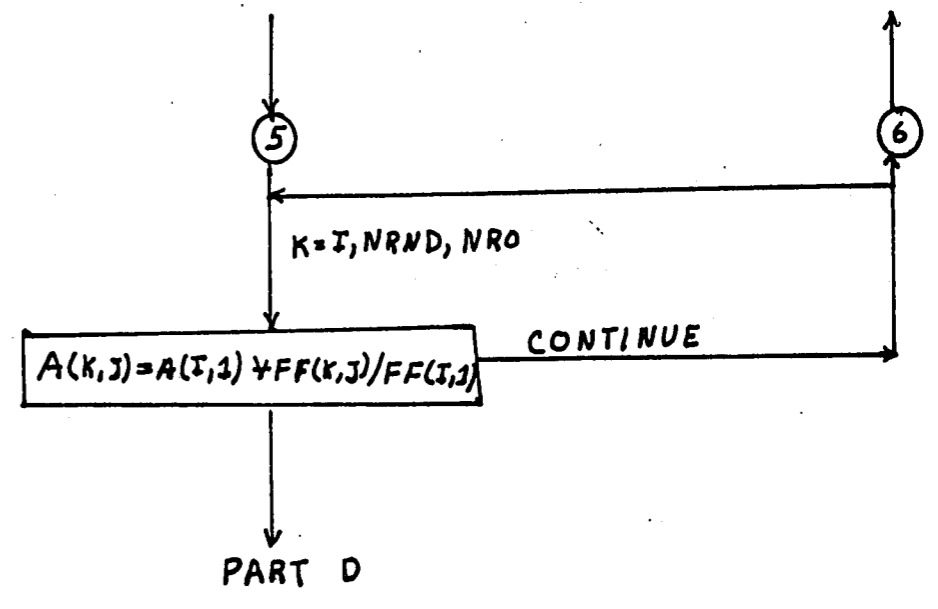


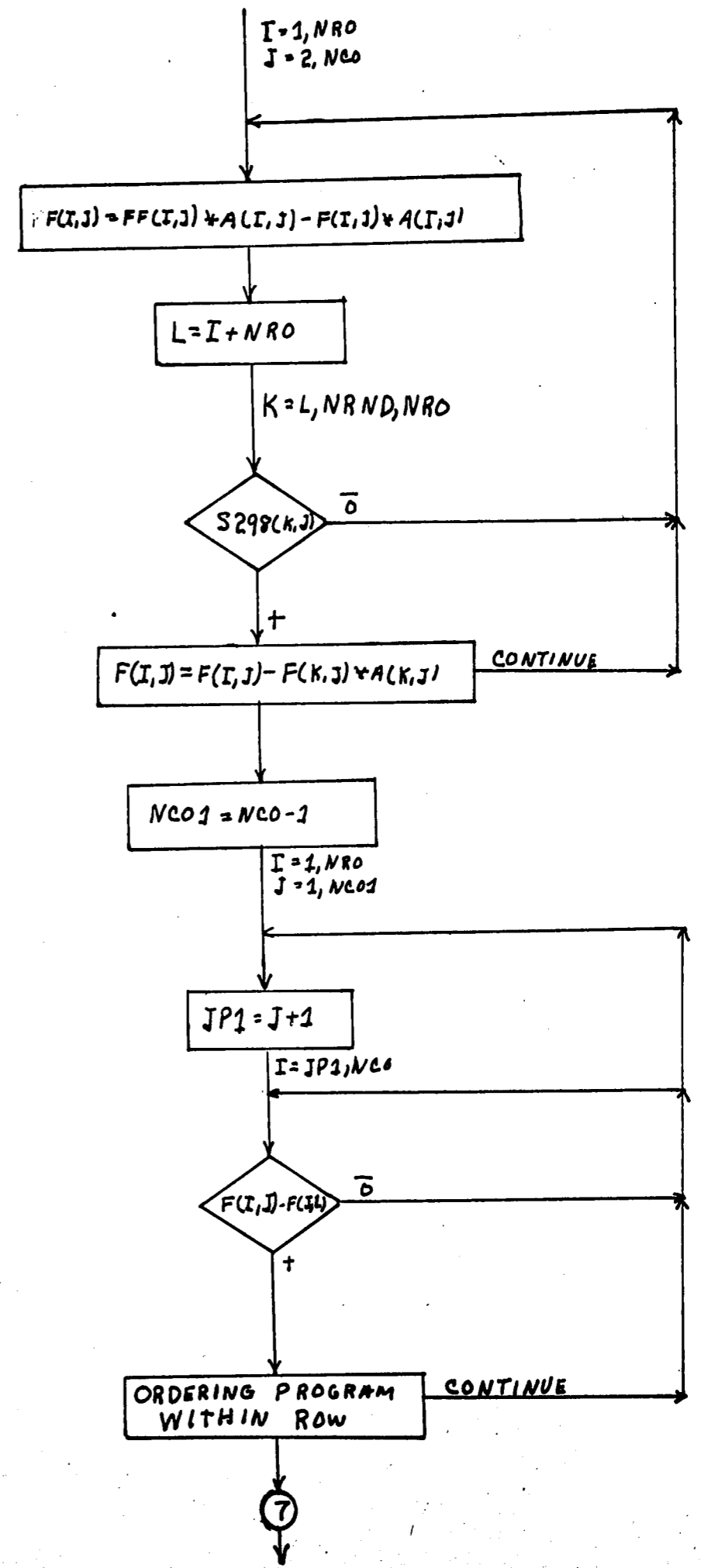
Part 0

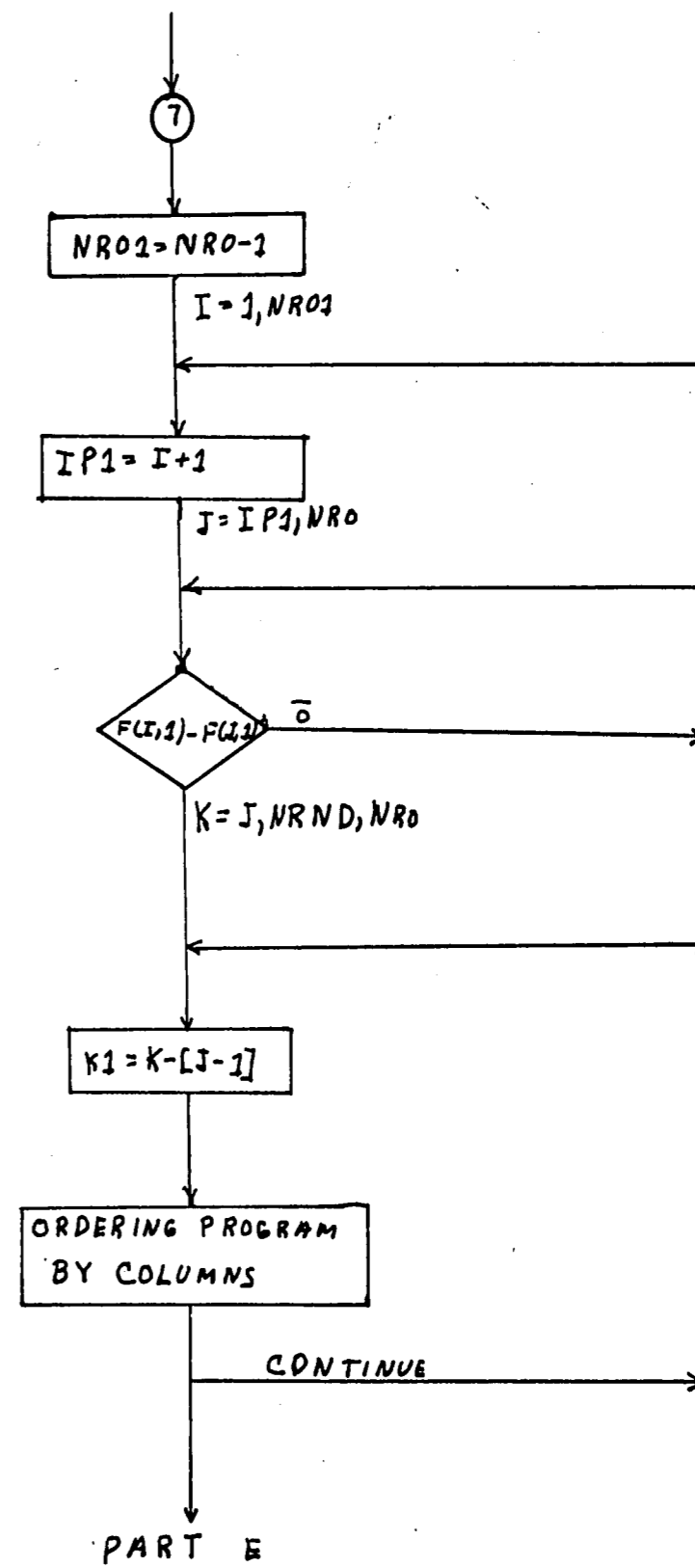




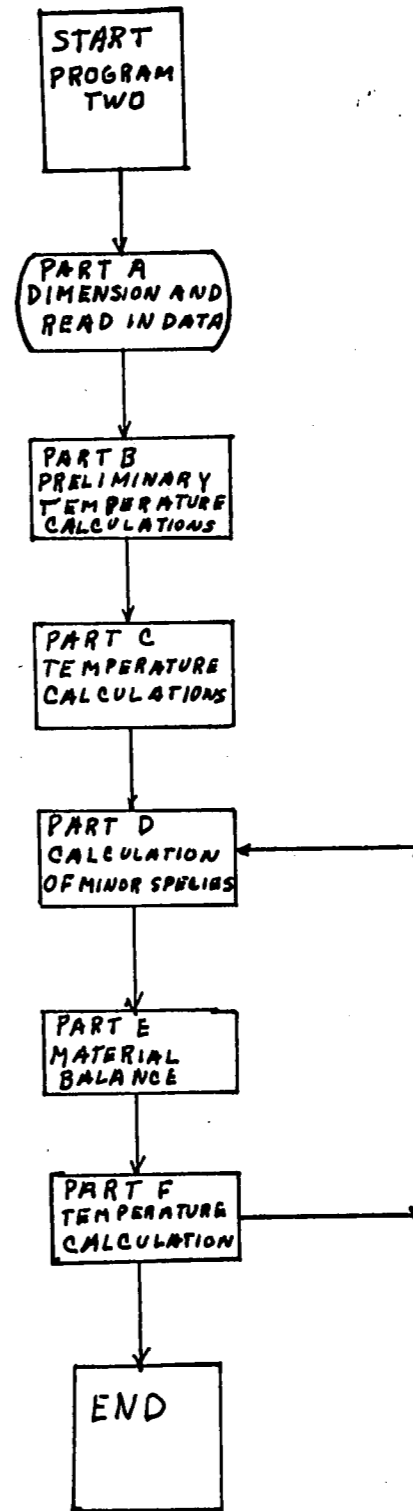




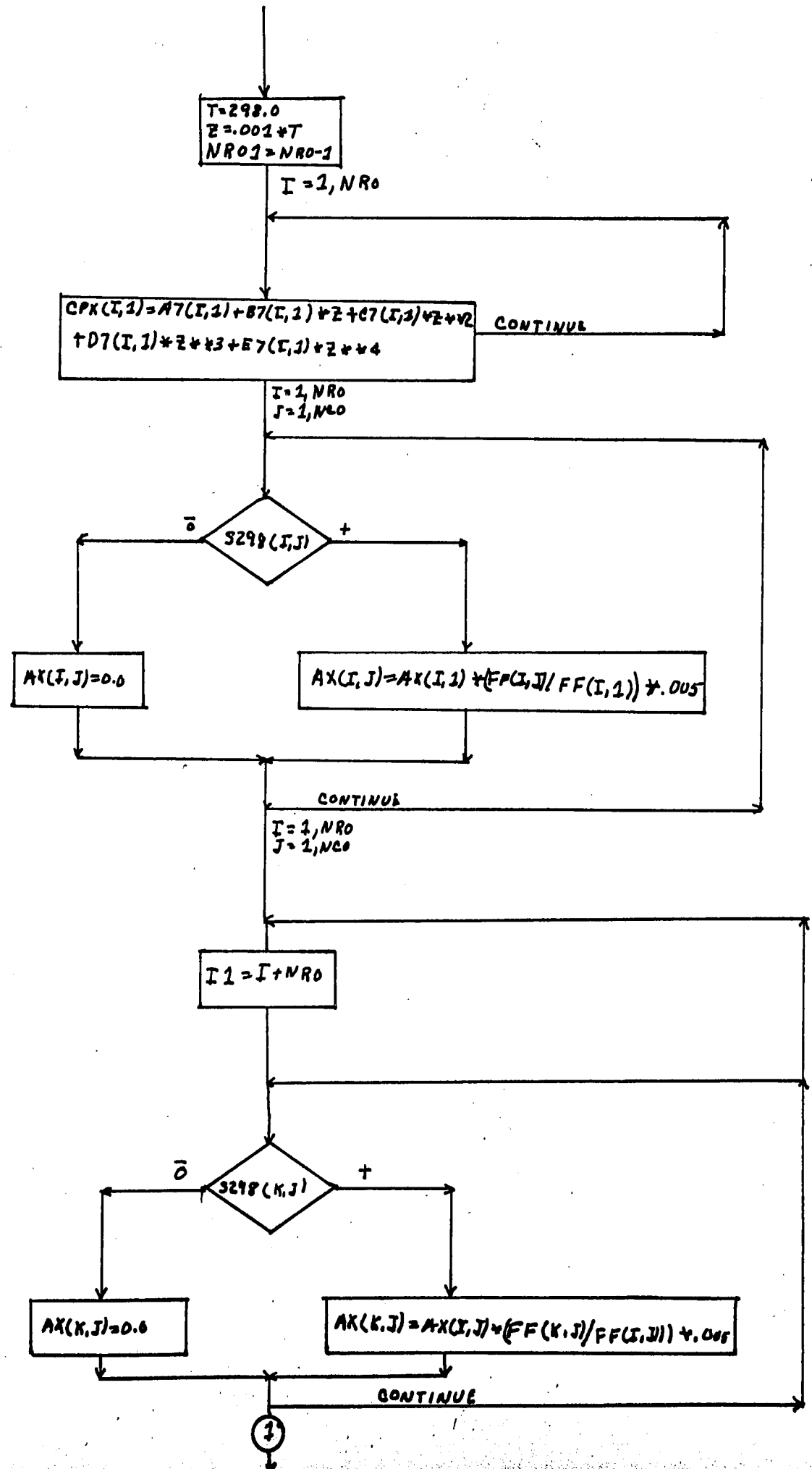


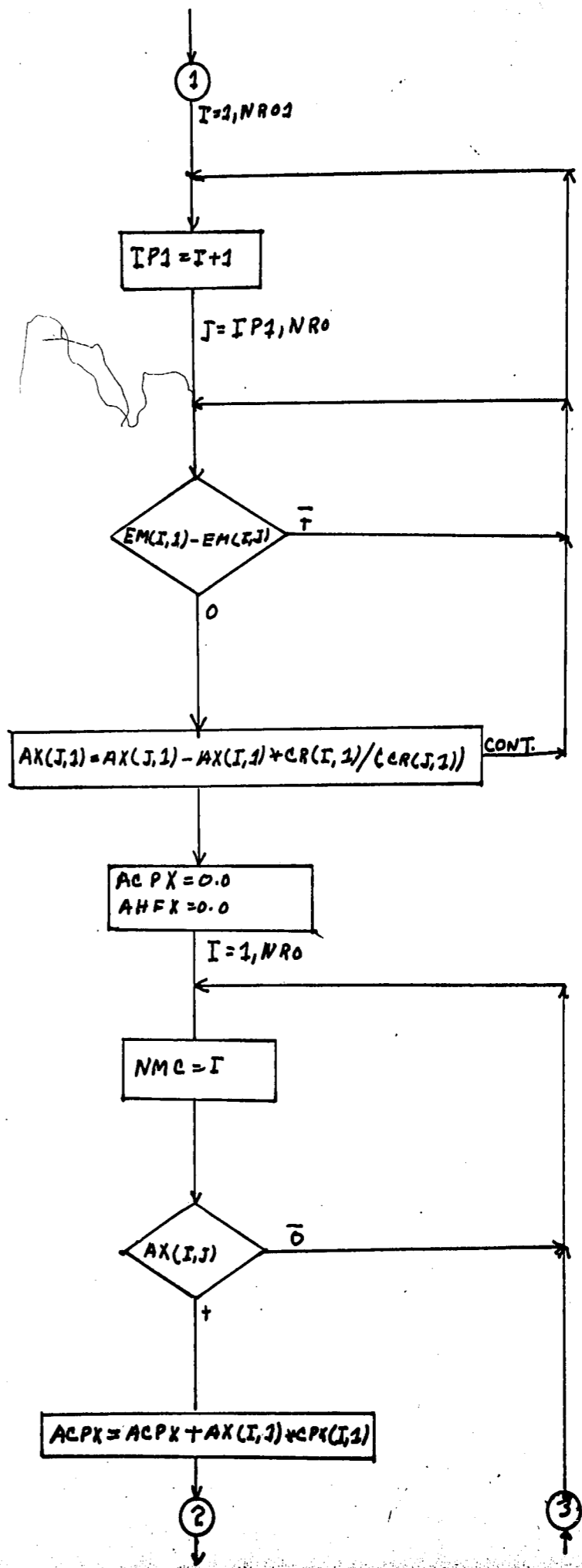


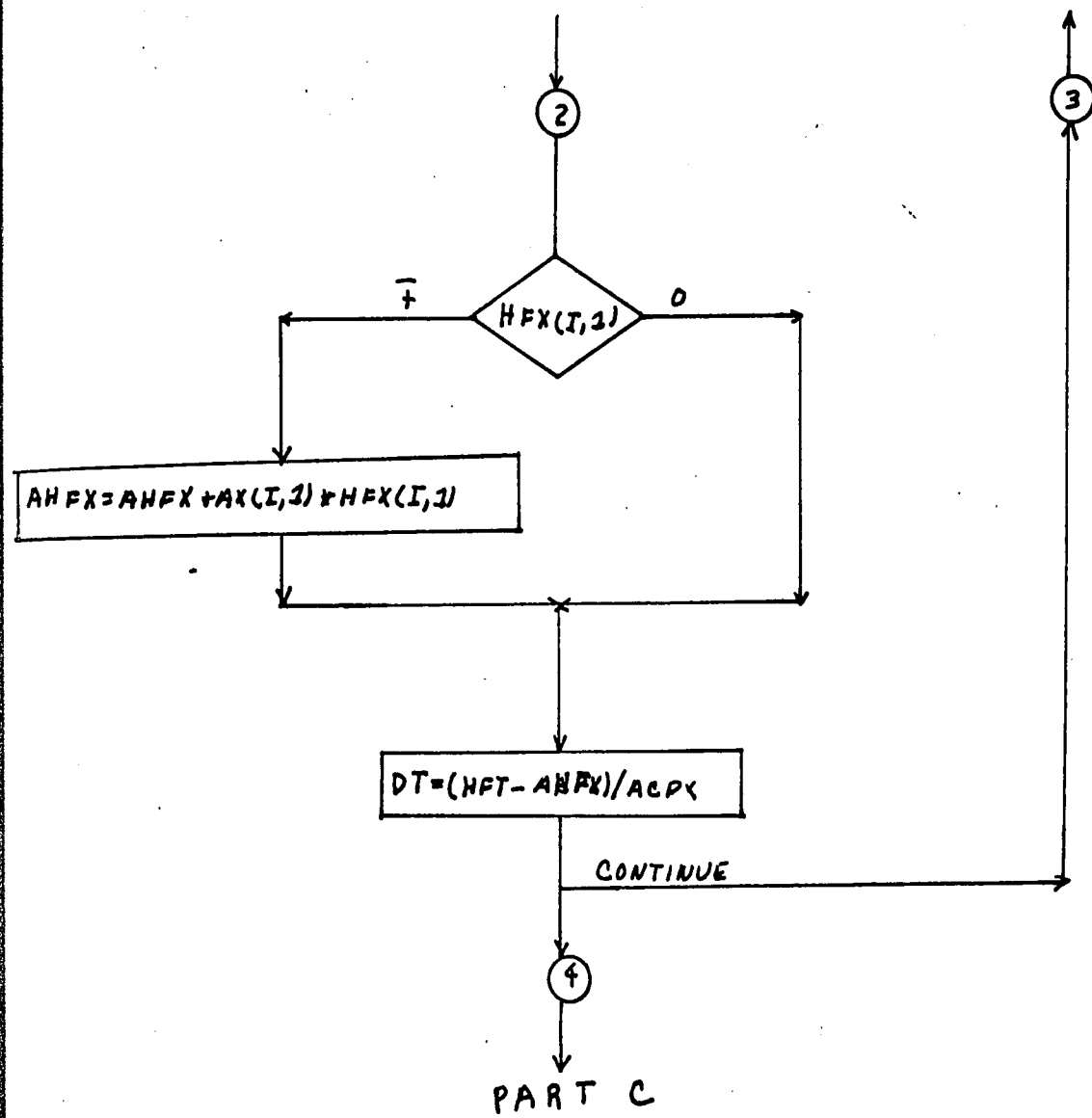
Program Two



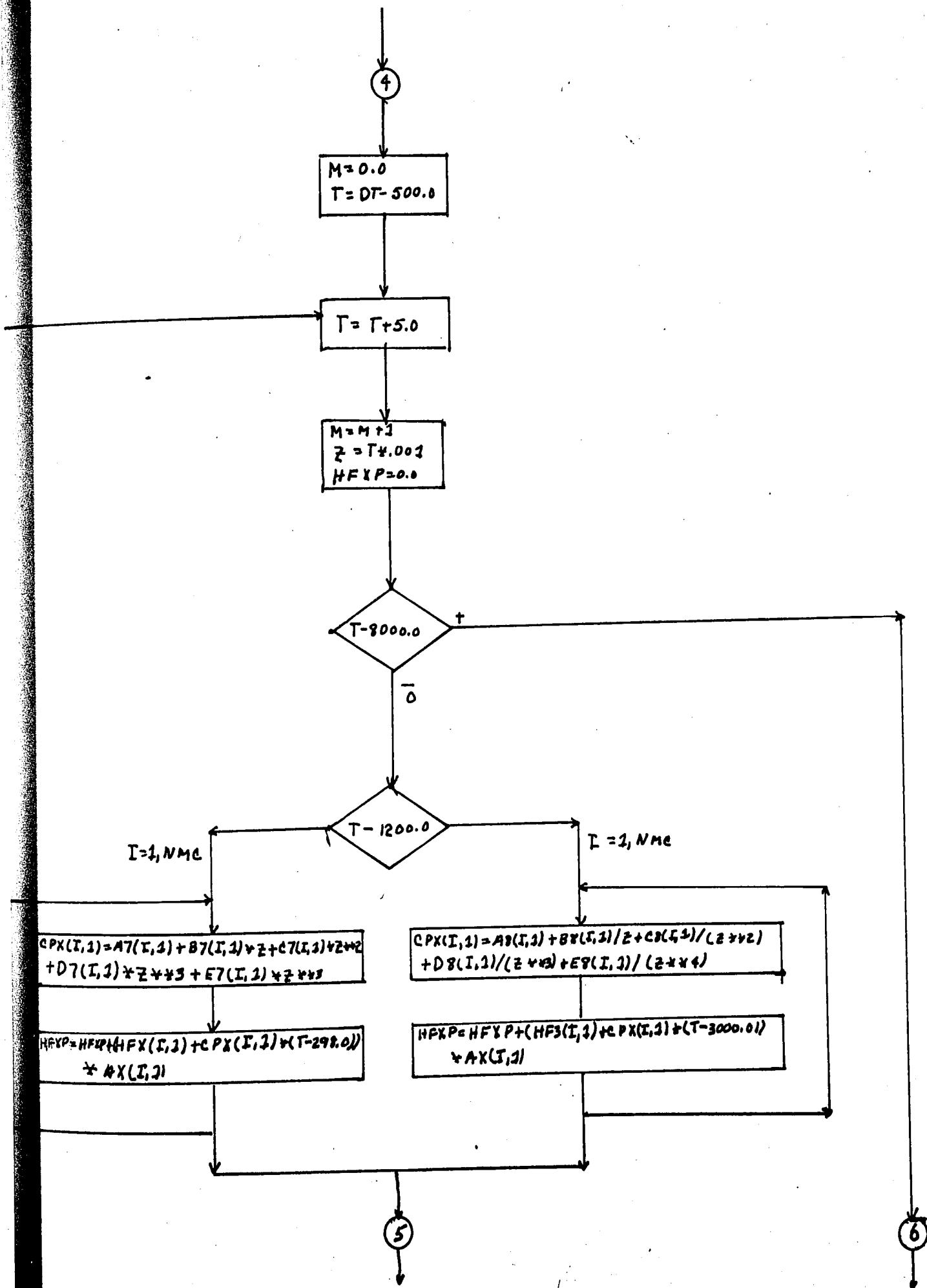
Part B

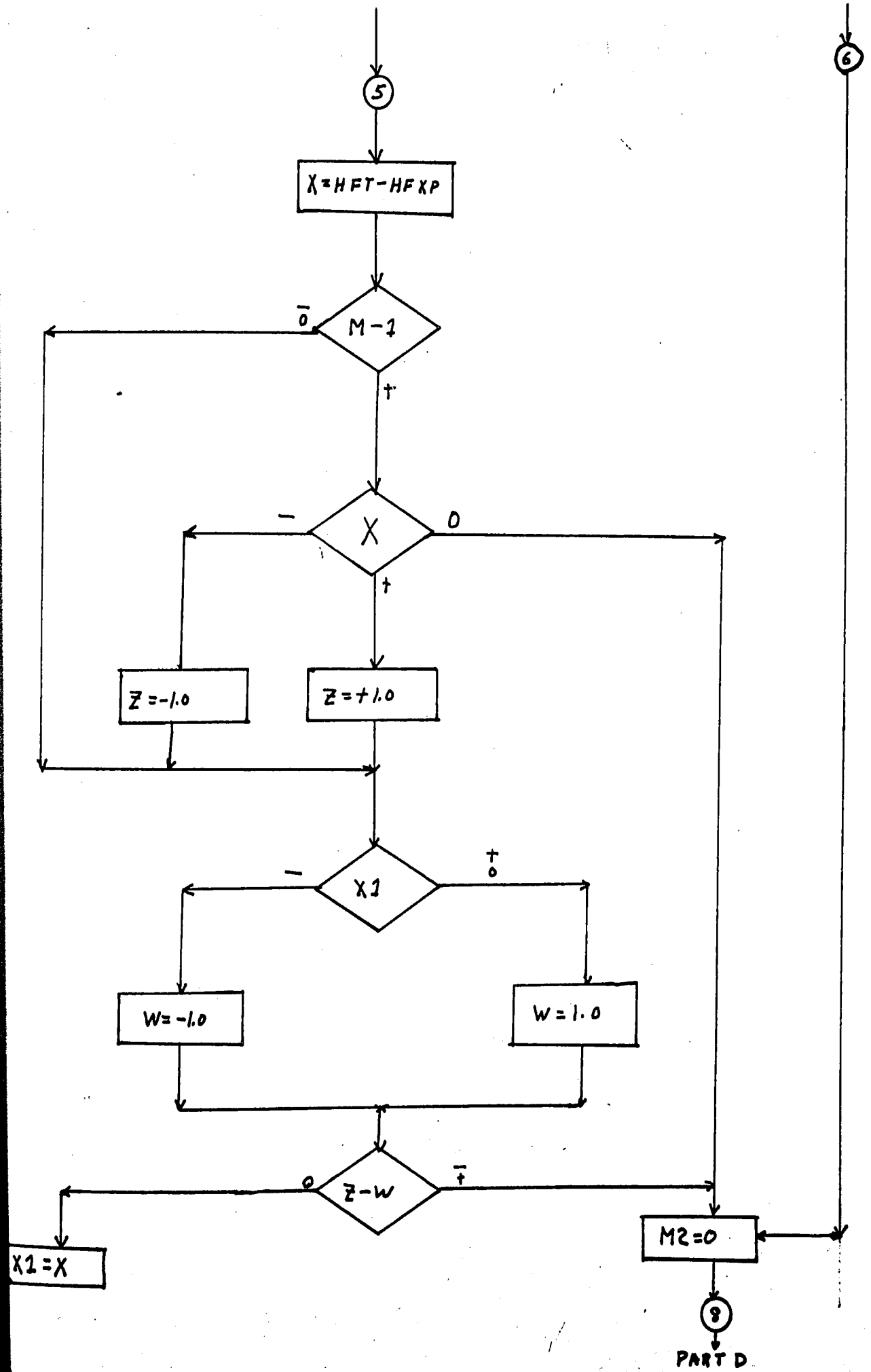




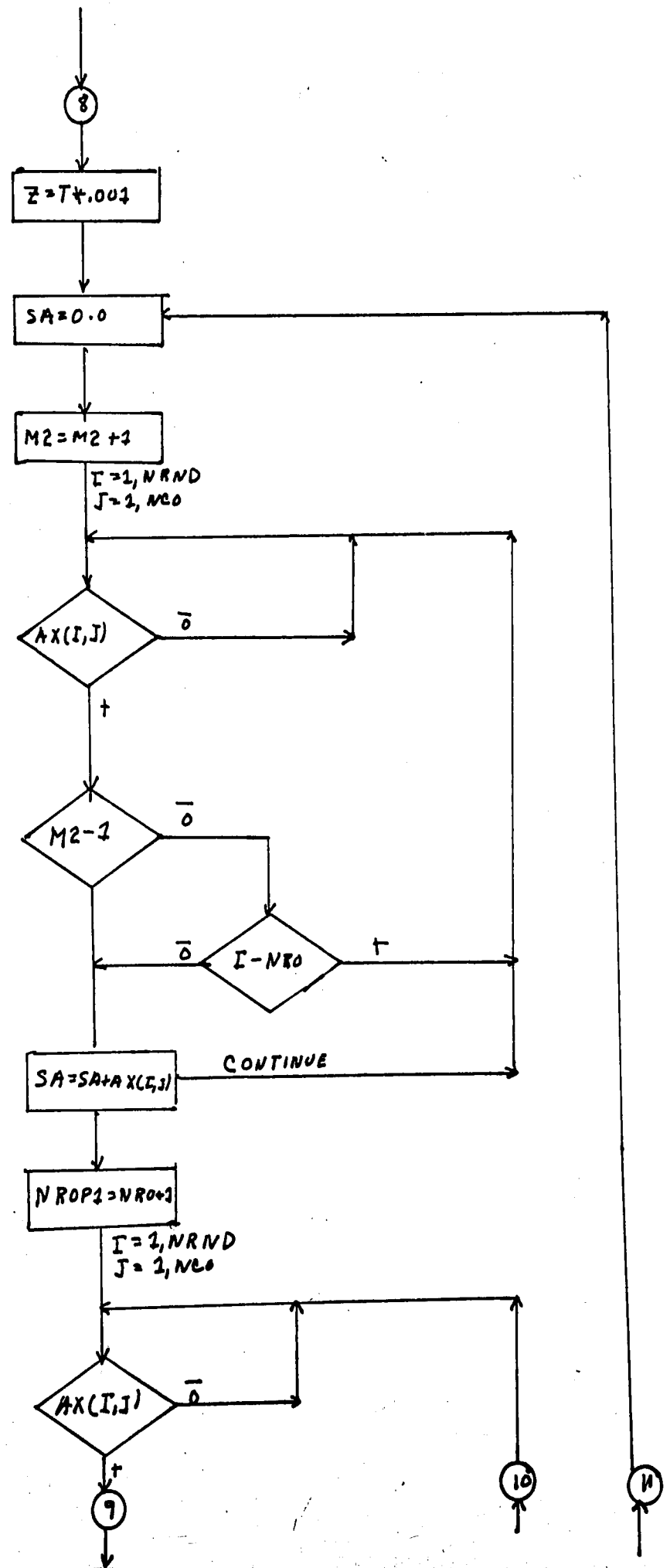


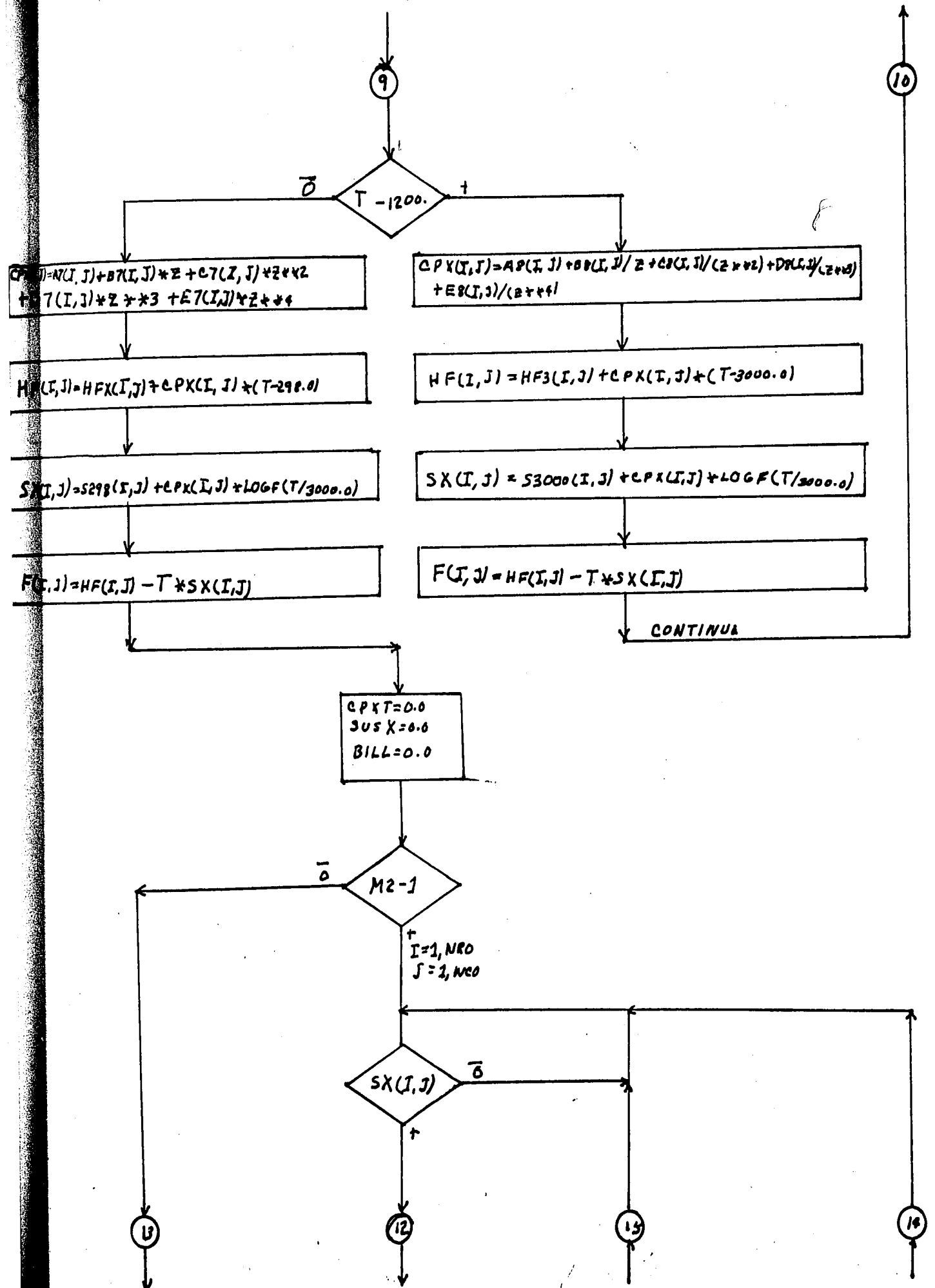
Part C

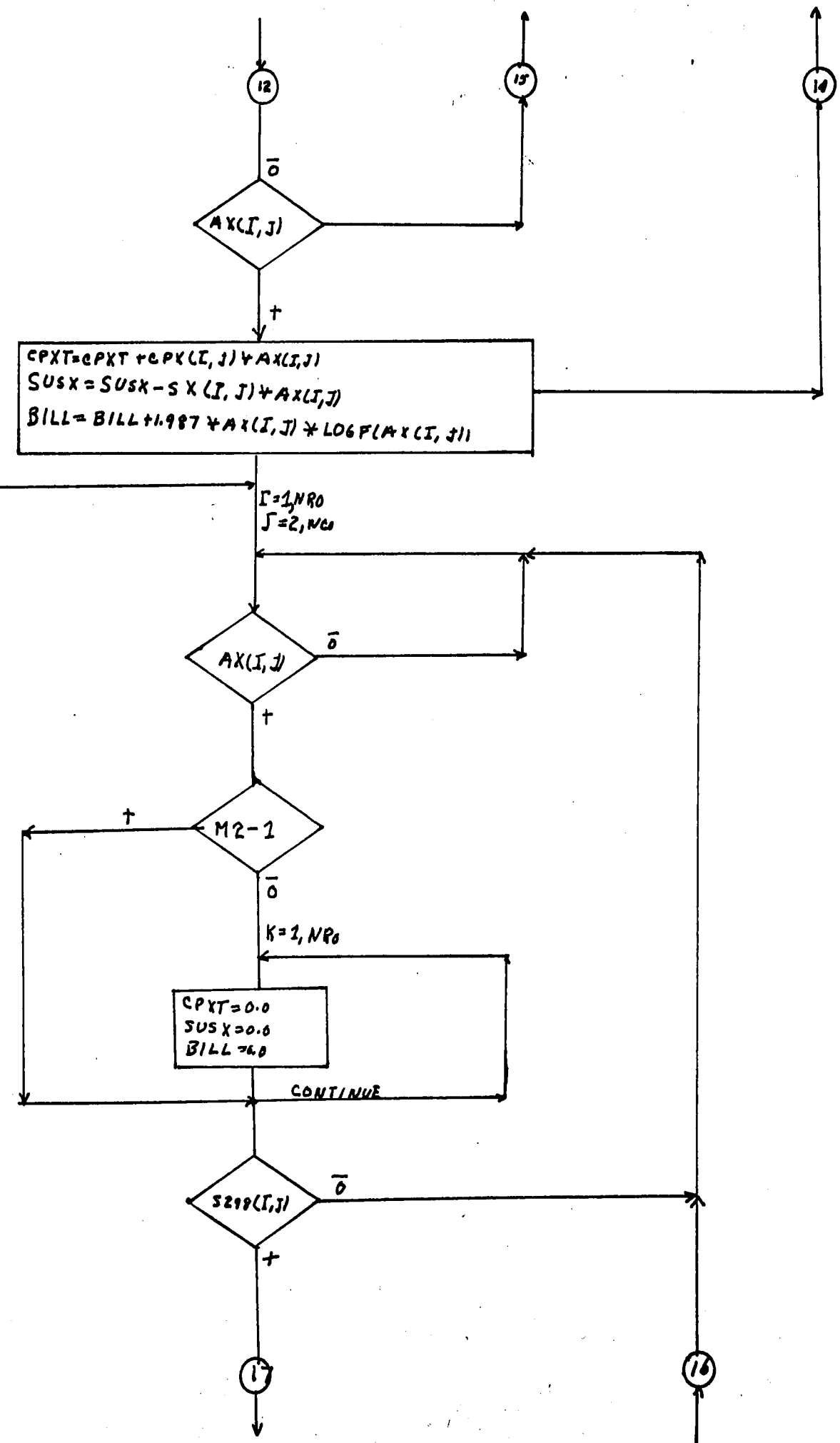


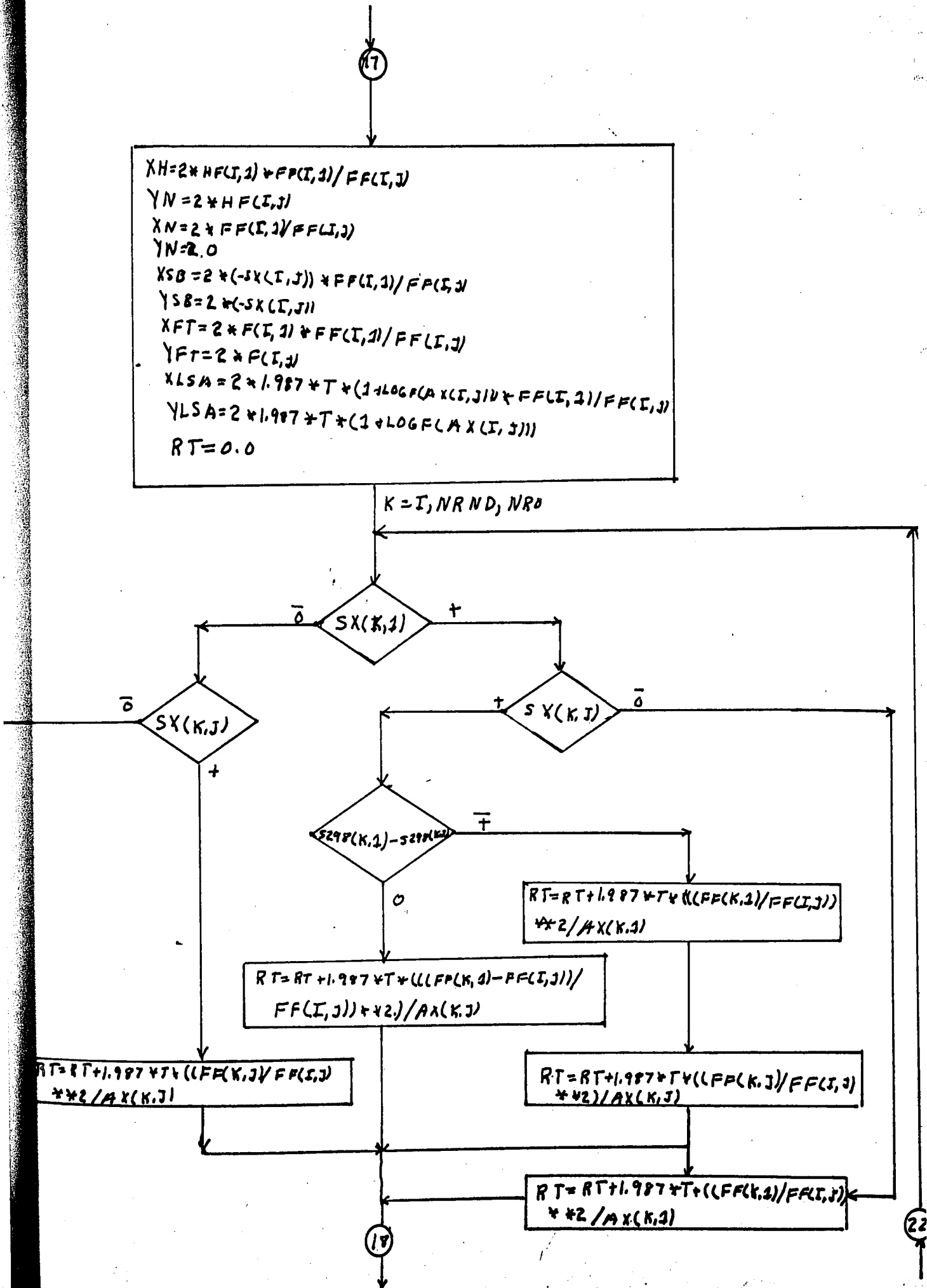


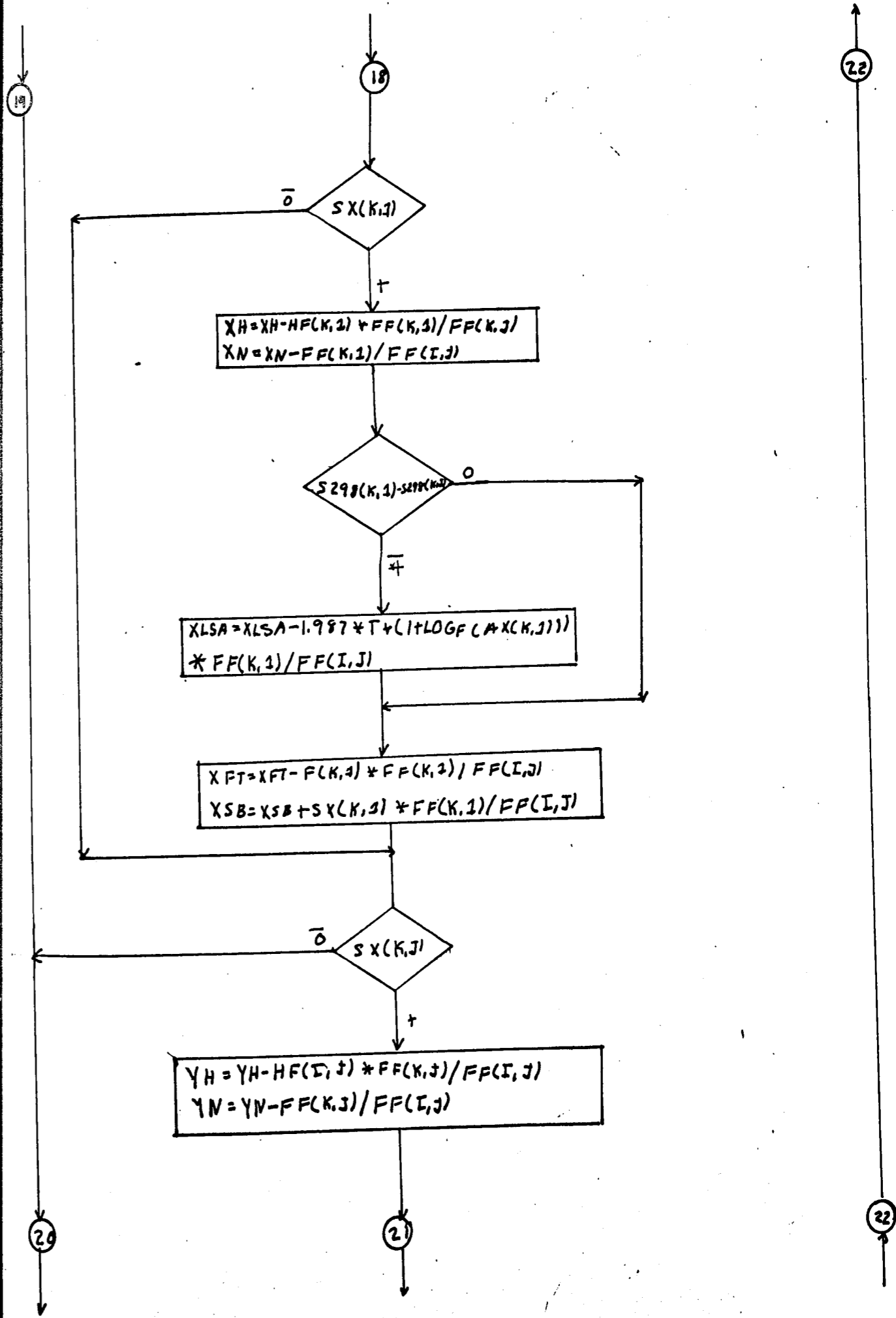
Part D.

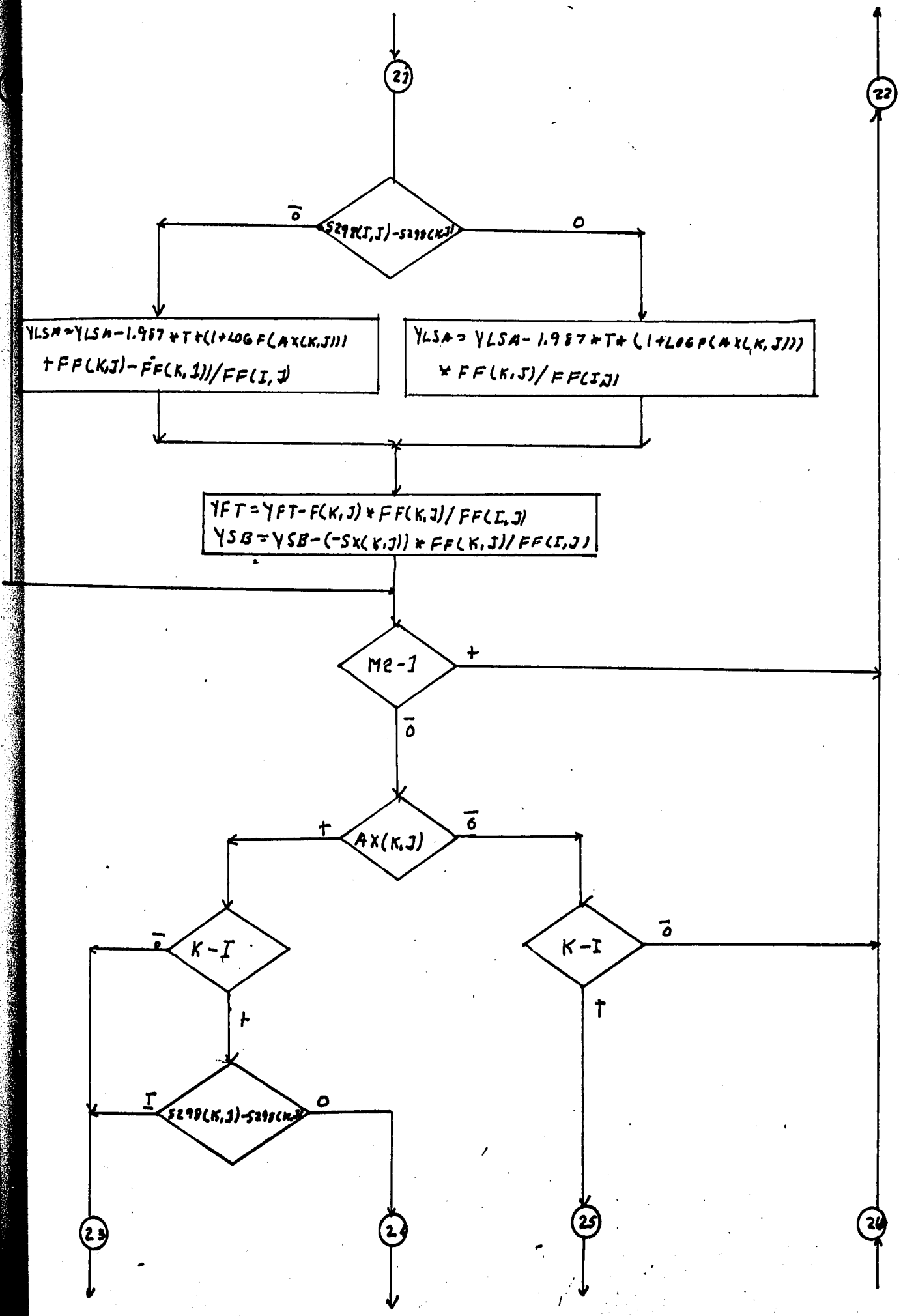


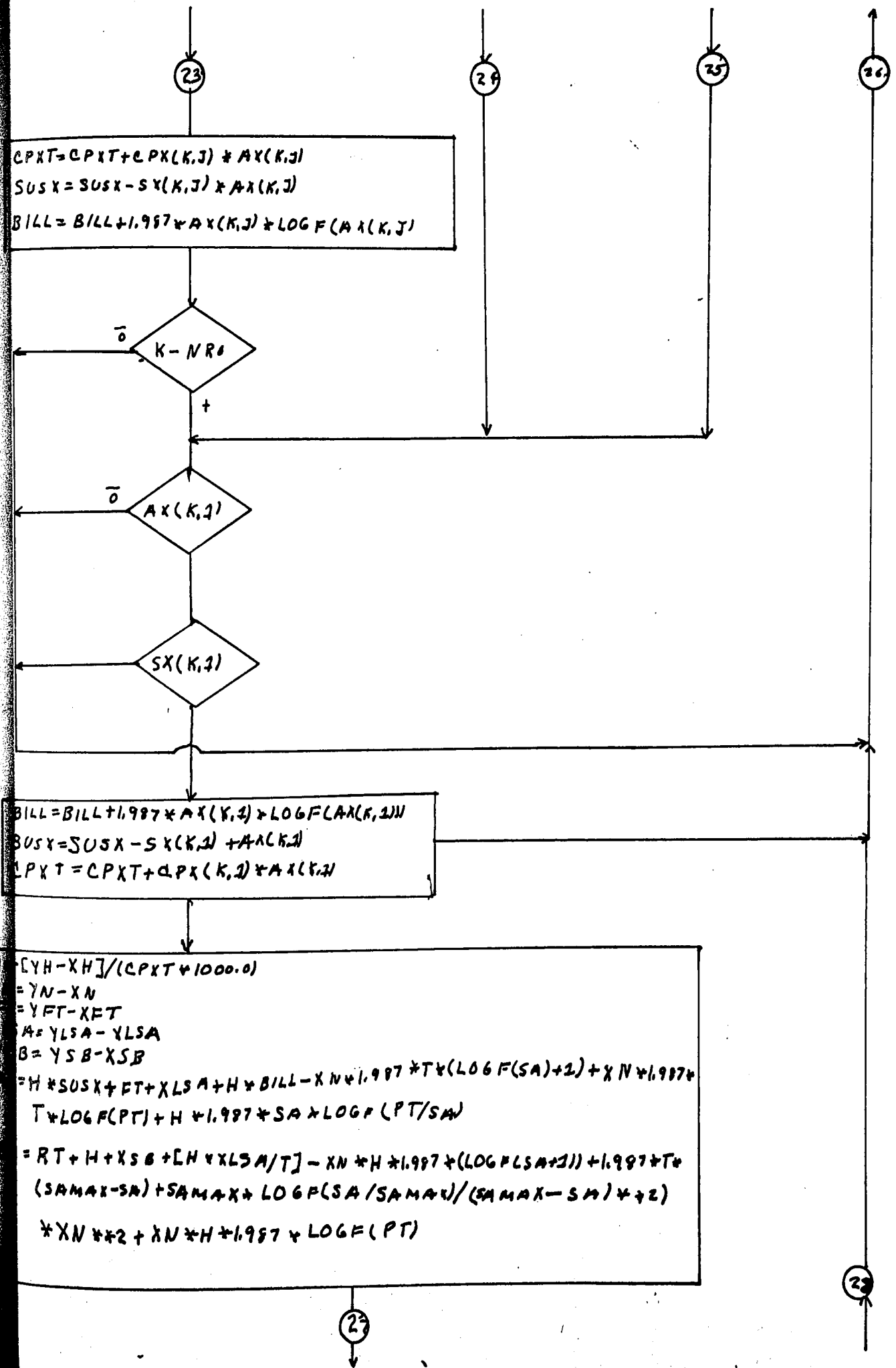


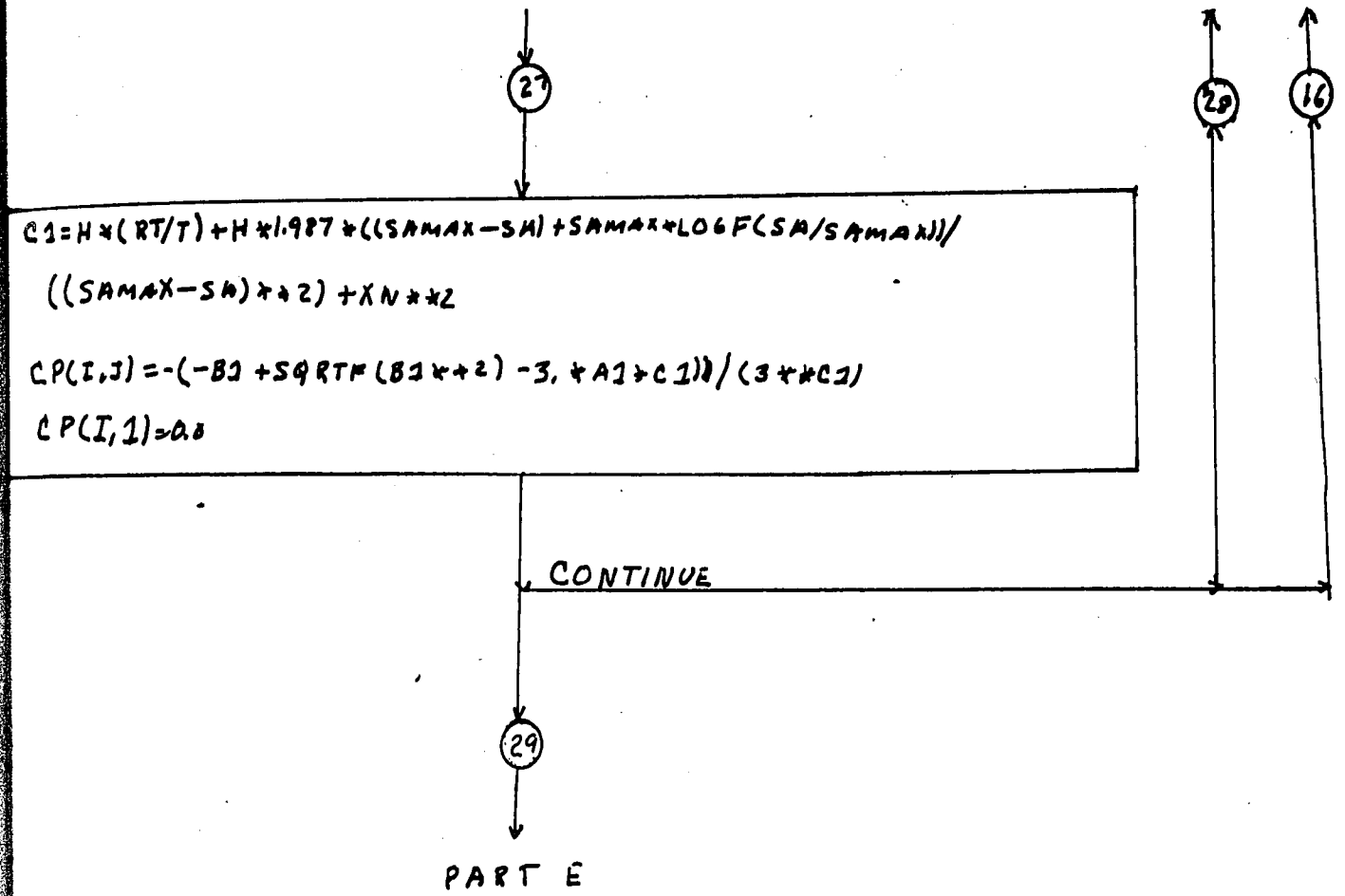




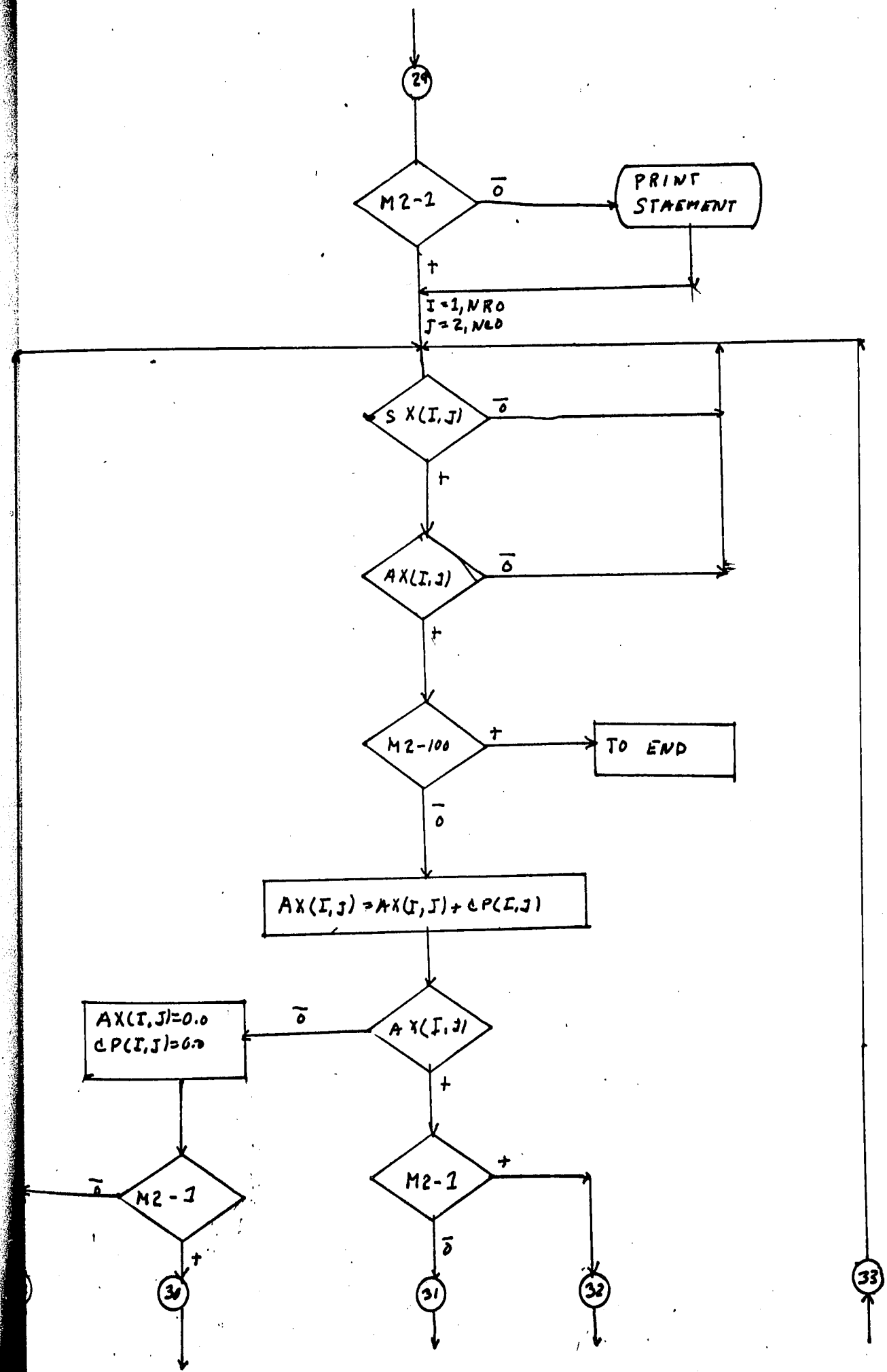


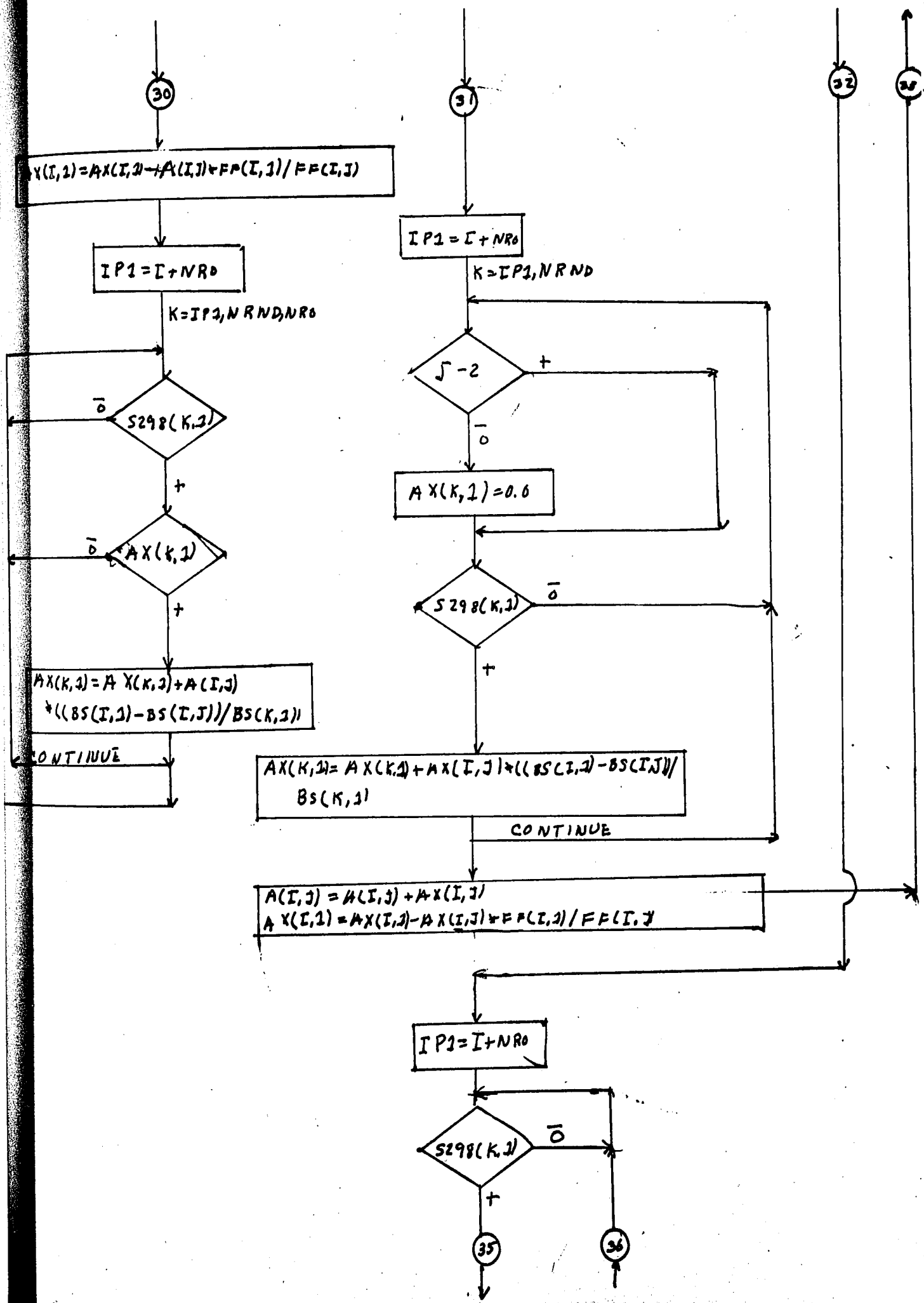


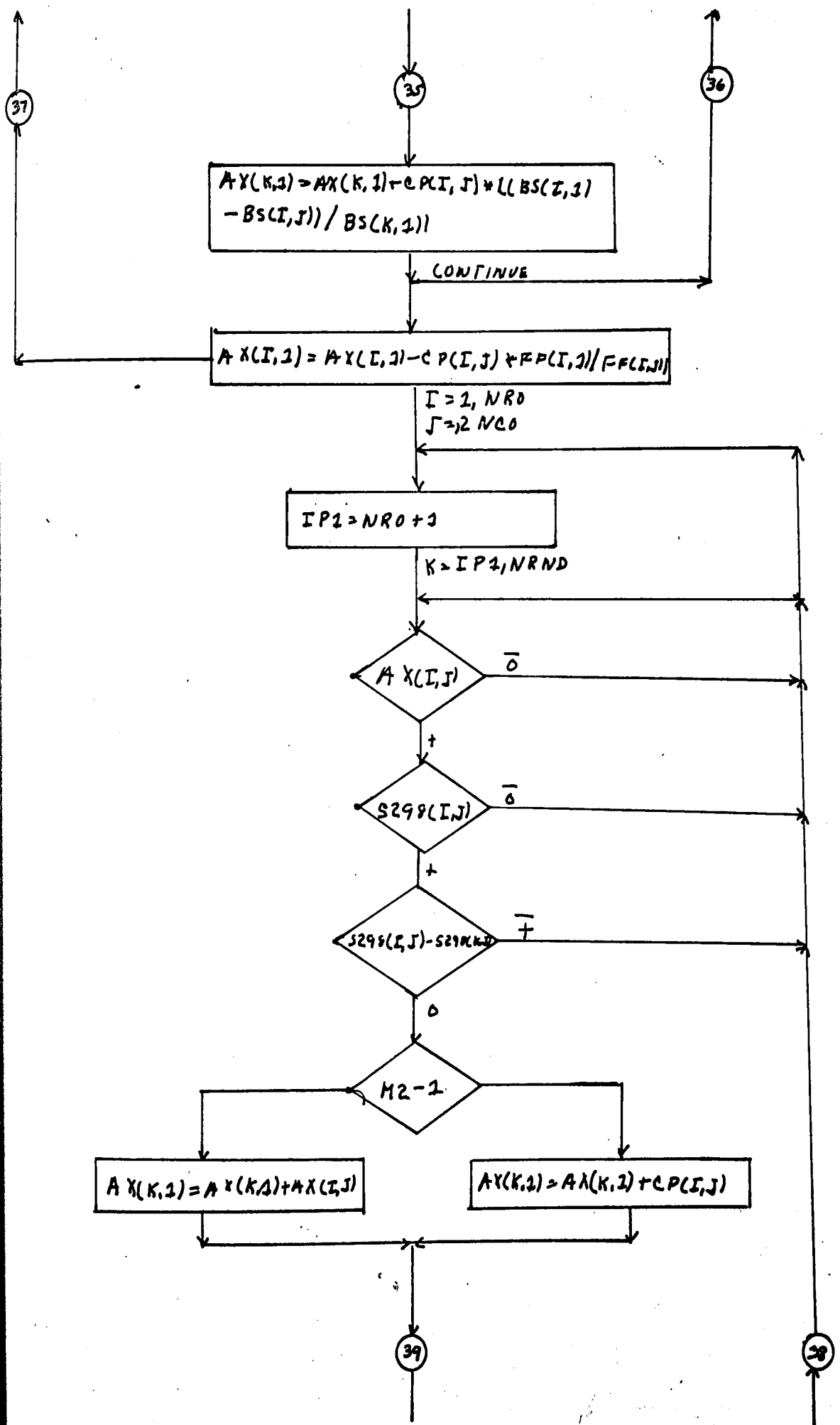


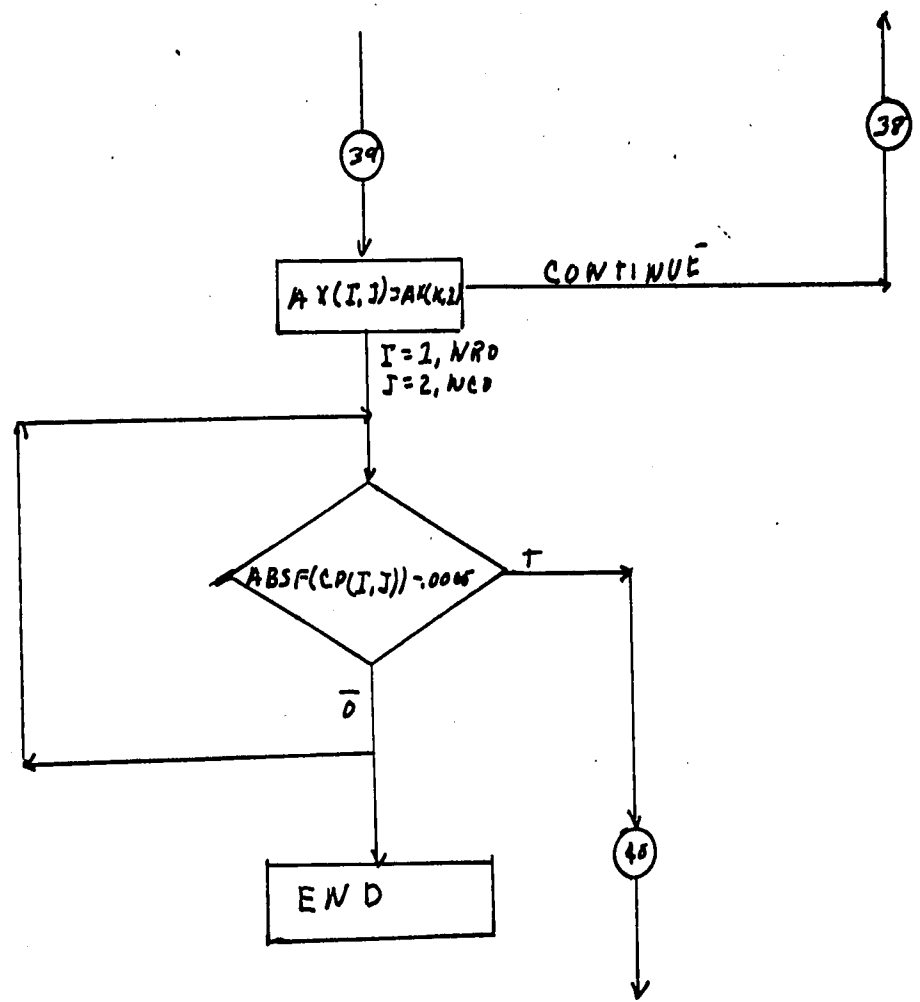


Part E

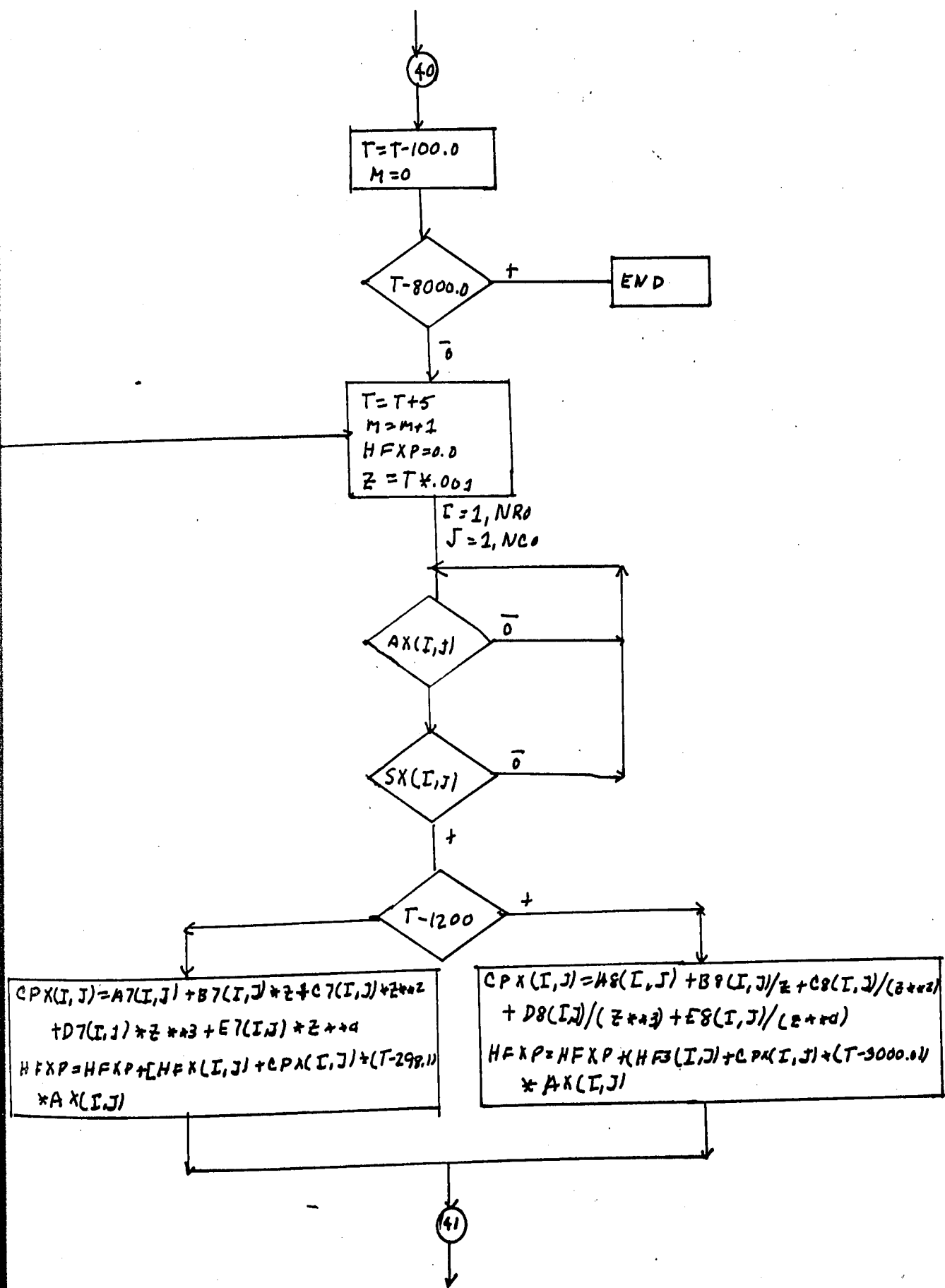


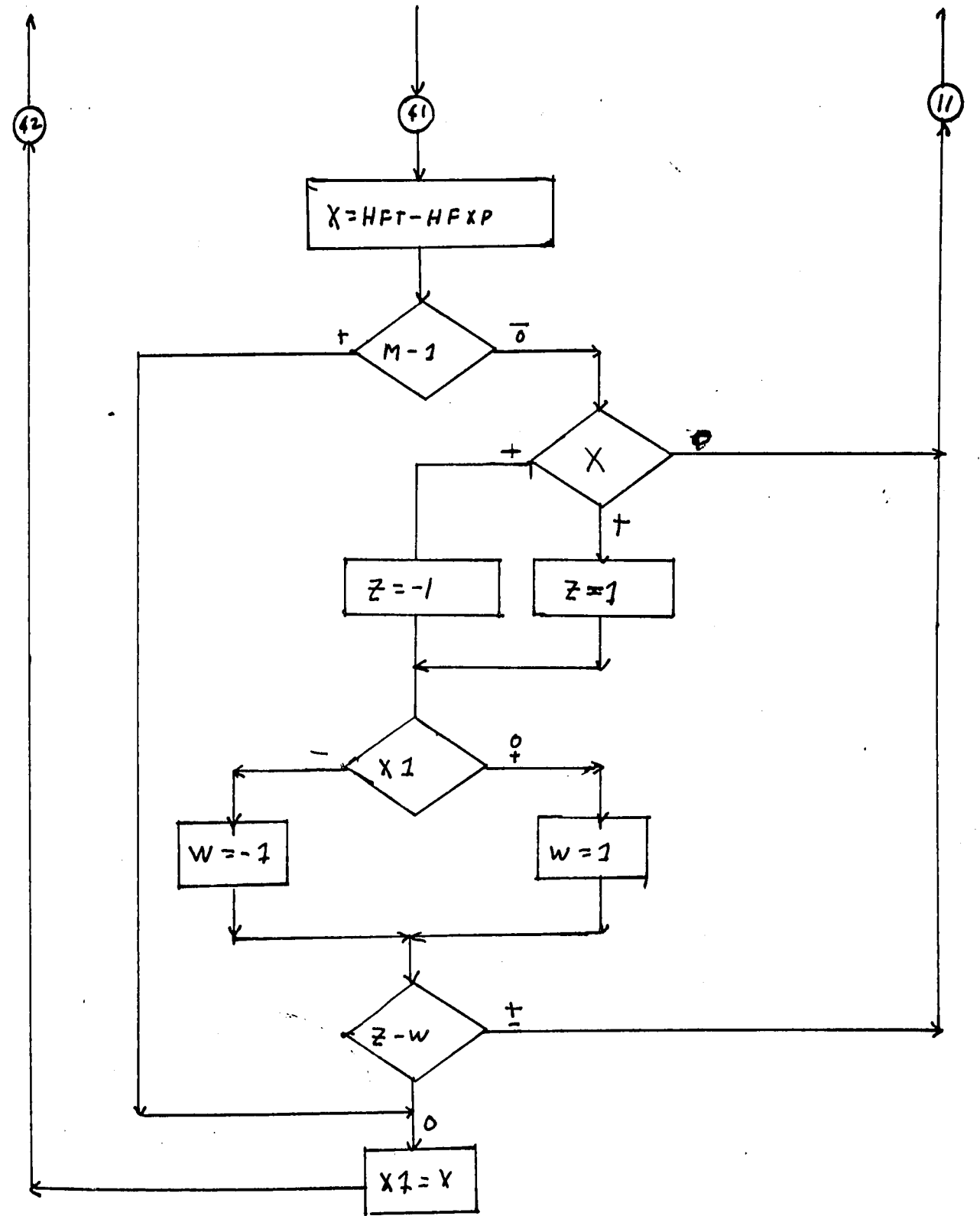






Part F





PROGRAM ONE

A

FOLLOWING DIMENSION STATEMENTS ARE NEEDED FOR ALL SUBSCRIPTED VARIABLES USED IN THE PROGRAM. THE DIMENSION STATEMENTS ARE THE SAME FOR EVERY PROGRAM AND DO NOT HAVE TO BE CHANGED.

```

DIMENSION E(6,4),A(6,4),AX(6,4),HF(6,4),HFX(6,4),S298(6,4)
DIMENSION S3000(6,4),SX(6,4),CPX(6,4),FF(6,4),A7(6,4),B7(6,4)
DIMENSION C7(6,4),D7(6,4),E7(6,4),A8(6,4),B8(6,4),C8(6,4),B8T(6,4)
DIMENSION D8(6,4),E8(6,4),HF3(6,4),CP(6,4),F(6,4),CR(6,4),EM(6,4)

```

B

READ STATEMENTS IN PART B ARE ALL THE DATA WHICH MUST BE READ INTO THE PROGRAM. THE INPUT DATA WILL BE DIFFERENT FOR EACH CASE RUN. THE INPUT DATA WHICH MUST BE READ IN WILL BE DISCUSSED IN DETAIL IN THE SECTION OF THE REPORT DEALING WITH INPUT DATA

```

READ 1,NRO,NQO,NDEP,PT,HFT
NRND=NRO*NDEP
DO 2 I=1,NRND
  READ 3,(HF(I,J),J=1,NC0)
2 CONTINUE
DO 4 I=1,NRND
  READ 3,(HF3(I,J),J=1,NC0)
4 CONTINUE
DO 5 I=1,NRND
  READ 3,(S298(I,J),J=1,NC0)
5 CONTINUE
DO 6 I=1,NRND
  READ 3,(S3000(I,J),J=1,NC0)
6 CONTINUE
DO 7 I=1,NRND
  READ 14,(FF(I,J),J=1,NC0)
7 CONTINUE
DO 108 I=1,NRND
  READ 14,(CR(I,J),J=1,NC0)
108 CONTINUE
DO 1024 I=1,NRND
  READ 14,(BS(I,J),J=1,NC0)
1024 CONTINUE
DO 208 I=1,NRND
  READ 14,(EM(I,J),J=1,NC0)
208 CONTINUE
DO 8 I=1,NRND
  READ 3,(A(I,J),J=1,NC0)
8 CONTINUE
DO 9 I=1,NRND
  READ 10,(E(I,J),J=1,NC0)
9 CONTINUE
DO 11 I=1,NRND
  DO 11 J=1,NC0
  READ 12,(A7(I,J),B7(I,J),C7(I,J),D7(I,J),E7(I,J))
11 CONTINUE
DO 13 I=1,NRND
  DO 13 J=1,NC0
  READ 12,(A8(I,J),B8(I,J),C8(I,J),D8(I,J),E8(I,J))

```

PROGRAM ONE

PART A

THE FOLLOWING DIMENSION STATEMENTS ARE NEEDED FOR ALL SUBSCRIPTED VARIABLES USED IN THE PROGRAM. THE DIMENSION STATEMENTS ARE THE SAME FOR EVERY PROGRAM AND DO NOT HAVE TO BE CHANGED.

```

DIMENSION E(6,4),A(6,4),AX(6,4),HF(6,4),HFX(6,4),S298(6,4)
DIMENSION S3000(6,4),SX(6,4),CPX(6,4),FF(6,4),A7(6,4),B7(6,4)
DIMENSION C7(6,4),D7(6,4),E7(6,4),A8(6,4),B8(6,4),C8(6,4),BS(6,4)
DIMENSION D8(6,4),E8(6,4),HF3(6,4),CP(6,4),F(6,4),CR(6,4),EM(6,4)

```

PART B

THE READ STATEMENTS IN PART B ARE ALL THE DATA WHICH MUST BE READ INTO THE PROGRAM. THE INPUT DATA WILL BE DIFFERENT FOR EACH CASE RUN. THE INPUT DATA WHICH MUST BE READ IN WILL BE DISCUSSED IN DETAIL IN THE SECTION OF THE REPORT DEALING WITH THE INPUT DATA

```

READ 1,NRO,NC0,NDEP,PT,HFT
NRND=NRO+NDEP
DO 2 I=1,NRND
  READ 3,(HF(I,J),J=1,NC0)
2 CONTINUE
DO 4 I=1,NRND
  READ 3,(HF3(I,J),J=1,NC0)
4 CONTINUE
DO 5 I=1,NRND
  READ 3,(S298(I,J),J=1,NC0)
5 CONTINUE
DO 6 I=1,NRND
  READ 3,(S3000(I,J),J=1,NC0)
6 CONTINUE
DO 7 I=1,NRND
  READ 14,(FF(I,J),J=1,NC0)
7 CONTINUE
DO 108 I=1,NRND
  READ 14,(CR(I,J),J=1,NC0)
108 CONTINUE
DO 1024 I=1,NRND
  READ 14,(BS(I,J),J=1,NC0)
1024 CONTINUE
DO 208 I=1,NRND
  READ 14,(EM(I,J),J=1,NC0)
208 CONTINUE
DO 8 I=1,NRND
  READ 3,(A(I,J),J=1,NC0)
8 CONTINUE
DO 9 I=1,NRND
  READ 10,(E(I,J),J=1,NC0)
9 CONTINUE
DO 11 I=1,NRND
  DO 11 J=1,NC0
  READ 12,(A7(I,J),B7(I,J),C7(I,J),D7(I,J),E7(I,J))
11 CONTINUE
DO 13 I=1,NRND
  DO 13 J=1,NC0
  READ 12,(A8(I,J),B8(I,J),C8(I,J),D8(I,J),E8(I,J))

```

13 CONTINUE

1 FORMAT (3I10,2F10.4)

3 FORMAT (4F15.5)

14 FORMAT(4F10.2)

10 FORMAT (4A3)

12 FORMAT (5F10.5)

PART C

THE TEMPERATURE AT WHICH THE PRODUCTS EXIST WILL BE ASSUMED TO BE 298 K AS A FIRST APPROXIMATION.

T=298.0

SA IS THE TOTAL NUMBER OF MOLES. IT IS INITIALIZED TO ZERO IN THIS STEP.

SA=0.0

DO 15 I=1,NRND

DO 15 J=1,NCO

THE FREE ENERGY, F, IS CALCULATED FOR EACH COMPONENT.

F(I,J)=HF(I,J)-T*S298(I,J)

IF(A(I,J)) 15,15,91

THE TOTAL NUMBER OF MOLES IS CALCULATED

91 SA=SA+A(I,J)

15 CONTINUE

SINCE IT WAS ASSUMED AS A FIRST APPROXIMATION THAT ALL THE PRODUCTS EXISTED AS A MONATOMIC GAS, SAMAX IS THE MAXIMUM NUMBER OF MOLES WHICH CAN EXIST.

SAMAX=SA

DO 16 I=1,NRO

DO 16 J=1,NCO

DO 16 K=1,NRND,NRO

IF(A(K,J)) 24,24,16

THE MONATOMIC GAS IS ASSUMED TO BE 2/3 OF THE MAXIMUM ALLOWABLE CONCENTRATION AS A FIRST APPROXIMATION

24 A(K,J)=(2./3.)*A(I,1)*(FF(K,J)/FF(I,1))

16 CONTINUE

DO 17 I=1,NRO

DO 17 J=2,NCO

S298 IS THE ENTROPY OF EACH SPECIES. THE MATRIX IS SET UP IN SUCH A WAY THAT SOME LOCATIONS IN THE MATRIX DO NOT CONTAIN ANY SPECIES BUT JUST A BLANK SPACE. THE BLANK SPACES ARE ASSIGNED AN ENTROPY OF ZERO. IF THE ENTROPY IS SOME POSITIVE NUMBER THEN IT WILL CALCULATE THE TERMS FT,XLSA,RT,AND XN.

IF(S298(I,J)) 17,17,18

18 FT=2.*F(I,J)-F(I,1)*FF(I,1)/FF(I,J)

FT IS THE FREE ENERGY OF THE REACTANTS AND PRODUCTS BEING CONSIDERED

XLSA IS EQUAL TO 1.987*T*(1+LOG(A(I,J))) OF THE REACTION BEING CONSIDERED. FOR THE REACTION 2N=N2, XLSA SHOULD BE -2*1.987*T*(1+LOG(N))+1.987*T*(1.LOG(N2)). THE FOLLOWING SEQUENCE OF STEPS IS DESIGNED TO GIVE THE ABOVE RESULT. THIS STEP GIVES XLSA=2*1.987*T*(1+LOGF(N2)).

XLSA=2.*1.987*T*(1.+LOGF(A(I,J)))

THE NEXT STEP GIVES XLSA=2*1.987*(1+LOG(N2))-1.987*T*(1+LOG(N))*2

XLSA=XLSA-1.987*T*(1.+LOGF(A(I,1)))*FF(I,1)/FF(I,J)

XN IS EQUAL TO THE CHANGE IN THE NUMBER OF MOLES PER REACTION.

PROGRAM ONE

IN THE NITROGEN CASE THIS WILL BE -1. THIS STEP GIVES $XN = -2+2$.

$$XN = -[FF(I,1)/FF(I,J)] + 2.$$

RT FOR THE NITROGEN EXAMPLE IS $4 \cdot R \cdot T / N + R \cdot T / N^2$. THE STEP GIVES

$$RT = R \cdot T \cdot 4 / N.$$

$$RT = 1.987 \cdot T \cdot [(FF(I,1)/FF(I,J)) \cdot 2] / A(I,1)$$

THE NEXT DUE LOOP WILL COMPLETE RT, XN, XLSA, AND FT

DO 19 K=I, NRND, NRO

IF(S298(K,J)) 19,19,20

$$20 \text{ FT} = \text{FT} - F(K,J) \cdot FF(K,J) / FF(I,J)$$

$$XLSA = 2 \cdot 1.987 \cdot [1 + \text{LOG}(N^2)] - 1.987 \cdot T \cdot [1 + \text{LOG}(N)] \cdot 2 -$$

$$1.987 \cdot T \cdot [1 + \text{LOG}(N^2)]$$

XLSA = $-2 \cdot 1.987 \cdot T \cdot [1 + \text{LOG}(N)] + 1.987 \cdot T \cdot [1 + \text{LOG}(N^2)]$ WHICH IS THE DESIRED RESULT.

$$XLSA = XLSA - 1.987 \cdot T \cdot [1 + \text{LOG}(A(K,J))] \cdot FF(K,J) / FF(I,J)$$

RT = $R \cdot T \cdot 4 / N + R \cdot T / N^2$ WHICH IS THE DESIRED RESULT.

$$RT = RT + 1.987 \cdot T \cdot [(FF(K,J)/FF(I,J)) \cdot 2] / A(K,J)$$

XN = $-2+2-1 = -1$ WHICH IS THE DESIRED RESULT

$$XN = XN - FF(K,J) / FF(I,J)$$

19 CONTINUE

A1 AND B1 ARE THE TWO TERMS IN THE MINIMIZATION OF FREE ENERGY EQUATION WHICH ARE NEEDED TO CALCULATE THE CORRECTION FACTOR FOR THE MOLES OF PRODUCT ASSUMED.

$$A1 = \text{FT} + XLSA - 1.987 \cdot T \cdot (\text{LOG}(SA) + 1) - 1.987 \cdot T \cdot \text{LOG}(PT)$$

$$B1 = RT + 1.987 \cdot T \cdot (-.5)$$

A IS THE CORRECTION FACTOR FOR THE MOLES OF PRODUCT ASSUMED.

$$A(I,J) = -A1 / (2 \cdot B1)$$

IF THE NUMBER OF MOLES OF PRODUCT IS GREATER THAN THE NUMBER OF MOLES OF REACTANTS, THE SUBMATRIX IS ASSIGNED A CONCENTRATION.

A SUBMATRIX IS ANY OTHER MATRIX BUT THE FIRST SHEET WHICH IS READ IN. IF A THREE DIMENSIONAL MATRIX IS CONSIDERED, THE SUBMATRICES ARE ALL OTHER MATRICES IN DEPTH BUT THE FIRST. ALTHOUGH IT IS IMPOSSIBLE TO HAVE MORE PRODUCT THAN REACTANTS THIS SHOWS THAT ALL THE REACTANT SHOULD EXIST AS PRODUCT.

ASSIGNS SUBMATRIX THE MAXIMUM ALLOWABLE CONCENTRATION.

IF(A(I,J) - A(I,1) * FF(I,J) / FF(I,1)) 17,17,200

200 DO 21 K=I, NRND, NRO

$$A(K,J) = A(I,1) \cdot FF(K,J) / FF(I,1)$$

21 CONTINUE

17 CONTINUE

PART D

PART D ORDERS THE REACTANTS AND PRODUCTS ACCORDING TO WHICH CAUSES THE GREATEST MINIMIZATION OF FREE ENERGY.

DO 22 I=1, NRO

DO 22 J=2, NCO

THE FREE ENERGY PER REACTION CONSIDERED IS CALCULATED.

$$F(I,J) = F(I,J) \cdot A(I,J) - F(I,1) \cdot A(I,1)$$

$$L = I + NRO$$

DO 22 K=L, NRND, NRO

IF(S298(K,J)) 22,22,240

$$240 \text{ F}(I,J) = \text{F}(I,J) - \text{F}(K,J) \cdot A(K,J)$$

22 CONTINUE

$$NCO1 = NCO - 1$$

DO 23 I=1, NRO

DO 23 J=1, NCO1

PROGRAM ONE

JP1=J+1

DO 23 L=JP1, NCO

THE FOLLOWING STATEMENT INITIATES THE ORDERING PROGRAM. EACH FREE ENERGY CHANGE IS COMPARED WITH ALL THE FREE ENERGY CHANGES IN THE MATRIX AND IT IS ARRANGED FROM THE LARGEST NEGATIVE FREE ENERGY TO THE LARGEST POSITIVE FREE ENERGY CHANGE.

IF(F(I,J)-F(I,L)) 23,23,28

28 DO 23 K=I, NRND, NRO

THE FIRST ORDERING PROGRAM ARRANGES THE MATRICES WITHIN THE ROW. SINCE EACH COMPONENT HAS ITS FREE ENERGY, NUMBER OF MOLES, ENTHALPY, ETC. STORED IN THE SAME LOCATION OF EACH MATRIX, WHEN THE FREE ENERGY MATRIX IS ORDERED ALL OTHER MATRICES MUST BE ORDERED IN THE SAME MANNER AS THE FREE ENERGY MATRIX.

TEMP=F(K,L)

F(K,L)=F(K,J)

F(K,J)=TEMP

AX(K,J)=A(K,J)

AX(K,L)=A(K,L)

TEMP=AX(K,L)

AX(K,L)=AX(K,J)

AX(K,J)=TEMP

TEMP=E(K,L)

E(K,L)=E(K,J)

E(K,J)=TEMP

HFX(K,J)=HF(K,J)

HFX(K,L)=HF(K,L)

TEMP=HFX(K,L)

HFX(K,L)=HFX(K,J)

HFX(K,J)=TEMP

TEMP=HF3(K,L)

HF3(K,L)=HF3(K,J)

HF3(K,J)=TEMP

TEMP=S298(K,L)

S298(K,L)=S298(K,J)

S298(K,J)=TEMP

TEMP=S3000(K,L)

S3000(K,L)=S3000(K,J)

S3000(K,J)=TEMP

TEMP=A7(K,L)

A7(K,L)=A7(K,J)

A7(K,J)=TEMP

TEMP=B7(K,L)

B7(K,L)=B7(K,J)

B7(K,J)=TEMP

TEMP=C7(K,L)

C7(K,L)=C7(K,J)

C7(K,J)=TEMP

TEMP=D7(K,L)

D7(K,L)=D7(K,J)

D7(K,J)=TEMP

TEMP=E7(K,L)

E7(K,L)=E7(K,J)

E7(K,J)=TEMP

TEMP=A8(K,L)

A8(K,L)=A8(K,J)

PROGRAM ONE

```

A8(K,J)=TEMP
TEMP=B8(K,L)
R8(K,L)=R8(K,J)
R8(K,J)=TEMP
TEMP=C8(K,L)
C8(K,L)=C8(K,J)
C8(K,J)=TEMP
TEMP=D8(K,L)
D8(K,L)=D8(K,J)
D8(K,J)=TEMP
TEMP=E8(K,L)
F8(K,L)=E8(K,J)
F8(K,J)=TEMP
TEMP=FF(K,L)
FF(K,L)=FF(K,J)
FF(K,J)=TEMP
TEMP=CR(K,L)
CR(K,L)=CR(K,J)
CR(K,J)=TEMP
TEMP=BS(K,L)
RS(K,L)=RS(K,J)
RS(K,J)=TEMP
TEMP=EM(K,L)
EM(K,L)=EM(K,J)
EM(K,J)=TEMP

```

23 CONTINUE

THE SECOND ORDERING PROGRAM, ORDERS ACCORDING TO COLUMNS.
THEREFORE, THE PROGRAM HAS BEEN COMPLETELY ORDERED. FIRST BY ROWS
THEN BY COLUMNS.

```

NR01=NR0-1
DO 31 I=1,NR01
  IP1=I+1
  DO 31 J=IP1,NR0
    IF(F(I,1)-F(J,1)) 31,31,32
32 DO 61 K=J,NRND,NR0
  K1=K-(J-I)
  DO 61 I1=1,NC0
    TEMP=F(K,I1)
    F(K,I1)=F(K1,I1)
    F(K1,I1)=TEMP
    TEMP=AX(K,I1)
    AX(K,I1)=AX(K1,I1)
    AX(K1,I1)=TEMP
    TEMP=E(K,I1)
    F(K,I1)=E(K1,I1)
    F(K1,I1)=TEMP
    TEMP=HFX(K,I1)
    HFX(K,I1)=HFX(K1,I1)
    HFX(K1,I1)=TEMP
    TEMP=HF3(K,I1)
    HF3(K,I1)=HF3(K1,I1)
    HF3(K1,I1)=TEMP
    TEMP=S298(K,I1)
    S298(K,I1)=S298(K1,I1)
    S298(K1,I1)=TEMP

```

PROGRAM ONE

```

TEMP=S3000(K,I1)
S3000(K,I1)=S3000(K1,I1)
S3000(K1,I1)=TEMP
TEMP=A7(K,I1)
A7(K,I1)=A7(K1,I1)
A7(K1,I1)=TEMP
TEMP=B7(K,I1)
B7(K,I1)=B7(K1,I1)
B7(K1,I1)=TEMP
TEMP=C7(K,I1)
C7(K,I1)=C7(K1,I1)
C7(K1,I1)=TEMP
TEMP=D7(K,I1)
D7(K,I1)=D7(K1,I1)
D7(K1,I1)=TEMP
TEMP=E7(K,I1)
E7(K,I1)=E7(K1,I1)
E7(K1,I1)=TEMP
TEMP=A8(K,I1)
A8(K,I1)=A8(K1,I1)
A8(K1,I1)=TEMP
TEMP=B8(K,I1)
B8(K,I1)=B8(K1,I1)
B8(K1,I1)=TEMP
TEMP=C8(K,I1)
C8(K,I1)=C8(K1,I1)
C8(K1,I1)=TEMP
TEMP=D8(K,I1)
D8(K,I1)=D8(K1,I1)
D8(K1,I1)=TEMP
TEMP=E8(K,I1)
E8(K,I1)=E8(K1,I1)
E8(K1,I1)=TEMP
TEMP=FF(K,I1)
FF(K,I1)=FF(K1,I1)
FF(K1,I1)=TEMP
TEMP=CR(K,I1)
CR(K,I1)=CR(K1,I1)
CR(K1,I1)=TEMP
TEMP=BS(K,I1)
BS(K,I1)=BS(K1,I1)
BS(K1,I1)=TEMP
TEMP=EM(K,I1)
EM(K,I1)=EM(K1,I1)
EM(K1,I1)=TEMP

```

61 CONTINUE

31 CONTINUE

PART F

AFTER ALL THE DATA IN THE MATRICES HAS BEEN ORDERED, IT IS THEN PUNCHED OUT AS OUTPUT. THE PUNCH OUTPUT IS THEN USED IN

PROGRAM TWO.

PRINT 1031

1031 FORMAT(1H1,10X,20HPRINT OUT NUMBER ONE)

PRINT 1098

```

1098 FORMAT(1H0,/)
      PRINT 1753
1753 FORMAT(1H0,10X,45HTHE FOLLOWING PRINT OUT IS THE ORDER IN WHICH/
110X,34HTHE COMPONENTS HAVE BEEN ARRANGED.12HTHE MOLES OF/
210X,32HEACH COMPONENT ARE LISTED BELOW./
310X,49HTHE PRINT OUT DOES NOT HAVE TO SATISFY A MATERIAL/
410X,37HBALANCE AT THIS POINT IN THE PROGRAM.1
      DO 1026 I=1, NRND
      PRINT 1027, (E(I,J), J=1, NCO)
      PRINT 1030, (AX(I,J), J=1, NCO)
      PRINT 1101
1026 CONTINUE
1027 FORMAT(1H ,10X,A3,10X,A3,10X,A3,10X,A3)
1030 FORMAT(1H ;3X,4F13.5)
1101 FORMAT(1H0)
      PUNCH 1, NR0, NCO, NDEP, PT, HFT
      DO 1002 I=1, NRND
      PUNCH 3, (HF(I,J), J=1, NCO)
1002 CONTINUE
      DO 1004 I=1, NRND
      PUNCH 3, (HF3(I,J), J=1, NCO)
1004 CONTINUE
      DO 1005 I=1, NRND
      PUNCH 3, (S298(I,J), J=1, NCO)
1005 CONTINUE
      DO 1006 I=1, NRND
      PUNCH 3, (S3000(I,J), J=1, NCO)
1006 CONTINUE
      DO 1007 I=1, NRND
      PUNCH 14, (FF(I,J), J=1, NCO)
1007 CONTINUE
      DO 1080 I=1, NRND
      PUNCH 14, (CR(I,J), J=1, NCO)
1080 CONTINUE
      DO 1025 I=1, NRND
      PUNCH 14, (RS(I,J), J=1, NCO)
1025 CONTINUE
      DO 1208 I=1, NRND
      PUNCH 14, (EM(I,J), J=1, NCO)
1208 CONTINUE
      DO 1008 I=1, NRND
      PUNCH 3, (A(I,J), J=1, NCO)
1008 CONTINUE
      DO 1009 I=1, NRND
      PUNCH 10, (E(I,J), J=1, NCO)
1009 CONTINUE
      DO 1011 I=1, NRND
      DO 1011 J=1, NCO
      PUNCH 12, A7(I,J), B7(I,J), C7(I,J), D7(I,J), E7(I,J)
1011 CONTINUE
      DO 1013 I=1, NRND
      DO 1013 J=1, NCO
      PUNCH 12, A8(I,J), B8(I,J), C8(I,J), D8(I,J), E8(I,J)
1013 CONTINUE
      PUNCH 1021, SAMAX

```


PROGRAM ONE

```
1021 FORMAT(F10.5)
      DO 1022 I=1, NRND
      PUNCH 3, (AX(I,J), J=1, NCO)
1022 CONTINUE
      DO 1023 I=1, NRND
      PUNCH 3, (HFX(I,J), J=1, NCO)
1023 CONTINUE
      CALL EXIT
      END
```

PROGRAM TWO

```

DIMENSION E(6,4),A(6,4),AX(6,4),HF(6,4),HFX(6,4),S298(6,4)
DIMENSION S3000(6,4),SX(6,4),CPX(6,4),FF(6,4),A7(6,4),B7(6,4)
DIMENSION C7(6,4),D7(6,4),E7(6,4),A8(6,4),B8(6,4),C8(6,4),BS(6,4)
DIMENSION D8(6,4),E8(6,4),HF3(6,4),CP(6,4),F(6,4),CR(6,4),EM(6,4)

```

PART A

THE FOLLOWING READ STATEMENTS ARE READ IN FROM THE DATA FROM PROGRAM ONE.

```

READ 1,NRO,NCO,NDEP,PT,HFT
NRND=NRO+NDEP
DO 2 I=1,NRND
  READ 3,(HF(I,J),J=1,NCO)
2 CONTINUE
DO 4 I=1,NRND
  READ 3,(HF3(I,J),J=1,NCO)
4 CONTINUE
DO 5 I=1,NRND
  READ 3,(S298(I,J),J=1,NCO)
5 CONTINUE
DO 6 I=1,NRND
  READ 3,(S3000(I,J),J=1,NCO)
6 CONTINUE
DO 7 I=1,NRND
  READ 14,(FF(I,J),J=1,NCO)
7 CONTINUE
DO 108 I=1,NRND
  READ 14,(CR(I,J),J=1,NCO)
108 CONTINUE
DO 200 I=1,NRND
  READ 14,(BS(I,J),J=1,NCO)
200 CONTINUE
DO 208 I=1,NRND
  READ 14,(EM(I,J),J=1,NCO)
208 CONTINUE
DO 8 I=1,NRND
  READ 3,(A(I,J),J=1,NCO)
8 CONTINUE
DO 9 I=1,NRND
  READ 10,(E(I,J),J=1,NCO)
9 CONTINUE
DO 11 I=1,NRND
DO 11 J=1,NCO
  READ 12, A7(I,J),B7(I,J),C7(I,J),D7(I,J),E7(I,J)
11 CONTINUE
DO 13 I=1,NRND
DO 13 J=1,NCO
  READ 12, A8(I,J),B8(I,J),C8(I,J),D8(I,J),E8(I,J)
13 CONTINUE
READ 1021,SAMAX
DO 1022 I=1,NRND
  READ 3,(AX(I,J),J=1,NCO)
1022 CONTINUE
DO 1023 I=1,NRND
  READ 3,(HFX(I,J),J=1,NCO)

```

PROGRAM TWO

1023 CONTINUE

1 FORMAT (3I10,2F10.4)

3 FORMAT (4F15.5)

14 FORMAT(4F10.2)

10 FORMAT (4A3)

12 FORMAT (5F10.5)

1021 FORMAT(F10.5)

PART R

THE PROGRAM NOW CONSIDERS WHAT PRODUCTS WILL OCCUR AT THE ACTUAL TEMPERATURE OF REACTION INSTEAD OF THE HYPOTHETICAL TEMPERATURE OF 298 K. THE PRODUCTS CALCULATED IN PROGRAM ONE WILL BE THE MAIN SPECIES PRESENT, AND WILL BE TERMED THE MAJOR SPECIES. THE PRODUCTS DUE TO DISSOCIATION CALCULATED IN PROGRAM TWO WILL BE TERMED THE MINOR SPECIES. THE TEMPERATURE AT WHICH THE PRODUCTS EXIST WILL BE ASSUMED TO BE 298 K AS A FIRST APPROXIMATION.

T=298.0

Z=.001*T

NR01=NR0-1

DO 132 I=1,NR0

THE HEAT CAPACITY OF EACH COMPONENT IS CALCULATED USING A FIVE CONSTANT EQUATION.

$$CPX(I,1)=A7(I,1)+B7(I,1)*Z+C7(I,1)*Z**2+D7(I,1)*Z**3+E7(I,1)*Z**4$$

132 CONTINUE

DO 145 I=1,NR0

DO 145 J=2,NCO

THE PROGRAM ASSIGNS AN INITIAL CONCENTRATION TO AN ASSUMED PRODUCT IF IT EXISTS IN THE MATRIX, IF S298 IS A POSITIVE QUANTITY.

IF(S298(I,J)) 151,151,150

IF S298 IS ZERO, IT ASSIGNS A VALUE OF ZERO TO THE COMPOSITION MATRIX.

151 AX(I,J)=0.0

GO TO 145

IF S298 IS POSITIVE IT ASSIGNS A VALUE OF .005 OF THE MAXIMUM POSSIBLE CONCENTRATION TO THE PRODUCT BEING CONSIDERED. THE PROGRAM IS NOT GUARANTEED TO CONVERGE WITH THIS INITIAL ASSUMPTION AND OTHER TRIAL COMPOSITIONS MAY HAVE TO BE TRIED. THE TRIAL ASSUMPTIONS WHICH ARE USED ARE ARBITRARY.

150 AX(I,J)=AX(I,1)*(FF(I,J)/FF(I,1))*0.005

145 CONTINUE

DO 152 I=1,NR0

DO 152 J=1,NCO

A(I,J)=0.0

I1=I+NR0

THE FOLLOWING DO LOOP ASSIGNS THE CONCENTRATIONS TO THE SUBMATRICES.

DO 152 K=I1,NRND,NR0

IF(S298(K,J)) 164,164,165

164 AX(K,J)=0.0

GO TO 152

165 AX(K,J)=AX(I,J)*(FF(K,J)/FF(I,J))*0.005

152 CONTINUE

DO 133 I=1,NR01

IP1=I+1

PROGRAM TWO

```
DO 133 J=IP1,NRO
```

IT IS IMPOSSIBLE FOR THE COMPUTER TO KNOW IF FOR EXAMPLE H2O AND OH BOTH CONTAIN H. THE PROGRAMER CAN TELL BY LOOKING, BUT THE COMPUTER MUST BE TOLD. IN A MATRIX TERMED EM ALL COMPONENTS CONTAINING H ARE GIVEN A SPECIFIC NUMBER SUCH AS 5. WHEN THE COMPUTER SCANS THE MATRIX IT CAN TELL ALL SPACES CONTAINING THE NUMBER 5 CONTAIN H. THE EM STATEMENT IS EXPLAINED IN MORE DETAIL IN THE SECTION DEALING WITH INPUT DATA.

```
IF(EM(I,1)-EM(J,1)) 133,134,133
```

CR IS SIMILAR TO FF AND IS EXPLAINED IN MORE DETAIL IN THE INPUT DATA SECTION. CR IS A DEVICE FOR MAINTAINING A MATERIAL BALANCE BETWEEN ROWS.

```
134 AX(J,1)=AX(J,1)-AX(I,1)*CR(I,1)/CR(J,1)
133 CONTINUE
```

```
1100 PRINT 1100
1100 FORMAT(1H1,10X,20HPRINT OUT NUMBER TWO)
1101 PRINT 1101
```

```
1101 FORMAT(1H0,/)
1105 PRINT 1104
```

1104 FORMAT(1H ,10X,50HTHE MOLES OF EACH COMPONENT LISTED BELOW SHOULD BE/10X,54HPOSITIVE INTEGERS. THE REACTANTS IN COLUMN ONE OF THE/210X,51HPRIMARY MATRIX SHOULD SATISFY THE MATERIAL BALANCE.)

```
DO 1102 I=1,NRND
PRINT 1103, (E(I,J),J=1,NC0)
PRINT 1108, (AX(I,J),J=1,NC0)
PRINT 1105
```

```
1102 CONTINUE
1103 FORMAT(10X,A3,10X,A3,10X,A3,10X,A3)
1108 FORMAT(5X,4F13.5)
```

```
PRINT 1101
PRINT 1109
1109 FORMAT(1H0,10X,22HPRINT OUT NUMBER THREE)
PRINT 1101
```

ACPX IS EQUAL TO THE SUM OF THE HEAT CAPACITIES TIMES THE NUMBER OF MOLES FOR EACH COMPONENT. IT IS INITIALIZED TO ZERO IN THIS STEP.

ACPX=0.0
AHFX IS EQUAL TO THE SUM OF THE ENTHALPIES TIMES THE NUMBER OF MOLES FOR EACH COMPONENT. IT IS INITIALIZED TO ZERO IN THIS STEP.

```
AHFX=0.0
DO 33 I=1,NRO
NMC IS THE NUMRER IF MAJOR COMPONENTS
NMC=I
```

```
IF(AX(I,1)) 33,33,63
63 ACPX=ACPX+AX(I,1)*CPX(I,1)
IF(HFX(I,1)) 64,65,64
64 AHFX=AHFX+AX(I,1)*HFX(I,1)
```

PART C

PART C COMBUSTION CHAMBER CALCULATION
THE TEMPERATURE AT WHICH THE PRODUCTS EXISTS IS EQUAL TO DT. THE CALCULATION ASSUMES THAT THE HEAT CAPACITIES AND ENTHALPIES ARE INDEPENDENT OF TEMPERATURE. THE HEAT CAPACITIES AND ENTHALPIES ARE DEPENDENT ON TEMPERATURE, SO THIS IS ONLY A CRUDE APPROXIMATION.

PROGRAM TWO

65 DT=(HFT-AHFX)/ACPX

33 CONTINUE

THE FOLLOWING SEQUENCE OF STEPS GIVES AN EXACT TEMPERATURE.
M IS A COUNTER USED IN THE TEMPERATURE EVALUATION SECTION

M=0

THE TEMPERATURE IS INCREMENTED IN 5 DEGREE INTERVALS. THE PROGRAM DOES NOT CONTAIN ANY PROVISION FOR MAKING THE TEMPERATURE CALCULATION CONVERGE IF THE ASSUMED TEMPERATURE IS ASSUMED TO BE LARGER THAN THE ACTUAL TEMPERATURE. BY ASSUMING A TEMPERATURE 500 DEGREES LESS THAN THE DT TEMPERATURE CALCULATED IT IS ASSUMED THAT THIS FIRST APPROXIMATION TEMPERATURE WILL BE LESS THAN THE ACTUAL TEMPERATURE AND WILL THUS CONVERGE.

34 T=DT-500.0

38 T=T+5.0

M=M+1

Z=T*.001

HFXP=0.0

THE FOLLOWING STATEMENT IS A SAFETY FACTOR. IF THE TEMPERATURE CALCULATION DOES NOT CONVERGE BY 8000 K, THE PROGRAM WILL CONTINUE

IF(T-8000.0) 35,35,43

THE HEAT CAPACITY, ENTHALPY, AND ENTROPY DATA ARE READ INTO THE PROGRAM FOR TWO TEMPERATURE RANGES, ABOVE AND BELOW 1200 K. THE IF STATEMENT TELLS THE PROGRAM WHICH SET OF DATA TO USE.

35 IF(T-1200.) 36,36,37

36 DO 39 I=1,NMC

CPX(I,1)=A7(I,1)+B7(I,1)*Z+C7(I,1)*Z**2+D7(I,1)*Z**3+E7(I,1)*Z**4
HFXP IS THE ENTHALPY OF A COMPONENT AT A PARTICULAR TEMPERATURE.

HFXP=HFXP+(HFX(I,1)+CPX(I,1)*(T-298.0))*AX(I,1)

39 CONTINUE

GO TO 41

37 DO 40 I=1,NMC

CPX(I,1)=A8(I,1)+B8(I,1)/Z+C8(I,1)/(Z**2)+D8(I,1)/(Z**3)

CPX(I,1)=CPX(I,1)+E8(I,1)/(Z**4)

HFXP=HFXP+(HFX(I,1)+CPX(I,1)*(T-3000.0))*AX(I,1)

40 CONTINUE

X IS THE DIFFERENCE BETWEEN THE ENTHALPY OF THE PRODUCTS AND REACTANTS. SINCE THIS IS A CONSTANT ENTHALPY PROCESS WHEN X IS ZERO THE PROGRAM HAS CONVERGED AT THE PROPER TEMPERATURE.

41 X=HFT-HFXP

THE FIRST TIME THROUGH THE LOOP X1=X. AFTER THE PROGRAM HAS GONE THROUGH THE LOOP ONCE IT GOES TO STATEMENT 111.

IF(M-1) 110,110,111

IF X IS ZERO IT MEAN MEANS THE PROGRAM HAS CONVERGED AND THE PROGRAM PROCEEDS ONTO THE NEXT SET OF CALCULATIONS. IF X IS NEGATIVE IT GOES TO STATEMENT 42 AND IF POSITIVE TO STATEMENT 131 AFTER GOING THROUGH BOTH STATEMENTS 42 OR 131 THE PROGRAM GOES TO STATEMENT 106.

111 IF(X) 42,43,131

42 Z=-1.0

GO TO 106

131 Z=1.0

STATEMENT 106 CHECKS TO SEE IF THE PRECEDING ITERATION WAS POSITIVE OR NEGATIVE.

IF IT WAS NEGATIVE IT ASSIGNS W EQUAL TO -1, IF IT WAS POSITIVE IT ASSIGNS W EQUAL TO +1.

662
PROGRAM TWO

63

106 IF(X1) 107,138,138

107 W=-1.0

GO TO 109

138 W=1.0

STATEMENT 109 CHECKS TO SEE IF X HAS CHANGED SIGN FROM THE PRECEDING ITERATION. IF IT CHANGES SIGN IT MUST HAVE GONE THROUGH X=0. IF X CHANGED SIGN IT MUST HAVE CONVERGED WITHIN 5 K OF THE LAST TEMPERATURE CALCULATED. IF X CHANGES SIGN IT PROCEEDS WITH THE NEXT PROGRAM, OTHERWISE IT REPEATS THE LOOP UNTIL X CHANGES SIGN AND THE PROGRAM CONVERGES.

109 IF(Z-W) 43,110,43

110 X1=X

GO TO 38

43 M2=0

PART D

PART D CALCULATES THE MINOR SPECIES. THIS PART OF THE PROGRAM IS VERY SIMILAR TO THE CALCULATION OF THE MAJOR SPECIES OF PROGRAM ONE.

Z=T*.001

THE NUMBER OF MOLES OF REACTANT AND PRODUCT IS AGAIN INITIALIZED TO ZERO

PRINT 1110,T

1110 FORMAT(1H ,10X,48H THE TEMPERATURE AT WHICH THE REACTION OCCURS IS 1F10.4/10X,59H IF THE TEMPERATURE IS EQUAL TO 8000 DEGREES THE TEMPERATURE/10X,28H CALCULATED DID NOT CONVERGE.)

PRINT 1111

1111 FORMAT(1H1,10X,21H PRINT OUT NUMBER FOUR)

832 SA=0.0

M2 IS A COUNTER

M2=M2+1

DO 144 I=1,NRND

DO 144 J=1,NC0

IF AX, THE NUMBER OF MOLES OF A PARTICULAR SPECIES, IS POSITIVE IT GOES TO STATEMENT 154.

IF(AX(I,J)) 144,144,154

STATEMENT 154 CHECKS TO SEE IF THIS IS THE FIRST TIME THROUGH THE LOOP. IF IT IS THE FIRST TIME THROUGH THE LOOP THE TOTAL NUMBER OF MOLES OF PRODUCTS AND REACTANTS SA WILL BE CALCULATED.

IF THIS IS NOT THE FIRST TIME THROUGH THE PROGRAM, THE SUM OF THE MOLES OF REACTANTS AND PRODUCTS IN THE FIRST MATRIX WILL BE CALCULATED. THE SUM OF THE MOLES OF PRODUCTS OF THE SUBMATRICES DOES NOT HAVE TO BE CALCULATED AFTER THE FIRST TIME THROUGH THE LOOP.

154 IF(M2-1) 66,66,163

66 IF(I-NR0) 163,163,144

163 SA=SA+AX(I,J)

144 CONTINUE

NR01=NR0+1

DO 44 I=1,NRND

DO 44 J=1,NC0

IF THE NUMBER OF MOLES OF COMPONENT AX IS POSITIVE THE HEAT CAPACITY (CPX), THE ENTHALPY (HF), THE ENTROPY (SX), AND THE FREE ENERGY (F) WILL BE CALCULATED.

IF(AX(I,J)) 44,44,67

PROGRAM TWO

STATEMENT 67 SHOWS THE COMPUTER WHICH SET OF DATA TO USE, THE SET FOR T LESS THAN 1200 K OR THE SET FOR T GREATER THAN 1200 K.

```

67 IF(T-1200.0) 45,45,46
45 CPX(I,J)=A7(I,J)+B7(I,J)*Z+C7(I,J)*Z**2+D7(I,J)*Z**3+E7(I,J)*Z**4
HF(I,J)=HF1(I,J)+CPX(I,J)*(T-298.0)
SX(I,J)=S298(I,J)+CPX(I,J)*LOGF(T/298.0)
F(I,J)=HF(I,J)-T*SX(I,J)
GO TO 444
46 CPX(I,J)=A8(I,J)+B8(I,J)/Z+C8(I,J)/(Z**2)+D8(I,J)/(Z**3)
CPX(I,J)=CPX(I,J)+E8(I,J)/(Z**4)
HF(I,J)=HF3(I,J)+CPX(I,J)*(T-3000.0)
SX(I,J)=S3000(I,J)+CPX(I,J)*LOGF(T/3000.0)
F(I,J)=HF(I,J)-T*SX(I,J)

```

44 CONTINUE
CPXT IS THE SUM OF THE HEAT CAPACITIES TIMES THE NUMBER OF MOLES FOR EACH COMPONENT.

```
444 CPXT=0.0
```

SUSX IS THE SUM OF THE ENTROPIES TIMES THE NUMBER OF MOLES FOR EACH COMPONENT.

```
SUSX=0.0
```

BILL IS THE SUM OF THE QUANTITIES 1.987*AX(I,J)*LOGF(AX(I,J)) FOR EACH COMPONENT.

```
RILL=0.0
```

THE FIRST TIME THROUGH THE PROGRAM IT GOES TO STATEMENT 74. THE SECOND AND SUCCEEDING TIMES THE PROGRAM GOES TO STATEMENT 96.

```
IF(M2-1) 74,74,96
```

```
96 DO 71 I=1,NRO
DO 71 J=1,NCO
```

IF THE MATRIX LOCATION HAS A REAL COMPONENT WITH A NON NEGATIVE CONCENTRATION CPXT, SUSX, AND BILL WILL BE CALCULATED FOR THE PRODUCTS AND REACTANTS IN THE PRIMARY MATRIX. IF THE MATRIX HAS A NON NEGATIVE CONCENTRATION AND IT IS THE FIRST TIME THROUGH THE LOOP CPXT, SUSX, AND BILL WILL BE CALCULATED FOR THE REACTANTS OF THE PRIMARY MATRIX.

```

IF(SX(I,J)) 71,71,72
72 IF(AX(I,J)) 71,71,333
333 CPXT=CPXT+CPX(I,J)*AX(I,J)
SUSX=SUSX-SX(I,J)*AX(I,J)
BILL=BILL+1.987*AX(I,J)*LOGF(AX(I,J))
71 CONTINUE
74 DO 48 I=1,NRO
DO 48 J=2,NCO

```

IF THE MATRIX HAS A NON NEGATIVE CONCENTRATION, AND IT IS THE FIRST TIME THROUGH THE LOOP CPXT, SUSX, AND BILL WILL BE CALCULATED FOR THE REACTANTS OF THE PRIMARY MATRIX.

```

IF(AX(I,J)) 48,48,803
803 IF(M2-1) 60,60,801
60 CPXT=0.0
SUSX=0.0
RILL=0.0

```

```

DO 70 K=1,NRO
CPXT=CPXT+CPX(K,1)*AX(K,1)
SUSX=SUSX-SX(K,1)*AX(K,1)
BILL=BILL+1.987*AX(K,1)*LOGF(AX(K,1))
70 CONTINUE

```

PROGRAM TWO

IF THE MATRIX LOCATION HAS A REAL COMPONENT, STATEMENTS 92 TO 335
CALCULATE XH, YH, XN, YN, XSB, YSB, XFT, YFT, XLSA, YLSA, AND RT. THE
ABOVE FACTORS ARE NEEDED FOR CALCULATING THE THREE FACTOR FREE
ENERGY EQUATION.

IT SHOULD BE NOTED THAT ALL THE FACTORS BEGINNING WITH X DEAL WITH
THE REACTANT, WHILE ALL THE FACTORS BEGINNING WITH Y DEAL WITH
THE PRODUCT.

801 IF (IS298(I, J)) 48, 48, 92

XH, YH, AND CPXT ARE NEEDED TO CALCULATE THE FACTOR H. FOR THE
EXAMPLE H₂=2H, H=[ENTHALPY OF H-1/2 ENTHALPY OF H₂]/A(I, J)*CPX
FOR THE H₂ EXAMPLE XH=2*HF(H₂)(1/2)

92 XH=2.*HF(I, 1)*FF(I, 1)/FF(I, J)

YH=2*HF(2H)

YH=2.*HF(I, J)

XN AND YN ARE NEEDED TO CALCULATE THE CHANGE IN THE TOTAL
NUMBER OF MOLES FOR THE REACTION, XN=2*1/2=1

XN=2.*FF(I, 1)/FF(I, J)

YN=2.0

XSR AND YSB ARE NEEDED TO CALCULATE THE ENTROPY TERM IN THE FREE
ENERGY EQUATION.

XSB=2*(-SX(H₂))*1/2

XSR=2.*(-SX(I, 1))*FF(I, 1)/FF(I, J)

YSB=2*(-SX(2H))

YSR=2.*(-SX(I, J))

XFT AND YFT ARE NEEDED TO CALCULATE THE FREE ENERGY TERM.

XFT=2*F(H₂)*1/2

XFT=2.*F(I, 1)*FF(I, 1)/FF(I, J)

YFT=2*F(2H)

YFT=2.*F(I, J)

XLSA AND YLSA ARE NEEDED TO CALCULATE THE LOG TERMS.

XLSA=2.1.987*T*(1+LOG(H₂))*1/2

XLSA=2.*1.987*T*(1+LOG(AX(I, 1)))*FF(I, 1)/FF(I, J)

YLSA=2*1.987*T*(1+LOG(2H))

YLSA=2.*1.987*T*(1+LOG(AX(I, J)))

RT IS INITIALIZED TO ZERO IN THIS STEP.

RT=0.0

DO LOOP 50 COMPLETES THE CALCULATION OF THE ABOVE TERMS.

DO 50 K=I, NRND, NRO

IF THE REACTANT IN THE MATRIX EXISTS STATEMENT 52 IS CALLED.

IF THE REACTANT IN THE MATRIX DOES NOT EXIST STATEMENT 51 IS
CALLED.

IF (SX(K, 1)) 51, 51, 52

STATEMENT 51 BYPASSES THE LOOP AND GOES TO STATEMENT 335 IF THE
PRODUCT IN THE MATRIX IS NON EXISTENT. IF THE PRODUCT IS EXISTENT
IT GOES TO STATEMENT 89.

51 IF (SX(K, J)) 335, 335, 89

STATEMENT 52 GOES TO 68 IF THE PRODUCT IS NON EXISTENT, AND TO
STATEMENT 69 IF IT IS EXISTENT.

52 IF (SX(K, J)) 68, 68, 69

FOR THE H₂=2H EXAMPLE SX(K, 1) IS POSITIVE AND SX(K, J) IS POSITIVE
SO THE PROGRAM GOES TO STATEMENT 69.

STATEMENT 69 CHECKS TO SEE IF IN THE SUBMATRIX THE REACTANT AND
PRODUCT ARE THE SAME. IN THE PARTICULAR EXAMPLE BEING CONSIDERED
THEY WILL NOT BE, BUT IN AN EXAMPLE USING H₂O AND OH THEY WILL BE.
THE READER IS REFERRED TO THE PICTURE OF THE MATRIX PRESENTED

PROGRAM TWO

EARLIER IN THE REPORT FOR VERIFICATION OF THE ABOVE STATEMENT
CONCERNING THE H2O AND OH EXAMPLE.

69 IF(S298(K,1)-S298(K,J)) 120,121,120
121 RT=RT+1.987*T*(((FF(K,1)-FF(K,J))/FF(I,J))**2)/AX(K,1)
GO TO 56

RT=(1.987*T*1/4)/H2
120 RT=RT+1.987*T*(((FF(K,1)/FF(I,J))**2)/AX(K,1))

RT=(1.987*T*1/4)/H2+(1.987*T)/H
RT=RT+1.987*T*(((FF(K,J)/FF(I,J))**2)/AX(K,J))

GO TO 56
68 RT=RT+1.987*T*(((FF(K,1)/FF(I,J))**2)/AX(K,1))

GO TO 56

89 RT=RT+1.987*T*(((FF(K,J)/FF(I,J))**2)/AX(K,J))

56 IF(SX(K,1)) 57,57,58

XH =2*HF(H2)(1/2)-HF(H2)(1/2)(H2)=1/2(HF)(H2)

58 XH=XH-HF(K,1)*FF(K,1)/FF(I,J)

XN=1-1/2=1/2

XN=XN-FF(K,1)/FF(I,J)

IF THE PRODUCT AND REACTANT IN THE SUBMATRICES ARE THE SAME AS IN
THE EXAMPLE OF H2O AND OH THE PROGRAM SKIPS STATEMENT 123. IF THE
PRODUCT AND REACTANT ARE NOT THE SAME AS IN THE EXAMPLE OF H2 AND
OH, THEN THE PROGRAM GOES TO STATEMENT 122.

IF(S298(K,1)-S298(K,J)) 122,123,122

XLSA=2*1.987*T*(1+LOG(H2))**1/2-1.987*T*(1+LOG(H2))**1/2=
1/2*1.987*T*(1+LOG(H2))

122 XLSA=XLSA-1.987*T*(1+LOG(AX(K,1)))*FF(K,1)/FF(I,J)

XFT=2*F(H2)*1/2-F(H2)*1/2=(1/2)F(H2)

123 XFT=XFT-F(K,1)*FF(K,1)/FF(I,J)

XSB=2*(-SX(H2))*1/2-(-SX(H2))*1/2=(1/2)(-SX(H2))

XSB=XSB+(SX(K,1))*FF(K,1)/FF(I,J)

THE NEXT GROUP OF STATEMENTS CALCULATES THE Y FACTORS.

57 IF(SX(K,J)) 335,335,59

YH=2*HF(OH)-HF(OH)=HF(OH)

59 YH=YH-HF(K,J)*FF(K,J)/FF(I,J)

YN=2-1=1

YN=YN-FF(K,J)/FF(I,J)

IF(S298(K,1)-S298(K,J)) 124,125,124

125 YLSA=YLSA-1.987*T*(1+LOG(AX(K,1)))*((FF(K,J)-FF(K,1))/FF(I,J))

GO TO 126

YLSA=2*1.987*T*(1+LOG(OH))-1.987*T*(1+LOG(OH))=1.987*T*(1+LOG(OH))

124 YLSA=YLSA-1.987*T*(1+LOG(AX(K,J)))*FF(K,J)/FF(I,J)

YFT =2*F(OH)-F(OH)=F(OH)

126 YFT=YFT-F(K,J)*FF(K,J)/FF(I,J)

YSB=2*(-SX(OH))-(-SX(OH))=-SX(OH)

YSB=YSB-(-SX(K,J))*FF(K,J)/FF(I,J)

THE FIRST TIME THROUGH THE PROGRAM GOES THROUGH THE LOOP
BEGINNING WITH STATEMENT 75. THE SECOND AND SUCCEEDING TIMES THE
PROGRAM SKIPS THE LOOP BECAUSE THE DATA WAS ALREADY CALCULATED IN
STATEMENT 333.

335 IF(M2-1) 75,75,50

75 IF(AX(K,J)) 334,334,78

334 IF(K-I) 50,50,82

78 IF(K-I) 331,331,330

330 IF(S298(K,1)-S298(K,J)) 331,82,331

331 CPXT=CPXT+CPX(K,J)*AX(K,J)

PROGRAM TWO

```

SUSX=SUSX-SX(K,J)*AX(K,J)
BILL=BILL+1.987*AX(K,J)*LOGF(AX(K,J))
IF(K-NRO) 50,50,82
82 IF(AX(K,1)) 50,50,83
83 IF(SX(K,1)) 50,50,84
84 BILL=BILL+1.987*AX(K,1)*LOGF(AX(K,1))
SUSX=SUSX-SX(K,1)*AX(K,1)
CPXT=CPXT+CPX(K,1)*AX(K,1)
50 CONTINUE

```

THE FOLLOWING TERMS COMBINE ALL THE X AND Y FACTORS NEEDED IN THE FREE ENERGY EQUATION.
 $H = -(HF(2H) - 1/2 HF(H2)) / CPXT$ THE 1000 IS NEEDED IN ORDER TO CHANGE CALORIES TO KILOCALORIES.

```

H = -(YH - XH) / (CPXT * 1000.0)
XN = 1 - 1/2 = 1/2
XN = YN - XN
FT = F(2H) - 1/2 F(H2)
FT = YFT - XFT
XLSA = 1.987 * T * (1 + LOG(2H)) - 1/2 * 1.987 * T * (1 + LOG(H2))
XLSA = YLSA - XLSA
YSR = -SX(2H) - 1/2 (-SX(H2))
YSR = YSR - XSR

```

THE ABOVE FACTORS ARE THEN SUBSTITUTED INTO THE THREE FACTOR EQUATION A1, B1, AND C1 TO GIVE EXACTLY THE SAME RESULTS AS THE SAMPLE CALCULATIONS AT THE END OF THE REPORT.

```

A1 = H * SUSX + FT + XLSA + H * BILL - XN * 1.987 * T * (LOGF(SA) + 1.)
A1 = A1 + XN * 1.987 * T * LOGF(PT) + H * 1.987 * SA * LOGF(PT/SA)
B1 = RT + H * XSR + (H * XLSA / T) - XN * H * 1.987 * (LOGF(SA) + 1.)
B1 = B1 + B2 + XN * H * 1.987 * LOGF(PT)
C1 = H * (RT / T)
C2 = H * 1.987 * ((SAMAX - SA) + SAMAX * LOGF(SA / SAMAX)) / ((SAMAX - SA) ** 2)
C1 = C1 + C2 * XN ** 2

```

CP WAS PREVIOUSLY USED AS THE SYMBOL FOR HEAT CAPACITY. DUE TO THE LACK OF SPACE IN THE COMPUTER MEMORY THE SAME SYMROL WILL BE USED FOR THE CORRECTION FACTOR FOR THE NUMBER OF MOLES OF PRODUCT.

```

CP(I,J) = (-B1 + SQRTF((B1**2) - 3.*A1*C1)) / (3.*C1)
CP(I,1) = 0.0

```

```

48 CONTINUE
IF(M2-1) 1701,1701,1700
1701 PRINT 1101
PRINT 1112

```

1112 FORMAT(1H ,10X 55H THE FOLLOWING PRINT OUTS ARE THE CORRECTION FACTORS, CP. /10X, 60H IF THE CORRECTION FACTORS ARE TOO LARGE THE PROGRAM WILL NOT /10X, 60H CONVERGE AND THE PROGRAMER WILL HAVE TO ASSUME AN OTHER VALUE /10X, 42H FOR THE INITIAL PRODUCT TRIAL CALCULATION.)

```

DO 1702 I=1, NRND
PRINT 1103, (E(I,J), J=1, NCO)
PRINT 1108, (CP(I,J), J=1, NCO)
PRINT 1105

```

```

1702 CONTINUE
PART F

```

PART F IS THE MATERIAL BALANCE SECTION USED IN CALCULATING THE MOLES OF PRODUCT IN THE COMBUSTION CHAMBER.

PROGRAM TWO

1700 DO 1048 I=1,NRO
DO 1048 J=2,NCO

IF THE PRODUCT EXISTS THE PROGRAM PROCEEDS TO STATEMENT 1049,
OTHERWISE IT REPEATS THE LOOP.

IF(SX(I,J)) 1048,1048,1049

IF THE PRODUCT IS NON NEGATIVE WHICH IT WILL BE THE FIRST TIME
THROUGH THE LOOP, IT GOES TO STATEMENT 1050. ON THE SECOND AND
SUCCESSIVE TIMES THROUGH THE LOOP THE MOLES OF A PARTICULAR
PRODUCT MAY BE ZERO.

1049 IF(AX(I,J)) 1048,1048,1050

STATEMENT 1050 CHECKS TO SEE IF THE PROGRAM HAS GONE THROUGH 100
ITERATIONS. IF THE PROGRAM HAS GONE THROUGH 100 ITERATIONS AND
HAS NOT CONVERGED IT PRINTS OUT THE FINAL VALUES CALCULATED. IF
THE PROGRAM HAS NOT GONE THROUGH 100 ITERATIONS IT WILL CONTINUE
THROUGH THE LOOP.

1050 IF(M2-100) 681,681,682

THE NEW PRODUCT COMPOSITION IS CALCULATED USING THE CORRECTION
FACTOR.

681 AX(I,J)=AX(I,J)+CP(I,J)

IF THE COMPOSITION IS NEGATIVE, WHICH IS IMPOSSIBLE THE PROGRAM
ASSIGNS IT A VALUE OF ZERO.

IF(AX(I,J)) 662,662,663

662 AX(I,J)=0.0

CP(I,J)=0.0

A(I,J) IS NOW AN ADDITIVE CORRECTION FACTOR INSTEAD OF A
COMPOSITION AS IN PROGRAM ONE.

THE ADDITIVE CORRECTION FACTOR IS USED IF AFTER THE FIRST TIME
THROUGH THE LOOP A COMPONENT WHICH WAS ASSUMED TO BE PRESENT IS
SHOWN TO HAVE A NEGATIVE CONCENTRATION.

IF(M2-1) 1048,1048,1904

1904 AX(I,1)=AX(I,1)+A(I,J)*FF(I,1)/FF(I,J)

IP1=I+NRO

DO 1903 K=IP1,NRND,NRO

IF(S298(K,1)) 1903,1903,1905

1905 IF(AX(K,1)) 1903,1903,1906

1906 AX(K,1)=AX(K,1)+A(I,J)*((BS(I,1)-BS(I,J))/BS(K,1))

1903 CONTINUE

GO TO 1048

THE FIRST TIME THROUGH THE LOOP THE STATEMENT GOES TO STATEMENT
664. THE SECOND AND SUCCESSIVE TIMES IT GOES TO STATEMENT 665.

663 IF(M2-1) 664,664,665

664 IP1=I+NRO

DO 666 K=IP1,NRND

THE FIRST TIME A PARTICULAR ROW IN THE SECONDARY MATRIX IS
CONSIDERED, THE FIRST COLUMN OF THE SECONDARY MATRIX IS INITIALIZED
TO ZERO. IF THE PRODUCT IN THE FIRST COLUMN OF THE SECONDARY
MATRIX EXISTS, THE PROGRAM BEGINS TO CALCULATE ITS COMPOSITION.

IF(J-2) 690,690,691

690 AX(K,1)=0.0

691 IF(S298(K,1)) 666,666,667

THE PROGRAM BEGINS TO CALCULATE THE COMPOSITION OF THE REACTANT.

667 AX(K,1)=AX(K,1)+AX(I,J)*((BS(I,1)-BS(I,J))/RS(K,1))

666 CONTINUE

A(I,J)=A(I,J)+AX(I,J)

AX(I,1)=AX(I,1)-AX(I,J)*FF(I,1)/FF(I,J)

PROGRAM TWO

GO TO 1048

665 IP1=I+NR0

THE FOLLOWING DO LOOP BEGINS TO CALCULATE THE COMPOSITION OF THE PRODUCT AND REACTANT IN COLUMN ONE FOR THE SECOND AND SUCCESSIVE TIMES THROUGH THE PROGRAM.

DO 671 K=IP1, NRND

IF(S298(K,1)) 671,671,672

672 AX(K,1)=AX(K,1)+CP(I,J)*[(BS(I,1)-BS(I,J))/BS(K,1)]

671 CONTINUE

A(I,J)=A(I,J)+CP(I,J)

AX(I,1)=AX(I,1)-CP(I,J)*(FF(I,1)/FF(I,J))

1048 CONTINUE

THE FOLLOWING DO LOOPS ARE A FURTHER MATERIAL BALANCE CALCULATION. IF FOR EXAMPLE HYDROGEN IS FORMED FROM $H_2O=H+OH$ AND ALSO FROM $H_2=2H$, THE PROGRAM WILL ADD UP BOTH CONTRIBUTIONS.

DO 673 I=1, NR0

DO 673 J=2, NCO

IP1=NR0+1

DO 673 K=IP1, NRND

IF THE PRODUCT BEING CONSIDERED IS POSITIVE THE PROGRAM PROCEEDS TO STATEMENT 674. IF THE PRODUCT EXISTS THE PROGRAM PROCEEDS TO STATEMENT 1300.

IF(AX(I,J)) 673,673,674

674 IF(S298(I,J)) 673,673,1300

STATEMENT 1300 CHECKS TO SEE IF THERE ARE ANY TWO PRODUCTS THE SAME IN THE PROGRAM SUCH AS THE HYDROGEN FROM THE REACTION OF $H_2O=H+OH$ AND THE HYDROGEN FROM $H_2=2H$. IF THE TWO PRODUCTS ARE THE SAME THE PROGRAM PROCEEDS TO STATEMENT 675. THE FIRST TIME THROUGH THE LOOP THE PROGRAM PROCEEDS TO STATEMENT 1690, AND THE SECOND AND SUCCESSIVE TIMES IT GOES TO STATEMENT 1691. BOTH STATEMENTS 1691 AND 1690 ADD THE PRODUCTS TOGETHER IF THEY ARE THE SAME.

1300 IF(S298(I,J)-S298(K,1)) 673,675,673

675 IF(M2-1) 1690,1690,1691

1690 AX(K,1)=AX(K,1)+AX(I,J)

GO TO 692

1691 AX(K,1)=AX(K,1)+CP(I,J)

692 AX(I,J)=AX(K,1)

673 CONTINUE

DO 1310 I=1, NR0

DO 1310 J=2, NCO

IF(ABS(CP(I,J))-0.0005) 1310,1310,1311

1310 CONTINUE

GO TO 682

PART F

PART F IS A TEMPERATURE RECALCULATION.

PART F IS THE SAME AS PART C AND WILL NOT BE FURTHER EXPLAINED.

1311 T=T-100.0

M=0

IF(T-8000.0) 838,838,682

838 T=T+5.

M=M+1

HFXP=0.0

7=T*.001

DO 823 I=1, NR0

PROGRAM TWO

```

DO 823 J=1, NCO
  IF (AX(I,J)) 823,823,824
824 IF (SX(I,J)) 823,823,825
825 IF (T-1200.) 826,826,827
826 CPX(I,J)=A7(I,J)+B7(I,J)*Z+C7(I,J)*Z**2+D7(I,J)*Z**3+E7(I,J)*Z**4
  HFXP=HFXP+(HFX(I,J)+CPX(I,J)*(T-298.)) * AX(I,J)
  GO TO 823
827 CPX(I,J)=A8(I,J)+B8(I,J)/Z+C8(I,J)/(Z**2)+D8(I,J)/(Z**3)
  CPX(I,J)=CPX(I,J)+E8(I,J)/(Z**4)
  HFXP=HFXP+(HFX(I,J)+CPX(I,J)*(T-3000.)) * AX(I,J)
823 CONTINUE
  X=HFT-HFXP
  IF (M-1) 828,828,830
830 IF (X) 831,832,833
831 7=-1.
  GO TO 834
833 7=1.
834 IF (X1) 835,836,836
835 W=-1.
  GO TO 837
836 W=1.0
837 IF (Z-W) 832,828,832
828 X1=X
  GO TO 838
682 PRINT 1101
  PRINT 1113
1113 FORMAT(1H ,10X,21HPRINT OUT NUMBER FIVE)
  PRINT 1114,M2
1114 FORMAT(1H0,10X,66HTHE NUMBER OF ITERATIONS THE PROGRAM TOOK TO CON
1VERGE AT THE FINAL/10X,15HCOMPOSITION IS ,13/10X,67HIF THE PROGRAM
2 TOOK 100 ITERATIONS IT DID NOT ACTUALLY CONVERGE AND/10X,48HA NEW
3 INITIAL CALCULATION WILL HAVE TO BE TRIED.)
  PRINT 1115
1115 FORMAT(1H1,10X,20HPRINT OUT NUMBER SIX)
  PRINT 1101
  PRINT 1117
1117 FORMAT(1H ,10X,53HTHE FOLLOWING PRINT OUT IS THE LAST SET OF CORRE
1CTION/10X,19HFACTORS CALCULATED.24H THE CORRECTION FACTORS/10X29H
2SHOULD BE APPROXIMATELY ZERO.)
  DO 1703 I=1, NRND
  PRINT 1103, (E(I,J), J=1, NCO)
  PRINT 1108, (CP(I,J), J=1, NCO)
  PRINT 1105
1703 CONTINUE
  PRINT 1101
  PRINT 1118
1118 FORMAT(1H ,10X,22HPRINT OUT NUMBER SEVEN)
  PRINT 1101
  PRINT 1119.T
1119 FORMAT(1H ,10X,47HTHE REACTION TEMPERATURE INSIDE THE CHAMBER IS F
110.4)
  PRINT 1120
1120 FORMAT(1H1,10X,22HPRINT OUT NUMBER EIGHT)
  PRINT 1101
  PRINT 1121

```

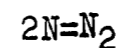
PROGRAM TWO

```
1121 FORMAT(1H ,10X,52H THE FINAL PRINT OUT LISTS THE COMPOSITION INSIDE  
1 THE/10X,19H COMBUSTION CHAMBER.)  
DO 1704 I=1,NRO  
PRINT 1103,(E(I,J),J=1,NC0)  
PRINT 1108,(AX(I,J),J=1,NC0)  
PRINT 1105  
1704 CONTINUE  
CALL EXIT  
END
```

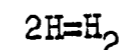
INPUT DATA INSTRUCTIONS FOR SUBMITTING PROGRAM

The most important job of the programmer will be to arrange the input data in the correct matrix form. In order for the program to be completely general the data is stored in matrix form. The only limit to the complexity of the system being considered is the size of the memory location. The following input instructions are meant to be a helpful guide to the programmer; however, the programmer may have to make some modifications of his own. In order to show what input data is needed and how the matrices should be set up, the example problem worked out at the end of the report will be programmed.

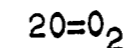
In the example being considered N_2H_4 and N_2O_4 may combine to give a variety of products. The only products which we will consider in this case will be $N, N_2, H, H_2, H_2O, O, OH, O_2$ and O . In setting up the matrix the products should be divided into elemental groups. First consider nitrogen:



Secondly consider hydrogen:



Thirdly consider oxygen:

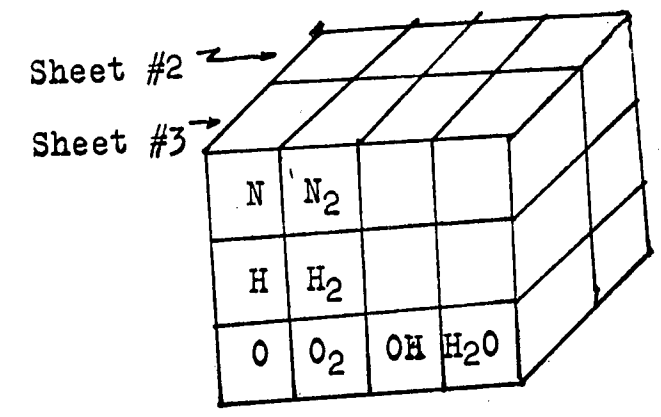


There are still two products which have not been considered, H_2O and OH . Since oxygen is the limiting element (7.2648 gram atoms of hydrogen and 1.8168 gram atoms of oxygen) we will group the OH and H_2O with the oxygen. The component should always be grouped with the limiting element.

Initially the matrix will be;

	Column			
	1	2	3	4
Row 1	N	N ₂		
2	H	H ₂		
3	O	O ₂	OH	H ₂ O

All of the products are now listed in the first sheet of the matrix. As long as the first column contains the monatomic gases, it doesn't matter how the rest of the row is arranged or in what order the rows are arranged, i.e. nitrogen could be listed last. The next step is to satisfy a material balance and fill in the remaining sheets. The term "sheets" refers to the way in which the matrices are stacked. If a three dimensional matrix is considered, the sheets would be the depth of the matrix.



Consider the reaction $2H=H_2O$. All of the reactants and products are present in the matrix but the hydrogen needed in the reaction is listed in row two and not in row three with the O_2 and H_2O . The program considers only one row at a time, but it can consider several sheets at the same

time. In order to satisfy the above material balance, the element H will be placed in sheet two, column 4, row 3. The same situation arises in the reaction $O + H = OH$, therefore the element H will also be placed in sheet 2, column 3, row 3. The final matrix is:

Sheet #1

N	N ₂		
H	H ₂		
O	O ₂	OH	H ₂ O

Sheet #2

		H	H

The following input data which is to be read in the program may be read in any desired format, but it must be in the above matrix form. The programmer will have to change the format statements for the read in and print out statements for every program run.

The following input data must be read in:

Read 1, NRO, NCO, NDEP, PT, HFT

NRO = The number of rows in matrix = 3

NCO = The number of columns in matrix = 4

NDEP = The number of sheets = 2

PT = Total Pressure in the chamber in atmospheres
= 34

HFT = Heat of Formation of propellant in calories/
100 grams = +19,400

Read 3, (HF(I,J),J=1,NC0)

HF = The enthalpy of the components at 298° K
in calories.

Read 3, (HF3(I,J),J=1,NC0)

HF3 = The enthalpy of the components at 3000°K
in calories.

Read 3, (S298(I,J),J=1,NC0)

S298 = The entropy of the components at 298°K
in calories.

Read 3, (S3000(I,J),J =1,NC0)

S3000 = The entropy of the components at 3000°K
in calories.

Read 14, (FF(I,J),J=1,NC0)

The factor FF(I,J) is used to maintain a material within the various rows. For the first reaction $2N=N_2$ a two is needed before the N in order to maintain a balance; therefore the first row of sheet one will be:

N ₂	N		
2.0	1.0	-	-

The two blanks may have any numbers assigned to them. For convenience a one will be listed for all the blanks. The second row for the reaction $2H = H_2$ will have the same factors. Row three will have the factors 2, 1 for the reaction $2O = O_2$; the factor 2,2, for the reaction $O + H = OH$, and the factors 2,2 for the reaction $O + 2H = H_2O$. In assigning the factor FF, the ratio of FF(reactant)/FF(product) is important and not the actual magnitude of

the factors. Before explaining the rule in more detail, first consider sheet two. Row three will be:

H H
1.0 1.0 2.0 4.0

The entire matrix will be:

Sheet #1

N	N ₂	--	---
2.0	1.0	1.0	1.0
H	H ₂	--	---
2.0	1.0	1.0	1.0
O	O ₂	OH	H
2.0	1.0	2.0	2.0

Sheet #2

--	--	--	--
1.0	1.0	1.0	1.0
--	--	--	--
1.0	1.0	1.0	1.0
--	--	H	H
1.0	1.0	2.0	2.0

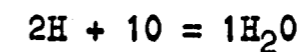
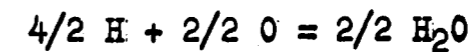
The rule for calculating FF is:

$$\text{Stoichiometric coefficient} = \frac{\text{FF (react)}}{\text{FF (product)}}$$

For the example of 2H + O = H₂O we have:

$$\left[\frac{\text{FF (H)}}{\text{FF (H}_2\text{O)}} \right] (\text{H}) + \left[\frac{\text{FF (O)}}{\text{FF (H}_2\text{O)}} \right] (\text{O}) = \left[\frac{\text{FF (H}_2\text{O)}}{\text{FF (H}_2\text{O)}} \right] (\text{H}_2\text{O})$$

or



Read 14, (CR(I,J), J = 1NCO)

The factor CR(I,J) is used to maintain a material balance between rows. If the reaction $2\text{H} + \text{O} = \text{H}_2\text{O}$ occurs, rows two and three will both be effected because every mole of O used from row three requires two moles of H from row two. The first sheet of the matrix will be:

N	N ₂	--	--
1.0	1.0	1.0	1.0
H	H ₂	--	--
1.0	1.0	1.0	1.0
O	O ₂	OH	H ₂ O
1.0	1.0	1.0	2.0

After the ordering program the matrix will be:

N ₂	--	--	N
1.0	1.0	1.0	1.0
H ₂ O	OH	O	O ₂
2.0	1.0	1.0	1.0
H ₂	--	--	--
2.0	1.0	1.0	1.0

The only place the factor CR(I,J) is used is in the equation-

$AX(J,1) = AX(J,1) - AX(I,1) + CR(I,1)/CR(J,1)$ of the second program. The above equation uses only the CR factors from primary matrix (sheet one) of column one. If two

components in column one contain the same element such as H₂ in row one, (H₂) and row two (H₂O), the above equation is then $AX(H_2) = AX(H_2) - AX(H_2O) (2/2)$. The equation nearly states that for every mole of H₂O used, one mole of H₂ is lost. The ratio and not the order of magnitude of the factors is important. The factors could have been (3/3) or (1/1). Only the first row of the rearranged primary matrix is important, all other locations can be assigned any arbitrary number. The programmer will have to initially guess how the matrix is going to be rearranged in program one. Program one prints out the rearranged order. If the programmer has made a mistake in his assumption, the output data can be corrected before using it as the input data for program two. In this way program one does not have to be re-run.

```
DO 14, (BS(I,J), J=1, NCO)
```

BS(I,J) is a factor used for maintaining a material balance for the submatrices. Again the programmer will have to make an initial assumption as to how program one will be rearranged. If the assumption is wrong, program one does not have to be re-run. The output of program one can be corrected and can then be submitted as the input of program two. The matrix should be:

Sheet #1

N ₂	--	--	N
1.0	1.0	1.0	1.0
H ₂ O	OH	0	O ₂
4.0	2.0	0.0	-4.0
H ₂	--	--	H
2.0	1.0	1.0	1.0

Sheet #2

--	--	--	--
1.0	1.0	1.0	1.0
H	H	--	--
4.0	.2.0	0.0	-4.0
--	--	--	--
2.0	1.0	1.0	1.0

The BS factor must satisfy the equation:

$$AX(K,1) = AX(K,1) + AX(I,J) + ((BS(I,1) - BS(I,J))/BS(K,1))$$

Consider the example $H_2O = 2H + O$

$$AX(H) = AX(H) + AX(O) * ((BS(H_2O) - BS(O))/BS(H))$$

or

$$AX(H) = AX(O) * (4 - 0) / 2$$

$$AX(H) = AX(H) + 2AX(O)$$

The above equation nearly shows that for every mole of O formed there are two moles of H formed. The programmer will have to work out each reaction by hand and then assign a BS factor for every component.

Read 14, (EM(I,J), J=1, NCO)

The EM(I,J) factor is a way of telling the computer what elements every component contains. The computer can not tell that OH contains both oxygen and hydrogen. Each element is assigned a number, oxygen=6, hydrogen=5. If the component OH is assigned the number 6, the program can tell it contains oxygen; and if it is assigned the number 5, the program can tell it contains hydrogen. The component can not be assigned both numbers, so it will be assigned

the number corresponding to the element with the largest composition, hydrogen. . . The matrix will be:

Sheet #1

N	N ₂	--	--
1.0	1.0	3.0	3.0
H	H ₂	--	--
5.0	5.0	3.0	3.0
O	O ₂	OH	H ₂ O
6.0	6.0	5.0	5.0

Sheet #2

--	--	--	--
3.0	3.0	3.0	3.0
--	--	--	--
3.0	3.0	3.0	3.0
--	--	H	H
3.0	3.0	5.0	3.0

The choice of numbers which maybe assigned to each component is arbitrary.

Read 3, (A(I,J),J=1,NC0)

A(I,J) = moles of each component initially assumed.

Read 10, (E(I,J),J=1,NC0)

E(I,J)=symbols of each component

H=atomic hydrogen

H₂=hydrogen

XN=atomic nitrogen

XN₂=nitrogen

OH=hydroxide

H₂O=water

XO=atomic oxygen

XO2=oxygen

XNP=no product

Read 12,A7(I,J),B7(I,J),C7(I,J),D7(I,J),E7(I,J)

Five constant heat capacity data at 298 K for each component.

Read 12,A8(I,J),B8(I,J),C8(I,J),D8(I,J),E'(I,J)

Five constant heat capacity data at 3000 K for for each component.

The programmer may find a complete set of input data used for the above example punched on the input data cards of program one which accompanys this report.

81
81

PRINT OUT NUMRER ONE

THE FOLLOWING PRINT OUT IS THE ORDER IN WHICH
THE COMPONENTS HAVE BEEN ARRANGED. THE MOLES OF
EACH COMPONENT ARE LISTED BELOW.
THE PRINT OUT DOES NOT HAVE TO SATISFY A MATERIAL
BALANCE AT THIS POINT IN THE PROGRAM.

XN2	XNP	XNP	XN
2.27040	1.51360	1.51360	1.51360

H2O	XOH	XO2	XO
1.81680	1.81680	1.81680	1.81680

H2	XNP	XNP	H
3.63240	2.42160	2.42160	2.42160

XNP	XNP	XNP	XNP
2.27040	1.51360	1.51360	1.51360

H	H	XNP	XNP
3.63360	3.63360	3.63360	1.81680

XNP	XNP	XNP	XNP
3.63240	2.42160	2.42160	2.42160

PRINT OUT NUMBER TWO

THE MOLES OF EACH COMPONENT LISTED BELOW SHOULD BE POSITIVE INTEGERS. THE REACTANTS IN COLUMN ONE OF THE PRIMARY MATRIX SHOULD SATISFY THE MATERIAL BALANCE.

XN2	XNP	XNP	XN
2.27040	0.	0.	0.02270

H2O	XOH	XO2	XO
1.81680	0.00908	0.00454	0.00908

H2	XNP	XNP	H
1.81560	0.	0.	0.03632

XNP	XNP	XNP	XNP
0.	0.	0.	0.

H	H	XNP	XNP
0.01817	0.00005	0.	0.

XNP	XNP	XNP	XNP
0.	0.	0.	0.

PRINT OUT NUMBER THREE

THE TEMPERATURE AT WHICH THE REACTION OCCURS IS 2674.7001 IF THE TEMPERATURE IS EQUAL TO 8000 DEGREES THE TEMPERATURE CALCULATED DID NOT CONVERGE.

PRINT OUT NUMBER FOUR

THE FOLLOWING PRINT OUTS ARE THE CORRECTION FACTORS, CP.
IF THE CORRECTION FACTORS ARE TOO LARGE THE PROGRAM WILL NOT
CONVERGE AND THE PROGRAMER WILL HAVE TO ASSUME ANOTHER VALUE
FOR THE INITIAL PRODUCT TRIAL CALCULATION.

XN2	XNP	XNP	XN
0.	0.	0.	-0.11703

H2O	XOH	XO2	XO
0.	0.00044	-0.00157	-0.00619

H2	XNP	XNP	H
0.	0.	0.	-0.00505

XNP	XNP	XNP	XNP
0.	0.	0.	0.

H	H	XNP	XNP
0.	0.	0.	0.

XNP	XNP	XNP	XNP
0.	0.	0.	0.

PRINT OUT NUMBER FIVE

THE NUMBER OF ITERATIONS THE PROGRAM TOOK TO CONVERGE AT THE FINAL
COMPOSITION IS 14
IF THE PROGRAM TOOK 100 ITERATIONS IT DID NOT ACTUALLY CONVERGE AND
A NEW INITIAL CALCULATION WILL HAVE TO BE TRIED.

PRINT OUT NUMBER SIX

THE FOLLOWING PRINT OUT IS THE LAST SET OF CORRECTION FACTORS CALCULATED. THE CORRECTION FACTORS SHOULD BE APPROXIMATELY ZERO.

XNP 0.	XNP 0.	XNP 0.	XN 0.
H2O 0.	XOH 0.00033	XO2 0.	XO 0.
H2 0.	XNP 0.	XNP 0.	H -0.00045
XNP 0.	XNP 0.	XNP 0.	XNP 0.
H 0.	H 0.	XNP 0.	XNP 0.
XNP 0.	XNP 0.	XNP 0.	XNP 0.

PRINT OUT NUMBER SEVEN

THE REACTION TEMPERATURE INSIDE THE CHAMBER IS 2634.7001

PRINT OUT NUMBER EIGHT

THE FINAL PRINT OUT LISTS THE COMPOSITION INSIDE THE COMBUSTION CHAMBER.

XN2	XNP	XNP	XN
2.27040	0.	0.	0.

H2O	XOH	XO2	XO
1.79983	0.01697	0.	0.

H2	XNP	XNP	H
1.83393	0.	0.	0.01571

Sample Calculations Using The Method of Minimization
Of Free Energy

1. Statement of the Problem

Reactants	Moles/100 grams propellant
N ₂ H ₄	1.8162
N ₂ O ₄	0.4542
Chamber Pressure= 500 PSIA	
Exhaust Pressure= 14.7 PSIA	
Density of Propellant= 1.148 g/cc	
Heat of Formation of Propellant= +19.44 Kcal/100gm	
Concentration of Ingredients per 100 grams of Propellant:	
H= 7.2648 gm-atoms	
N= 4.5408 gm-atoms	
O= 1.8168 gm-atoms	

2. Mass Balance

The moles of propellant are considered on a 100 gram basis. All reaction products that are possible could be considered on a high speed digital computer. In order to demonstrate the method for calculating the equilibrium composition inside a combustion chamber the reaction products will be limited to the following species: H₂, H₂O, N₂, H, N, OH, and O. The mass balances are-

$$\Sigma H = 7.2648 = 2N_{H_2} + 2N_{H_2O} + N_{OH} + N_H$$

$$\Sigma N = 4.5408 = 2N_{H_2O} + N_H$$

$$\Sigma O = 1.8168 = N_{H_2O} + N_{OH} + N_O$$

Through out all of the calculations it should be kept in mind that a mass balance must be maintained while simultaneously minimizing the free energy of the system.

3. Initial Conditions

The calculational routine is initiated by assuming that the entire propellant composition exists as a monatomic gas. This assumption gives a hypothetical composition which defines the maximum free energy and the maximum gaseous products for the system. Also, at constant enthalpy, the corresponding temperature of the monatomic gas mixture is a very low hypothetical one. The various products of combustion are introduced incrementally into the complex mixture. Each addition serves to reduce the free energy and increase the temperature of the mixture until equilibrium is obtained.

Initially assume that the monatomic gas products exist at 298°K. If the composition of the product being considered is initially zero, assume a value of 2/3 the maximum allowable concentration as the initial quantity to be introduced.

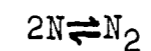
Physical Properties

Specie	n_j	ΔH_f 298 Kcal/mole	C_p -cal/deg-mole
N	4.5408	+113.0	4.97
H	7.2648	+52.09	4.968
O	<u>1.8168</u>	+59.55	5.24
	13.6224		

$$\begin{aligned} \text{Heat Formation of Propellant} &= n_j H_{f298} + C_p n_j \Delta T \\ &+ 19,440 \text{ cal.} = 998,500 \text{ cal.} + 68.1 \text{ cal/deg} \Delta T \\ \Delta T &= -14,400^\circ \text{K} \end{aligned}$$

This is the temperature at which the above hypothetical reaction mixture could exist. Whenever the temperature falls below 298°K , the thermodynamic data will be calculated at 298°K .

4. Formation of N_2



$$\frac{2\Delta n}{\text{N}_2} = -\frac{\Delta n}{\text{N}}$$

At 298°K the ideal entropy and free energy of N and N_2 are:

$$S_{\text{N}} = 36.61 \text{ cal/deg-mole}$$

$$S_{\text{N}_2} = 45.77 \text{ cal/deg-mole}$$

$$F_{\text{N}} = H - TS = +113.0 - 10.90 = +102.1 \text{ Kcal/mole}$$

$$F_{\text{N}_2} = H - TS = 0 - 13.65 = -13.65 \text{ Kcal/mole}$$

$$\Delta n_{\text{N}_2} = \frac{-B + \sqrt{B^2 - 3AC}}{3C}$$

Where-

$$\begin{aligned} A &= K n_{\text{N}} (-S_{\text{N}}) + K n_{\text{N}_2} (-S_{\text{N}_2}) + K n_{\text{H}} (-S_{\text{H}}) \\ &+ K n_{\text{O}} (-S_{\text{O}}) - 2(F_{\text{N}}) + (F_{\text{N}_2}) - 2RT \\ &(1 + \ln n_{\text{N}}) + RT(1 + \ln n_{\text{N}_2}) \\ &+ KR(n_{\text{N}} \ln n_{\text{N}}) + KR(n_{\text{N}_2} \ln n_{\text{N}_2}) \\ &+ KR(n_{\text{H}} \ln n_{\text{H}}) + KR(n_{\text{O}} \ln n_{\text{O}}) \\ &- RT(\ln n_{\text{T}} + 1) - RT \ln P \\ &+ KB_{\text{N}_2} \ln P_{\text{T}}/n_{\text{T}} = -224,217 \end{aligned}$$

$$\begin{aligned}
 B &= \frac{4RT}{\eta_N} + \frac{RT}{\eta_{N_2}} - 2K(-S_N) + K(-S_{N_2}) \\
 &- 2KR(1 + \ln \eta_N) + KR(1 + \ln \eta_{N_2}) \\
 &- KR(\ln \eta_T + 1) - KR \ln P_T \\
 &+ \frac{RT(\eta_{TMAX} - \eta_T) + \eta_{TMAX} \ln \frac{\eta_T}{\eta_{TMAX}}}{(\eta_{TMAX} - \eta_T)^2} = 616.7
 \end{aligned}$$

$$\begin{aligned}
 C &= \frac{4KR}{\eta_N} + \frac{KR}{\eta_{N_2}} + \frac{KR(\eta_{TMAX} - \eta_T)}{(\eta_{TMAX} - \eta_T)^2} \\
 &+ \eta_{TMAX} \ln \frac{\eta_T}{\eta_{TMAX}} = 0
 \end{aligned}$$

$$\Delta \eta_{N_2} = 181.8 \text{ MOLES}$$

Where-

$$K = \frac{H_{N_2} - 2N_H}{\sum n_j C_{Pj}}$$

This term is equal to zero when the temperature is below 298°K.

R = ideal gas constant = 1.987

n_{Tmax} = Maximum moles possible (monatomic gas) =
13.6224 moles

P_T = Total pressure in the atmosphere

If $(n_{Tmax} - n_T) = 0$

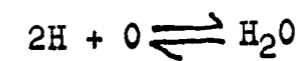
let

$$\frac{(n_{Tmax} - n_T) + n_{Tmax} \ln \frac{n_T}{n_{Tmax}}}{(n_{Tmax} - n_T)^2} = -0.5$$

The above calculations show that 181.8 moles of N_2 should exist at 298°K. This calculation shows that all the nitrogen should exist as N_2 instead of N. The free energy has been minimized by the following:

$$\Delta F = (2.270 \text{ moles}) (-13.65 \text{ Kcal/mole}) - (4.5408 \text{ moles}) (+102.1 \text{ Kcal/mole}) = -494.0 \text{ Kcal}$$

5. Formation of H_2O



$$\Delta n_{H_2O} = -\Delta n_O - 2\Delta n_H$$

From the oxygen balance, a maximum of 1.8168 moles of water could be formed.

From the hydrogen balance, a maximum of 3.6324 moles of water could be formed.

Hence, the oxygen balance is the restricting one.

At 298°K, the ideal entropy and free energy of H, O, and H₂O are:

$$S_H = 27.39 \text{ cal/deg-mole}$$

$$S_O = 38.47 \text{ cal/deg-mole}$$

$$S_{H_2O} = 45.11 \text{ cal/deg-mole}$$

$$F_H = +43.92 \text{ Kcal/mole}$$

$$F_O = +48.07 \text{ Kcal/mole}$$

$$F_{H_2O} = -71.21 \text{ Kcal/mole}$$

$$K = \frac{H_{H_2O} - H_O - 2H_H}{\sum n_j C_{Pj}} = 0, \quad T < 298^\circ K$$

$$A = -2(F_H) - (F_O) - 2RT(1 + \ln n_H)$$

$$- RT(1 + \ln n_O) + RT(1 + \ln n_{H_2O})$$

$$- RT(\ln n_T + 1) - RT \ln P_T = -215.119$$

$$B = \frac{4RT}{n_H} + \frac{RT}{n_O} + \frac{RT}{n_{H_2O}}$$

$$+ \frac{RT (n_{TMAX} - n_T) + n_{TMAX} \ln \frac{n_T}{n_{TMAX}}}{(n_{TMAX} - n_T)^2} = 844.7$$

$$C = 0$$

$$\Delta n_{H_2O} = 127.3$$

A maximum of 1.8168 moles of water can exist. Since Δn_{H_2O} exceeds this value, all oxygen should exist as water in preference to oxygen atoms. Furthermore, 3.6324 moles of hydrogen should also be combined to form H₂O. The ideal free energy change accompanying this concentration change is -

$$\Delta F = 1.8168 (-71.21) - 1.8168 (+48.07) - 3.6336 (+43.92) = -375.9 \text{ Kcal}$$

6. Introduction of Major Species

All other species are calculated in the same manner. The next step in the calculational procedure is to see which change caused the greatest single reduction in free energy, i.e. Transforming N to N₂.

Specie	N_j	ΔH_{f298}	$\Delta N_j \Delta H_f$	C_{P298}	$N_j C_P$
N_2	2.2704	0	0	6.96	15.8
H	7.2648	+52.09	+377.5	4.968	36.1
O	1.8168	+59.55	$\frac{+108.0}{+485.5}$	5.24	9.5

19,440 cal = 485,500 cal + 61.4 cal/deg ΔT
 $\Delta T = -7580^\circ K$

Since the introduction of N_2 was not sufficient to raise the temperature of the mixture to a realistic value, water will also be introduced:

Specie	N_j	ΔH_{f298}	$\Delta N_j \Delta H_f$	C_{P298}	$N_j C_P$
N_2	2.2704	0	0	6.96	15.8
H_2O	1.8168	-57.79	-105.0	8.03	14.6
H	3.6336	+52.09	$\frac{+189.0}{+84.0}$	4.968	$\frac{18.0}{48.4}$

19,400 cal = +84,000 cal + 48.4 Cal/deg ΔT
 $\Delta T = -1330^\circ K$

Next, let the rest of the H be introduced as H_2

Specie	N_j	ΔH_{f298}	$\Delta N_j \Delta H_f$	C_{P298}	$N_j C_P$
N_2	2.2704	0	0	6.96	15.8
H_2O	1.8168	-57.79	-105.0	8.03	14.6
H_2	$\frac{1.8168}{5.9040}$	0	$\frac{0}{-105.0}$	6.89	$\frac{12.5}{42.9}$

$$+19,400 = -105,000 + 42.9 \Delta T$$

$$\Delta T = 2900^\circ\text{K}$$

The ΔT of 2900°K corresponds to $T_0 = 3198^\circ\text{K}$, which is a reasonable temperature for the combustion chamber. The temperature will, however, have to be further corrected because the heat capacity data was extrapolated over a wide range. An enthalpy balance is therefore needed to adjust to the corresponding chamber temperature.

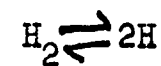
At 2687°K ,

$$\begin{aligned} & (\sum \eta_j \Delta H_{f,298})_{\text{reactants}} - (\sum \eta_j \Delta H_{f,298})_{\text{products}} = \\ & - (\sum \eta_j H_j)_{298}^{\text{T}} \\ & + 124.44 = 124.44 \end{aligned}$$

And the enthalpy balance is satisfied.

7. Introduction of Minor Species

At 2687°K there will be some dissociation into H, N, OH, O, etc. The preceding calculations must be repeated for minor species. The minor species are all other components, existing in relatively small composition, other than the major species calculated in part six. First, atomic hydrogen will be reconsidered. An initial composition of .005 times the maximum possible concentration was tried as a first approximation.



$$2 \Delta N_{\text{H}_2} = \Delta n_{\text{H}}$$

$$\Delta N_{\text{T}} = +\frac{1}{2} \Delta N_{\text{H}}$$

$$K = \frac{H_{\text{H}} - \frac{1}{2} H_{\text{H}_2}}{\sum n_j C_{p_j}} = -0.928$$

$$S_{\text{H}_2} = 47.23 \text{ cal/deg-mole}$$

$$S_{\text{H}} = 38.34 \text{ cal/deg-mole}$$

$$F_{\text{H}_2} = -109.6 \text{ Kcal/mole}$$

$$F_{\text{H}} = -39.4 \text{ Kcal/mole}$$

At this point, the species H_2 , N_2 , H_2O , and H are present as products of combustion. The constants for the quadratic equation are:

$$\begin{aligned} A = & K n_{\text{H}_2} (-S_{\text{H}_2}) + K n_{\text{H}} (-S_{\text{H}}) + K' n_{\text{N}_2} (-S_{\text{N}_2}) \\ & + K n_{\text{H}_2\text{O}} (-S_{\text{H}_2\text{O}})_T - \frac{1}{2} (F_{\text{H}_2}) + (F_{\text{H}}) \\ & - \frac{1}{2} RT (1 + \ln n_{\text{H}_2}) + RT (1 + \ln n_{\text{H}}) \\ & + KP (n_{\text{H}_2} \ln n_{\text{H}_2}) + KR (n_{\text{H}} \ln n_{\text{H}}) \\ & + KR (n_{\text{N}_2} \ln n_{\text{N}_2}) + KR (n_{\text{H}_2\text{O}} \ln n_{\text{H}_2\text{O}}) \\ & - \frac{1}{2} RT (\ln n_{\text{T}} + 2) + \frac{1}{2} RT \ln P_{\text{T}} \\ & + KR n_{\text{T}} \ln \frac{P_{\text{T}}}{n_{\text{T}}} = +281.56 \end{aligned}$$

$$\begin{aligned}
 B &= \frac{RT}{4N_{H_2}} + \frac{RT}{\gamma_H} - \frac{1}{2} K (-S_{H_2}) + K (-S_H) \\
 &\quad - \frac{1}{2} KR (1 + \ln \gamma_{H_2}) + KR (1 + \ln \gamma_H) \\
 &\quad - \frac{1}{2} KR (\ln N_{T+1}) + \frac{RT(N_{TMAX} - N_T) + N_{TMAX} \ln \frac{N_T}{N_{TMAX}}}{4(N_{TMAX} - N_T)^2} \\
 &\quad + \frac{1}{2} KR \ln P_T = 170,443.4
 \end{aligned}$$

$$\begin{aligned}
 C &= \frac{KR}{4N_{H_2}} + \frac{KR}{\gamma_H} + \frac{KR(N_{TMAX} - N_T) + N_{TMAX} \ln \frac{N_T}{N_{TMAX}}}{4(N_{TMAX} - N_T)^2} \\
 &= -58.578
 \end{aligned}$$

$$\Delta \gamma_H = \frac{-B + \sqrt{B^2 - 3AC}}{3C} = -0.0114$$

An initial composition of $2/3$ of the maximum possible value was chosen so that $N_H = 2.312$ gram-atoms.

By continuing the iteration until all species have been re-introduced and the free energy of the system has been minimized, the gas composition is found to be:

$$N_{H_2} = 1.83393$$

$$N_{H_2O} = 1.79983$$

$$N_{H_2} = 2.27040$$

$$N_H = 0.01571$$

$$N_{OH} = 0.01697$$

$$N_O = 0.0000$$

$$N_N = 0.0000$$

CONCLUSION

The most difficult step in running the program is to submit the data in the proper matrix form. The programmer should not have any trouble using the program if he follows the rules for properly submitting the data. The program is thoroughly explained in the report so the programmer should be able to remedy any problems which are incurred in running it. There are several intermediate print outs which are useful in detecting any errors in the program. It is hoped that this report will be a useful tool in the calculation of performance parameters of combustion mixtures.

Bibliography

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LIST OF NOMENCLATURE

A=Moles of each component in program one; additive correction factor in program two.

A7, B7, etc.=Heat capacity constants at 298 K

A8, B8, etc.=Heat capacity constants at 3000 K

ACPX=The sum of the moles of each component times its heat capacity

AHFX=The sum of the moles of each component times its enthalpy

AX=Moles of each component in program two

BILL=Sum of the moles of each component times 1.987 times the Log of the composition of each component

BS=Material balance factor between submatrices

CP=Heat capacity of each component in program one; correction factor in program two

CPX=Heat capacity of each component in program two

CPXT=Sum of the moles of each component times its heat capacity

CR=Material balance factor between rows

DT=First approximation of the temperature inside the combustion chamber.

E=Component name

EM=Component identification factor

F=Free energy of each component

FF=Material balance factor within rows

HF=Enthalpy of component at 298 K

HF3=Enthalpy of component at 3000 K

HFT=Enthalpy of reactants per 100 grams

HFX=Enthalpy of each component at some temperature other than 298K or 3000K.

NCO=Number of columns in matrix

NDEP=Number of sheets in matrix

NMC=Number of major components

NRND=NRO-NDEP

NRO=Number of rows in matrix

PT=Total pressure in atmospheres

S298=Entropy of component at 298 K

S3000=Entropy of component at 3000 K

SA=Total number of moles of product and reactant

SAMAX=Maximum number of moles of product which could exist

SUSX=Sum of the moles of each component times its entropy

SX=Entropy of each component at some temperature other than 298 K or 30000 K

T=Temperature in K