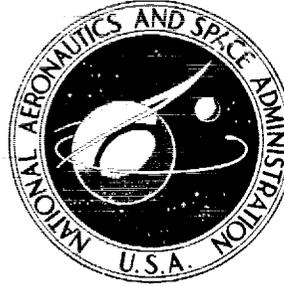


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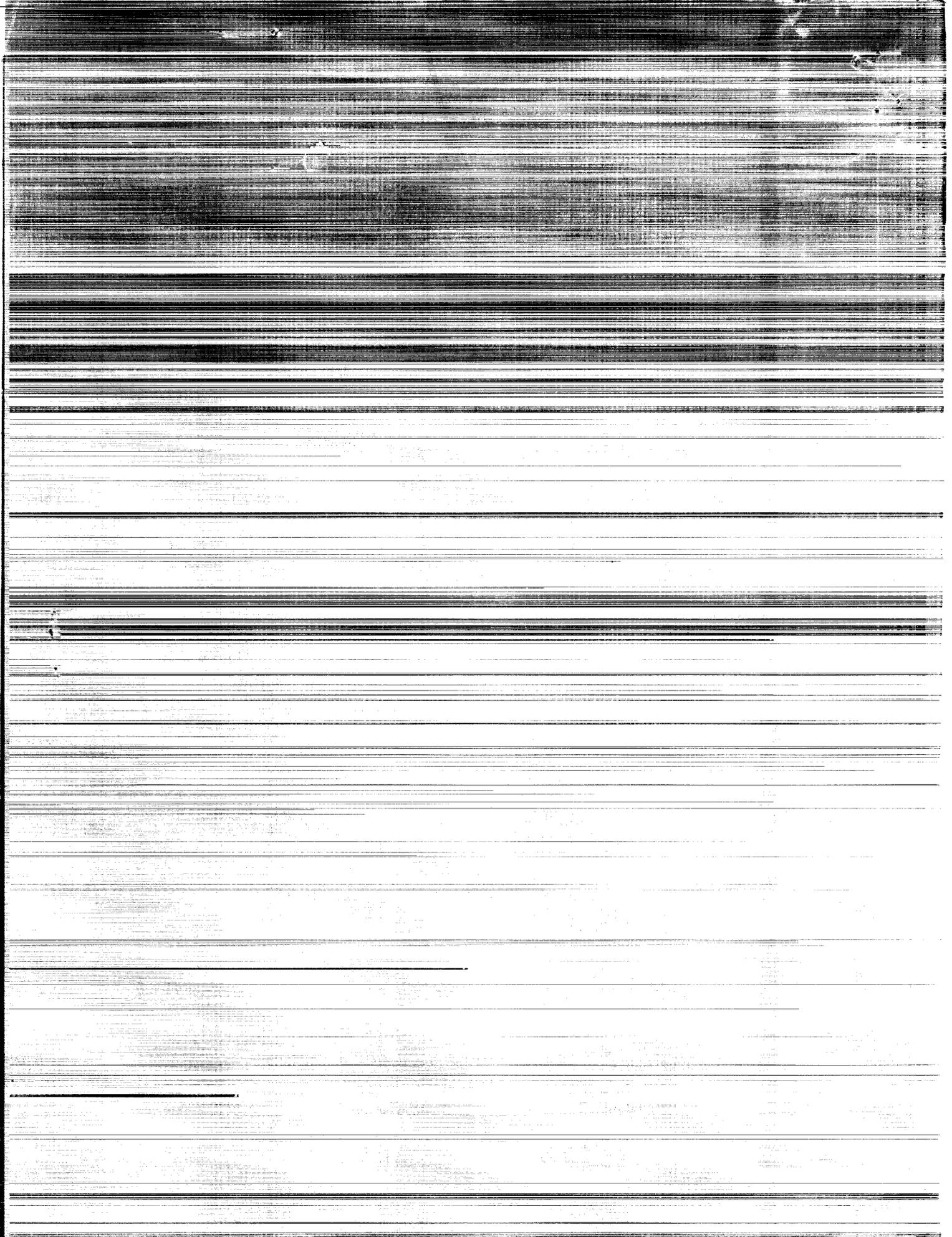
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COMPUTER PROGRAM FOR THE NUMERICAL SOLUTION OF
NONEQUILIBRIUM EXPANSIONS OF
REACTING GAS MIXTURES

By J. A. Lordi, R. E. Mates, and J. R. Moselle

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FOREWORD

The preparation of this report has been sponsored by the National Aeronautics and Space Administration under Contract No. NASr-109. The initial development of this computer program was sponsored under Contract No. AF 49(638)-792 by the United States Air Force Office of Scientific Research, under Contract No. AF 40(600)-804 by the USAF, as part of Project Defender by the Advanced Research Projects Agency, Department of Defense, and by Cornell Aeronautical Laboratory Internal Research. Modifications of the original program have been made in connection with research performed under Contract No. NASr-109 for the NASA and Contract No. AF 33(657)-8860 for the Aerospace Research Laboratories of the USAF.

The original version of the program was coded for use on an IBM 704 computer by Dr. John Fleck, Department Head, and Duane Larson of the Computer Services Department of CAL. The program was recoded in FORTRAN IV language for use on an IBM 7044 computer by Mrs. Camille Fiore, also of the Computer Services Department.

ABSTRACT

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This report describes a computer program developed at CAL for the numerical solution of quasi-one-dimensional, inviscid expansions of reacting mixtures. The analytical techniques employed and results obtained using the program have been previously reported. The details of the coding and operation of the program are discussed in this report. Program cards which have been written in FORTRAN IV language for use on an IBM 7044 computer are available upon request.

The computer program in its present form is capable of handling a general gas mixture, including up to 20 chemical species and 64 reactions. The species are assumed to undergo vibrational and electronic excitation in addition to coupled chemical reactions. The vibrational and electronic degrees of freedom are assumed to remain in thermodynamic equilibrium while the chemical reactions may be assumed to be either frozen, in equilibrium, or to proceed at finite reaction rates. Additional options in the program are provided for treating ionized nozzle flows, assuming the degree of vibrational excitation to be frozen at the reservoir value, or including the effects of moderate virial imperfections on high-density nozzle flows.

While the basic program computes the properties of an expansion from an equilibrium reservoir state through a nozzle of specified geometry, modifications of the program have been made to permit specifying the stream-tube pressure variation rather than an area distribution and to permit a finite-velocity, equilibrium or nonequilibrium initial state. The program cards for these modified versions of the program are also available upon request.

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List of Symbols

Note: Primed symbols denote dimensional quantities

- a_j constant in thermo-fit and harmonic oscillator expressions for chemical potential.
- A ratio of streamtube cross-sectional area to minimum cross-sectional area.
- A_i coefficients in polynomial expressions for $A(x)$ or $p(x)$ in the upstream region, also constant factor in i th reaction-rate constant.
- b_j coefficient of T' in thermo-fit expression for species enthalpy, also constant factor to be specified in harmonic-oscillator description of species properties as defined by Eq. (77).
- b_0 co-volume of molecules in excluded-volume correction for gas imperfections (Eq. (83)).
- B_i coefficients in polynomial expression for $A(x)$ and $p(x)$ in downstream region.
- c number of elements in mixture.
- c_j coefficient of $(T')^2$ in thermo-fit expression for species enthalpy.
- C_{p_j} specific heat at constant pressure for j th species ($C_{p_j} = C'_{p_j} / R_0$)
- C constant in density-fit relation (Eq. (45)).
- d_j coefficient of $(T')^3$ in thermo-fit expression for species enthalpy.
- D, D_1, D_2 intermediate variables defined by Eq. (52).
- e_j coefficient of $(T')^4$ in thermo-fit expression for species enthalpy.
- E'_{act_i} activation energy of i th reaction (cal/mole-°K).
- f mass flow per unit area.
- f_i slope at point i in Runge-Kutta integration scheme.

- F' specific Gibbs free energy (cal/gm).
- F_j functions defined by Eqs. (7) and (21).
- F_n exponential functions defined by Eq. (71).
- g function defined by Eq. (47).
- g_{lj} degeneracy of the l th electronic state of the j th species.
- h Planck's constant (6.62×10^{-27} erg-sec).
- h_j molar enthalpy of j th species ($h_j = h'_j/R_o T_o'$).
- h_{j_o}' formation enthalpy of j th species (cal/mole).
- H specific enthalpy of mixture ($H = H' m_o/R_o T_o'$).
- k Boltzmann's constant (1.379×10^{-16} erg/ $^{\circ}$ K/particle).
- k_j constant in thermo-fit expression for the chemical potential of the j th species.
- k_{f_i}, k_{r_i} forward and reverse rate constants for the i th reaction (cc/mole-sec or cc²/mole²-sec).
- K_{p_i} equilibrium constant for the i th reaction based on partial pressure.
- l characteristic length of nozzle (cm).
- m mass flow rate at minimum cross-section.
- m_j' mass of the j th particle (gm).
- M Mach number.
- M molecular weight (gms/mole).
- n_j number of atoms in the j th species.

- N_0 Avogadro's number (6.023×10^{23} particles/mole).
- p pressure ($p = p'/p_0'$).
- P intermediate variable in modified Runge-Kutta numerical integration scheme (Eq. (72)).
- P_i variable defined by Eq. (32).
- q_j mole-fraction of j th component when only independent species are present in a mixture.
- q_i exponent of third-body factor in i th reaction rate constant (Eq. (82)).
- Q_k number of gram-atoms of k th element in mixture.
- ν number of reactions included in chemical-kinetic model.
- R_0 universal gas constant ($1.98647 \text{ cal/mole-}^\circ\text{K}$, $82.0535 \frac{\text{cc atm}}{\text{mole } ^\circ\text{K}}$).
- R_{f_i}, R_{r_i} forward and reverse rates of the i th reaction (mole/cc-sec).
- s number of species in mixture.
- s_j molar entropy of j th species ($s_j = s_j'/R_0$).
- S' specific entropy of mixture (cal/gm $^\circ$ K).
- T temperature ($T = T'/T_0'$).
- u velocity ($u = u'/\sqrt{R_0 T_0'/m_0}$).
- U_{ij} third-body matrix defined by Eq. (82).
- x distance along nozzle axis or mid-plane ($x = x'/l$).
- X_j mole-fraction of j th species.
- y independent variable used to describe numerical integration procedure in Section 3.5.

- z compressibility factor.
- α constant in density-fit relation (Eq. (45)).
- α_{ij} matrix which specifies the elements and species present in the chemical model of a mixture.
- β_{ij} difference between the stoichiometric coefficients of the j th species on the product and reactant sides of the i th reaction.
- $\beta_i = \sum_j \beta_{ij}$.
- τ_j concentration of the j th species in units of moles of j per gram of mixture.
- ϵ_{lj} energy of the l th electronic state of the j th species ($\epsilon_{lj} = \frac{\epsilon'_{lj}}{R_0 T_0}$).
- $\epsilon_{\kappa i}$ value of $\delta \tau_i$ at which numerical integration of nonequilibrium solution is begun.
- η_i exponent of temperature in i th forward reaction-rate constant.
- θ_{rj} characteristic rotational temperature of the j th species ($\theta_{rj} = \theta'_{rj} / T_0'$).
- θ_{vj} characteristic vibrational temperature of the j th species ($\theta_{vj} = \theta'_{vj} / T_0'$).
- μ_j chemical potential of the j th species ($\mu_j = \mu'_j / R_0 T_0'$).
- ν_{ij}, ν'_{ij} stoichiometric coefficient of the j th species on the reactants and products side, respectively, of the i th reaction.
- $\nu_i = \sum_j \nu_{ij}$.
- ρ density ($\rho = \rho' / \rho_0'$).

$\tilde{\rho}$ effective density defined by Eq. (84) ($\tilde{\rho} = \tilde{\rho}'/\tilde{\rho}'_0$).

σ diameter of hard-sphere molecule.

τ_i variable defined by Eq. (33).

Subscripts

o reservoir conditions.

i pertaining to i th reaction.

j pertaining to j th species.

k pertaining to k th element.

l pertaining to l th electronic level.

Superscripts

()' prime symbol denotes dimensional quantity.

($\bar{\quad}$) bar symbol denotes infinite-rate equilibrium-flow value.

o refers to standard pressure condition (i. e. at 1 atm).

* conditions at throat of converging-diverging nozzle.

1. INTRODUCTION

In high temperature expansions of reacting gas mixtures the flow transit times are usually not sufficient to maintain equilibrium. Departures from equilibrium in turn affect the gasdynamic properties of the flow. Thus, in order to define the flows in high-temperature, hypersonic wind tunnels and rocket nozzles, and around hypersonic vehicles, the nonequilibrium effects on the fluid-mechanical properties of the flows must be taken into account. In the course of studying nonequilibrium phenomena in high-speed flows a computer program has been developed at CAL to obtain numerical solutions for quasi-one-dimensional, inviscid expansions of chemically reacting mixtures.¹ This program, which is also capable of generating solutions for the limiting cases of frozen and equilibrium flow, has proved to be a useful tool, not only in the above-mentioned situations, but also in the design and interpretation of fundamental experiments on nonequilibrium flows.

The purpose of this report is to describe the methods of solution contained in the program and the use of the program. The report is intended to accompany a copy of the program cards, which are available upon request. The program cards are in FORTRAN IV language and are coded for use on an IBM 7044 computer. This report is similar in purpose to Reference 2 which describes the program developed at CAL for computing the nonequilibrium flow behind normal and bow shock waves.

Several authors have reported numerical solutions for nonequilibrium expanding flows (e.g. Refs. 3-6). The initial work in this area at CAL was performed by Hall and Russo⁷ who obtained exact solutions for the nonequilibrium nozzle flow of a diatomic gas and a diatomic gas in an inert diluent. Then Boyer, Eschenroeder, and Russo⁸ reported equilibrium and approximate nonequilibrium solutions for nozzle expansions of air over a wide range of reservoir conditions. The approximate nonequilibrium solutions were obtained using the approximate freezing criterion of Reference 7 for the oxygen dissociation reaction. Then, the method of exact numerical solution for nonequilibrium expansion flows, which is contained in the computer program

described here, was presented by Eschenroeder, Boyer, and Hall.¹ Further development of this method, particularly for near equilibrium flow, was reported by Mates and Lordi.⁹ Applications of the computer program employed in the method of Reference 1 have included hypersonic wind tunnel flows of high-temperature air,^{10, 11} rocket-nozzle flows of hydrogen-carbon and hydrogen-oxygen mixtures,^{12, 13} and body streamtube flows of high-temperature air.¹⁴⁻¹⁷

The basic nozzle-flow computer program has the capability of obtaining numerical solutions for inviscid expansions of a reacting mixture from an equilibrium reservoir state through a streamtube of arbitrary geometry. The vibrational and electronic degrees of freedom are assumed to remain equilibrated with the translational and rotational modes; hence, the effects of vibrational and electronic relaxation on the chemistry are not included. The chemistry may be assumed to either be frozen, remain in equilibrium, or proceed at a finite rate in the expansion.

The method by which the composition and thermodynamic properties are found for a given mixture in chemical equilibrium at a specified temperature and pressure is discussed in Section 2.1. The extension of this method to describe an equilibrium expansion from the specified reservoir condition is discussed in Section 2.2. The computation for an expansion with frozen chemical composition is described in Section 2.3.

The procedure employed in the computer program for obtaining non-equilibrium expansions from a given reservoir condition is covered in Section 3. In Section 3.1, the general approach followed in solving the governing equations is described. The problem is basically one of obtaining the numerical solution for a system of coupled, first-order nonlinear differential equations.

Some difficulty is encountered in starting the solution in the reservoir because the gradients of the flow properties and composition are assumed to vanish there. The method employed to start the solution is to consider the nonequilibrium flow in the initial portion of the expansion to be a perturbation about the equilibrium solution. The analytical technique for locating a point in the expansion for starting the numerical integration is described in Section 3.2.

The modification of the technique of solution when the numerical integration is started upstream of the nozzle throat is covered in Section 3.3. The perturbation calculation used in the starting procedure is described in Section 3.4. Finally the numerical integration scheme used in the program and some of the numerical difficulties encountered in seeking nonequilibrium solutions are discussed in Section 3.5.

The method for specifying the kinetic model to be used in a given calculation is presented in Section 4. It is necessary to provide thermodynamic data for the specific enthalpy and chemical potential of each species included in the mixture. Also, the forward rate constants must be given for each reaction included in the gas model. The program which accompanies this report has a capacity for a gas model comprised of 20 species and 64 reactions. This capacity is determined only by the storage limitation. Certain options in the program could be eliminated if larger models need be considered.

The following alternative options, discussed in Section 5, are also included in the program. Nonequilibrium nozzle flows of ionized gases are considered by treating electrons as a separate chemical element. The vibrational mode can be assumed frozen at the reservoir degree of excitation while the chemical reactions are assumed to be frozen, in equilibrium or in nonequilibrium. Also, moderate gas imperfections may be accounted for in the initial near equilibrium portion of the expansion.

Instructions on the preparation of input data for the computer program are given in Section 6. Also, the calculation of a nozzle expansion of air is used to demonstrate the use of the program. Some of the results of this calculation are used to describe the form of the output data and to relate some of the experience gained in the use of the program. The results of the sample calculation also serve as a test case for the program.

In Section 7 a description of the function performed by each subroutine in the program is given. Flow charts are provided for the more complicated subroutines. These descriptions of the subroutines are intended as a guide in relating the analysis and governing equations presented in the report to the FORTRAN IV program. Also, a complete list of the FORTRAN symbols used in the program including a description of each is given in Section 7.

Modifications of the basic program have been made in order to treat other applications. One modification permits the solution of a nonequilibrium expansion from an equilibrium stagnation point through a specified pressure variation. This version of the program is applicable to the flow from a stagnation point through the streamtube nearest a body for which the surface pressure variation is known. The second modification of the program lends itself to the study of quasi-one-dimensional flows starting at a known nonequilibrium state and proceeding through either a specified area or pressure variation. This modification can be used to compute the relaxing flow behind shock waves (constant area streamtube) or along a streamline in the outer portion of a blunt-body flow field (specified pressure distribution). Yet another variation of the program is aimed at solving the nonequilibrium expansion from an equilibrium, but finite-velocity initial state. The application of this version of the program is to non-reflected-type shock tunnels or to the flow downstream of an MHD accelerator. The governing equations and the associated changes in the use of the program for these three modifications are discussed in the Appendix. The FORTRAN IV language program cards for each of the three modified versions of the program are also available upon request.

2. METHOD FOR COMPUTING EQUILIBRIUM RESERVOIR STATE, AND EQUILIBRIUM AND FROZEN FLOWS

The computer program calculates the equilibrium composition of a reservoir state for a specified temperature and pressure. Then the variation in composition and flow properties in an equilibrium expansion from the specified reservoir state can be computed. Also, the solution can be obtained for an expansion in which the composition is frozen at the reservoir value. The methods employed in these computations are described in this section.

2.1 Reservoir Calculation

The determination of the composition of a specified gas mixture for a given equilibrium state proceeds as follows. If there are c chemical elements and s chemical species in a multicomponent mixture the chemical formula of the i th species may be represented as

$$M_i = (\alpha_{i1}, \alpha_{i2}, \dots, \alpha_{ic}) \quad i = 1, 2, \dots, s \quad (1)$$

The specification of the species to be included in the calculation is then through the matrix α_{ij} , where α_{ij} is the number of atoms of the j th element per molecule of the i th species.

There are $(s-c)$ linearly independent relations which may be written as equilibrium formation reactions for the species in terms of the elements

$$M_i = \sum_{j=1}^c \alpha_{ij} M_j \quad i = c+1, c+2, \dots, s \quad (1a)$$

It is not necessary that the c chemical elements be chosen as independent species from which the other species are formed. In fact, the chemical elements are not necessarily included as separate species in the mixture. However, the independent species or components must be linearly independent combinations of the chemical elements. In other words, the rank of the α_{ij} matrix must be c .

As will be discussed in ensuing sections it is sometimes necessary to choose species other than the chemical elements as components. The species chosen as components are listed in the first c rows of the α_{ij} matrix. The computer program then writes the formation reactions for the $(s-c)$ dependent species in terms of the c components as

$$M_i = \sum_{j=1}^c \bar{\nu}_{ij} M_j \quad i = c+1, c+2, \dots, s \quad (2)$$

In addition to specifying the chemical species and the chemical elements to be included in a computation, the number of gram-atoms of each chemical element contained in the mixture Q_k must be given. The total number of gram-moles of the components which are present in the mixture is given by

$$\sum_{j=1}^c \alpha_{jk} q'_j = Q_k \quad k = 1, 2, \dots, c \quad (3)$$

This relation now specifies the element composition of the mixture in terms of the components rather than the chemical elements.

As shown in Reference 8, enforcing mass conservation in each of the formation reactions and global mass conservation lead to the following relation for the mole fractions of the components, X_j , in terms of the q'_j and the mole fractions of the other $(s-c)$ species

$$X_j = q_j - \sum_{i=c+1}^s [\bar{\nu}_{ij} - q_j (\bar{\nu}_i - 1)] X_i \quad j = c+1, c+2, \dots, s \quad (4)$$

where

$$q_j = \frac{q'_j}{\sum_j q'_j}, \quad \bar{\nu}_i = \sum_j \bar{\nu}_{ij}$$

At chemical equilibrium the dependent species concentrations are related to the concentrations of the components through the equilibrium constants for the formation reactions (Eq. (2)).

$$X_i = K_{p_i} p_i^{(\bar{v}_i - 1)} \prod_{j=1}^c X_j^{\bar{v}_{ij}} \quad i = c+1, c+2, \dots, s \quad (5)$$

where

$$K_{p_i} = \exp \left[\sum_{j=1}^s \bar{v}_{ij} \frac{\mu_j^\circ}{T} - \frac{\mu_i^\circ}{T} \right] \quad (6)$$

Equation (5) may be used to reduce Equations (4) to a set of c simultaneous equations for the concentrations of the independent species or components.

From the above development the calculation of the reservoir conditions for a given temperature and pressure is seen to require specification of the species included in the mixture, the chemical potential of these species, and the relative number of gram-atoms of each chemical element present. Having specified these items the g_j 's are used as initial estimates for the independent species concentrations. Using the condition of chemical equilibrium (Eq. (5)) the dependent species concentrations are computed and then the results are used to test whether Equation (4) is satisfied.

A Newton-Raphson iteration scheme is used to solve Equation (4) in the form

$$F_j(X_1, \dots, X_c) = g_j - \sum_{i=c+1}^s [\bar{v}_{ij} - g_j(\bar{v}_i - 1)] X_i - X_j = 0 \quad (7)$$

$j = 1, 2, \dots, c$

where again the $s-c$ dependent concentrations X_i , $i = c+1, s$ are found

from Equation (5). Newton's method for finding the $(n+1)$ correction to the estimates for X_j employs the linear term in a Taylor expansion about the previous value X_j^n . Enforcing the condition that $F_j = 0$ for the $(n+1)$ iteration, the fractional corrections for the n^{th} values of the X_j^n are found from

$$-F_j(X_j^n) = \sum_i \left(\frac{\partial F_j}{\partial X_i} \right)^n (X_i^{n+1} - X_i^n)$$

In the program these equations are written in the form

$$-F_j(X_j^n) = \sum_i X_i^n \left(\frac{\partial F_j}{\partial X_i} \right)^n \left(\frac{X_i^{n+1} - X_i^n}{X_i^n} \right) \quad (8)$$

Letting h_i^n denote the fractional correction

$$h_i^n = \frac{X_i^{n+1} - X_i^n}{X_i^n}$$

the $(n+1)$ estimates are obtained from

$$X_i^{n+1} = X_i^n (1 + h_i^n) \quad i = 1, \dots, c \quad (9)$$

If at a given step in the iteration, the $(n+1)$ guess for X_i found from Eq. (9) is zero or negative, then X_i^{n+1} is found from

$$X_i^{n+1} = X_i^n / 2 \quad (9a)$$

Once the species concentrations for the specified reservoir temperature and pressure have been found, the mixture molecular weight at the reservoir condition is calculated from

$$M = \sum_{j=1}^s X_j m_j \quad (10)$$

Then, the reservoir density may be computed from the equation of state

$$p' = p'(\rho', T', m) \quad (11)$$

For a mixture of ideal gases the equation is

$$p' = \frac{R_o \rho' T'}{m} \quad (11a)$$

Finally the specific reservoir or stagnation enthalpy is computed from

$$H = \sum_{j=1}^s X_j h_j \quad (12)$$

where, for a mixture of ideal gases, the species enthalpies, h_j , are functions only of temperature. In order to complete the reservoir computation both the species enthalpy and chemical potential must be specified. The method employed in the program for specifying these data is discussed in Section 4.

2.2 Equilibrium Expansions

In the above formulation, the determination of the equilibrium reservoir state was seen to require the condition of chemical equilibrium (Eq. (5)), the conservation of mass in the formation reactions (Eq. (4)), and global mass conservation. In addition, an equilibrium expansion requires the conservation of momentum and energy. For quasi-one-dimensional, inviscid flow the global conservation of mass, momentum and energy may be expressed as

$$\rho u A = m = \text{constant} \quad (13)$$

$$u du + \frac{1}{\rho} dp = 0 \quad (14)$$

$$H + \frac{1}{2} u^2 = H_o = \text{constant} \quad (15)$$

Now, the entropy of a chemically reacting mixture is⁹

$$\frac{S'}{R_o} = \frac{1}{\mathcal{M}} \sum_{j=1}^s X_j s_j = \frac{1}{\mathcal{M}} \left[\sum_{j=1}^s X_j s_j^{\circ} - \sum_{j=1}^s X_j \ln X_j - \ln p' \right] \quad (16)$$

where

$$s_j^{\circ} = \frac{h_j - \mu_j^{\circ}}{T} \quad (17)$$

The entropy change for a chemically reacting mixture may be written¹⁸

$$T' dS' = dH' - \frac{1}{\rho'} dp' - \sum_{j=1}^s \mu_j d\left(\frac{X_j}{\mathcal{M}}\right) \quad (18)$$

Then the condition of chemical equilibrium (Eq. (5)), may be rewritten as follows by enforcing a maximum in the free energy¹⁸

$$\sum_{j=1}^s \mu_j d\left(\frac{X_j}{\mathcal{M}}\right) = 0 \quad (19)$$

Also from Equations (14) and (15)

$$dH' = \frac{1}{\rho'} dp' \quad (20)$$

for a one-dimensional, inviscid flow. From Equations (18), (19), and (20) the inviscid flow of a mixture in chemical equilibrium is seen to be isentropic. Thus, an equilibrium expansion from a given reservoir state can be solved in the same manner as the reservoir state by adding the constraint that successive points in the expansion constitute an isentropic path.

The equilibrium solution is obtained by taking successive temperature steps from the reservoir value. The results of the previous step are used as initial estimates for the pressure and concentrations of the components, and the Newton-Raphson method is employed to find the correct pressure and composition at the specified temperature and entropy. The governing equation which must be satisfied by the c components and the pressure is

$$F_j = 0 \quad j = 1, \dots, c, c+1$$

where F_j for $j = 1, \dots, c$ is given by Equation (7) and

$$F_{c+1} = \sum_{i=1}^s X_i (s_i^\circ - \mathcal{M}_i S_o' - \ln X_i) - \ln p' \quad (21)$$

Equation (21), which specifies the isentropic path, provides the additional equation needed to find the pressure at successive temperature steps.

As cited above the equilibrium composition and pressure can be computed at successive temperature intervals. The other flow properties can then be found at each temperature as follows. Once the iteration for the pressure and composition converges, the local molecular weight is computed from Equation (10). Then the density is obtained from the equation of state (Eq. (11a)). If T' , p' , and ρ' are nondimensionalized by the reservoir values the state equation may be written

$$p = \rho \frac{T m_e}{m} \quad (11b)$$

The static enthalpy for the mixture is computed from Equation (12) and the velocity from the energy equation (Eq. (15)). The value of the Mach number at each point is obtained from the following formula.

$$M = u / (p - p_b / \rho - \rho_b)^{1/2} \quad (22)$$

where p_b and ρ_b are the values of p and ρ at the previous computational step.

In the above procedure the solution for an expansion in chemical equilibrium is obtained as a function of temperature. In a nozzle-flow expansion it is desired to obtain the solution as a function of area ratio. Here the following procedure is employed to find the equilibrium-flow solution as a function of area ratio. The equilibrium solution is obtained at successive temperature intervals, computing the flux, ρu , at each point. The maximum

ρu and the corresponding temperature determine the throat conditions and the critical mass flow for the equilibrium expansion. Having thus found the mass flow the area ratio corresponding to each temperature can be found from Equation (13).

In the computer program the throat, i. e., the maximum ρu is located and then the equilibrium-flow calculation is restarted at the reservoir. The solution is then obtained at fixed temperature intervals, computing the area ratio at each point. Since the temperature intervals become very small when seeking the critical mass flow, the results of that calculation are not printed except for the throat values. Relatively few steps are repeated by this restarting of the calculation at the reservoir.

The maximum value of ρu is found by the following method. At each temperature step the value of ρu is compared with the value at the previous two steps. Denoting the values of ρu as f_1 , f_2 , and f_3 in order of decreasing temperature, the computation is continued at the original interval in temperature until $f_3 \leq f_2$. Once ρu passes through a maximum, the temperature step size is refined to locate the maximum precisely.

The refinement of the temperature step proceeds on the following basis. If $f_3 = f_2$, the temperature interval is halved and the computation restarted at the temperature corresponding to f_2 . If $f_3 < f_2$ the computation is resumed with the smaller temperature interval starting at the temperature corresponding to f_1 . The temperature step is continually reduced whenever $f_3 \leq f_2$. When the temperature interval becomes less than a specified value the sharpness of the maximum is examined. If $(f_1 + f_3 - 2f_2)/f_2$ is less than .00001 the throat temperature is set equal to that corresponding to the current value of f_2 . If the above condition is not satisfied a parabolic fit for $f(T)$ is obtained from the current values of f_1 , f_2 , f_3 .

$$f = f_2 - \frac{f_3 - f_1}{2(\Delta T)} (T - T_2) + \frac{f_1 + f_3 - 2f_2}{2(\Delta T)^2} (T - T_2)^2 \quad (23)$$

where ΔT is the size of the temperature step and T_1 , T_2 , and T_3 are the temperatures corresponding to f_1 , f_2 , and f_3 . The throat temperature is then taken as that value for which df/dT obtained from Eq. (23) vanishes.

$$T^* = T_2 + \frac{(f_2 - f_1) \Delta T}{2(f_1 + f_3 - 2f_2)} \quad (24)$$

The equilibrium solution is obtained in intervals of T of .01. The solution can be terminated at any specified temperature below the throat temperature. Since intervals of .01 are taken, the specified temperature stop must be $\geq .01$ because the Newton-Raphson iteration procedure diverges for $T \approx 0$, within the digital accuracy. If the equilibrium solution were desired at temperatures below .01 T' then the program could be modified to decrease the step size below a given temperature.

2.3 Frozen Flow

The computer program also contains the option of generating the solution for an expansion in which the chemical composition is frozen at the reservoir state. As may be seen from Equation (18) an inviscid, frozen expansion is also isentropic. Using the value obtained for the reservoir entropy the frozen flow may be determined by direct algebraic computation.

The procedure employed for the frozen flow solution is to specify a temperature interval below the reservoir temperature. For the given temperature h_j and μ_j° are calculated for each species. Then using the reservoir entropy and composition the pressure is obtained from Equations (16) and (17).

$$p = \exp \left\{ - \frac{S_o' m_o}{R_o} + \left[\sum_{j=1}^s X_j (s_j^\circ - \ln X_j) \right] - \ln p_o' \right\} \quad (25)$$

Next the density and static enthalpy are calculated from the thermal and caloric equations of state (Equations (11b) and (12)). The velocity may then be evaluated from the energy equation (15) using the reservoir, or stagnation enthalpy.

By following the above procedure the frozen flow solution is obtained at specified temperatures. The solution is found in terms of the nozzle area ratio by the same method employed for the equilibrium solution. The

maximum in ρu is found in order to locate the nozzle throat. The area ratio is then found at each computational step using the continuity equation. Also a Mach number is computed at each step using Equation (22).

3. NONEQUILIBRIUM EXPANDING FLOWS

In this section the nonequilibrium flow computation is discussed. First the analysis, governing equations, and the general method employed in the solution are discussed. Then the method for starting the numerical integration and the perturbation calculation used in the starting procedure are described. Finally the numerical integration scheme used in the program is presented.

3.1 Analysis and Governing Equations

The fluid considered is a multicomponent mixture composed of s chemical species. These species undergo n coupled, chemical reactions of the form



where ν_{ij} and ν'_{ij} are the stoichiometric coefficients of the reactants and products and k_{fi} and k_{ri} are the reaction-rate constants for the forward and reverse reactions, respectively. Notice that these reactions differ from the formation reactions (Equation (1)) and that here n is not necessarily equal to $s-c$. However, the equilibrium formation reactions may appear in the nonequilibrium reaction mechanism.

The nonequilibrium flow is governed by the conditions of conservation of mass, momentum, and energy (Equations (13)-(15)), the thermal and caloric state equations (Equations (11) and (12)), and the species conservation equations. Again the enthalpy and chemical potential for each species must be specified. For the nonequilibrium flow the condition that the chemical elements be conserved is written

$$\sum_{j=1}^s \alpha_{jk} \gamma_j = Q_k \quad k = 1, 2, \dots, c \quad (27)$$

or alternatively

$$\sum_{j=1}^s \alpha_{jk} \frac{dx_j}{dx} = 0 \quad k = 1, 2, \dots, c \quad (28)$$

In the nonequilibrium calculation the equations are written using the concentration variable x_j , which is in units of moles per gram.

The relation between the concentration variable X_j used in the equilibrium flow calculation and that used in the nonequilibrium calculation, x_j , is

$$X_j = x_j M \quad (29)$$

Since the species gradients along the nozzle are connected by the element conservation equation (Eq. (28)) there are $(s - c)$ independent species conservation equations given by

$$\frac{dx_j}{dx} = \sum_{i=1}^c \beta_{ij} P_i x_i \quad j = c+1, c+2, \dots, s \quad (30)$$

where

$$\beta_{ij} \equiv \nu'_{ij} - \nu_{ij} \quad (31)$$

$$P_i = \frac{l R_{f_i}}{\rho' u'} = l \rho_0'^{(\nu_i-1)} \left(\frac{M_0}{R_0 T_0'} \right)^{1/2} \frac{\rho^{(\nu_i-1)}}{u} k_{f_i} \prod_{j=1}^s x_j^{\nu_{ij}} \quad (32)$$

$$x_i = 1 - \frac{R_{r_i}}{R_{f_i}} = 1 - \frac{\rho' \beta_i}{K_i} \prod_{j=1}^s x_j^{\beta_{ij}} \quad (33)$$

In the above equations x is the axial distance along the nozzle, x' , divided by the characteristic length l . Also, R_{f_i} and R_{r_i} are the forward and reverse rates of the i th reaction.

Due to the complexity of the chemical production terms on the right hand side of the species conservation equations, the nonequilibrium solution

is obtained numerically. However, since all the flow gradients are assumed zero in the reservoir the integration cannot be started there. In the case of nonequilibrium solutions for diatomic gases the integration has been started using a series expansion in inverse powers of the nozzle area ratios.⁷ This procedure would be quite complicated for a multicomponent mixture. However, in the initial portion of the nozzle, the solutions for a diatomic gas indicate that the flow remains very near equilibrium. Thus, the procedure used to start the numerical integration in the present case is to treat the initial portion of the nonequilibrium solution as a perturbation about the infinite-reaction-rate equilibrium solution. The computation of the perturbations is discussed in Section 3.4. The procedure for starting the numerical integration and the governing equations for the nonequilibrium computation are discussed below.

The nonequilibrium expansion is governed by 5+3 first order differential equations, element conservation, Equation (27), species conservation, Equation (30), and the conservation of mass, momentum, and energy. For the nozzle-flow problem the area distribution is specified and the unknowns are the species concentrations, u , T , and ρ . The thermal and caloric state equations are used to relate p and H to these dependent variables. In the computer program for the numerical solution of this problem the governing equations are arranged as follows. The energy and state equations are used to eliminate the pressure and velocity derivatives in the momentum and continuity equations. Differentiating Equations (13) and (15) and eliminating du/dx yields

$$\frac{d \ln \rho}{dx} + \frac{d \ln A}{dx} - \frac{1}{u^2} \frac{dH}{dx} = 0$$

Using Equation (12) to rewrite dH/dx yields

$$\sum_{j=1}^5 h_j \frac{dx_j}{dx} + \sum_{j=1}^5 x_j C_{p_j} \frac{dT}{dx} - \frac{u^2}{m_0} \frac{d \ln \rho}{dx} - \frac{u^2}{m_0} \frac{d \ln A}{dx} = 0 \quad (34)$$

where

$$C_{p_j} = \frac{dh_j}{dT} \quad (35)$$

Now differentiating Equations (11) and (15) and substituting the results in (14), the momentum equation becomes

$$-\frac{dH}{dx} + \frac{T m_o}{m} \frac{d \ln \rho}{dx} + \frac{m_o}{m} \frac{dT}{dx} - \frac{m_o T}{m^2} \frac{dm}{dx} = 0$$

Using Equation (12) and the fact that

$$\sum_{j=1}^s r_j = \frac{1}{m}$$

leads to

$$\sum_{j=1}^s (T - h_j) \frac{dr_j}{dx} + \sum_{j=1}^s r_j (1 - C_{p_j}) \frac{dT}{dx} + \frac{T}{m} \frac{d \ln \rho}{dx} = 0$$

Using Equation (34) this result becomes

$$\sum_{j=1}^s \frac{dr_j}{dx} + \frac{1}{T} \sum_{j=1}^s r_j \frac{dT}{dx} + \left(\frac{1}{m} - \frac{u^2}{m_o T} \right) \frac{d \ln \rho}{dx} - \frac{u^2}{m_o T} \frac{d \ln A}{dx} = 0 \quad (36)$$

For a prescribed geometry, Equations (28), (30), (34), and (36) are a set of $s+2$ equations for the unknown slopes $\frac{dr_j}{dx}$, $\frac{dT}{dx}$, and $\frac{d \ln \rho}{dx}$ at a point in the numerical integration. The quantity $d \ln \rho / dx$ is not eliminated from Equations (34) and (36) because of the procedure adopted for starting nonequilibrium solutions upstream of the nozzle throat.

As discussed in more detail in Section 6, the nozzle geometry may be specified in either of two ways. For a wedge, cone, or hyperboloid geometry the area ratio at a given nozzle station is given by a simple quadratic in x . Different shapes may be specified for the converging and diverging sections. Accordingly, for $x < 0$ the area ratio is given by

$$A(x) = A_1 + A_2 x + A_3 x^2 \quad (37)$$

and for $x > 0$

$$A(x) = B_1 + B_2 x + B_3 x^2 \quad (37a)$$

The other method of specifying the nozzle geometry is applicable to contoured shapes. In this case the nozzle area-ratio variation may be fitted with a polynomial in seven different intervals, two in the converging section and five in the diverging section. For reasons which become evident in Section 3.2 the polynomials in the first intervals in both sections must be quadratics. The polynomials in the other regions may be up to sixth order.

Once the state of the flow is known at a given nozzle station x and $\frac{d \ln A}{dx}$ is obtained from the specified $A(x)$, slopes $d\tau_j/dx$, dT/dx , and $d \ln \rho/dx$ may be calculated from the above set of $s+2$ differential equations. These equations may then be integrated numerically to obtain the temperature and composition at a new nozzle location. The numerical technique employed is discussed in Section 3.5. Once a new temperature and composition have been determined the enthalpy may be calculated from Equation (12), the velocity from Equation (15), the density from Equation (13), and the pressure from Equation (11). At each point in the nonequilibrium solution a Mach number is calculated based on a "speed of sound" given by $(dp/dx/d\rho/dx)^{1/2}$.

$$M = \frac{1}{\sqrt{1 + (d \ln A/dx / d \ln \rho/dx)}} \quad (38)$$

Notice that the above defined speed of sound is not in general the speed of propagation of small disturbances in a relaxing medium.¹⁹ Also, at each point a value of the entropy is computed from Equation (16).

In evaluating the density from the continuity equation (Equation (13)) it is tacitly assumed that m , the critical mass flow is known. If the flow is appreciably out of equilibrium upstream of the nozzle throat, m is not known at the outset of the calculation. The method for handling this situation is discussed below together with the description of the procedures for starting the numerical solution.

The nonequilibrium flow solution may be stopped at either a specified nozzle station or at the same temperature which is used for the frozen and equilibrium solutions. Since the nonequilibrium solution may be time consuming (i. e. longer than 15 minutes on an IBM 7044) for a complex, chemical-

kinetic model, provision can also be made for saving the computation at a given point, as described in Section 7.

3.2 Procedure for Starting a Nonequilibrium Solution

As mentioned above the nonequilibrium solution cannot be started in the reservoir. The solution is started by considering the nonequilibrium solution to be a perturbation about the equilibrium solution in the early stages of the expansion. Thus, as for the equilibrium flow, the nonequilibrium solution begins with taking fixed temperature steps from the reservoir state. At each temperature the equilibrium composition, pressure, density, and velocity are computed in the same manner as described in Section 2.2. In addition, the equilibrium values of dx_j/dx , dT/dx , and $d \ln p/dx$, which are needed in the perturbation calculation, are computed at each point. Equations (28), (34), and (36) remain valid for infinite-rate equilibrium flow. However, the rate Equations (30) cannot be used to determine the remaining ($s-c$) species gradients in equilibrium. These additional equations for the species gradients are obtained by differentiating the equation which expresses the condition of chemical equilibrium, i. e. Equation (5):

$$\frac{1}{x_j} \frac{dx_j}{dx} - \sum_{k=1}^c \frac{\bar{v}_{jk}}{x_k} \frac{dx_k}{dx} + \sum_{k=1}^c \frac{\bar{v}_{jk}}{T} \left(\frac{h_k}{T} - 1 \right) \frac{dT}{dx} - \left(\frac{h_j}{T^2} - \frac{1}{T} \right) \frac{dT}{dx} - (\bar{v}_j - 1) \frac{d \ln p}{dx} = 0 \quad j = c+1, \dots, s \quad (39)$$

The van't Hoff equation which can be written

$$\begin{aligned} \frac{\partial \ln K_j}{\partial T} &= \sum_{k=1}^c \frac{\bar{v}_{jk}}{T} \left(\frac{h_k}{T} - 1 \right) - \left(\frac{h_j}{T^2} - \frac{1}{T} \right) \\ &= - \frac{(\bar{v}_j - 1)}{T} + \frac{d(\mu_j^0/T)}{dT} - \sum_{k=1}^c \bar{v}_{jk} \frac{d(\mu_k^0/T)}{dT} \end{aligned} \quad (40)$$

has been used in deriving Equation (39). Equation (39) may also be obtained by enforcing the conditions of chemical equilibrium ($\tau_i = 0$ and $dx_i/dx = 0$) in Equation (33). The result is then

$$-\sum_{j=1}^s \frac{\beta_{ij}}{\chi_j} \frac{d\chi_j}{d\kappa} + \sum_{j=1}^s \frac{\beta_{ij}}{T} \left(\frac{h_j}{T} - 1 \right) \frac{dT}{d\kappa} - \beta_i \frac{d \ln p}{d\kappa} = 0 \quad (39a)$$

$i = 1, \dots, \kappa$

Only $(s-c)$ of Equations (39a) are linearly independent⁹ as may be seen by noting that the $\kappa \chi'_i$ may be written in terms of the $(s-c) \chi'_j$ for the equilibrium formation reactions (Equations (2)).

$$(1 - \chi_i) = \frac{R_{n_i}}{R_{f_i}} = \prod_{j=1}^{s-c} (1 - \chi_j)^{-\beta_{i,j+c}} \quad (41)$$

In other words, only the formation reactions need be considered for a flow in chemical equilibrium. If the β_{ij} matrix is written for the formation reactions it is seen that

$$\begin{aligned} \beta_{ij} &\longrightarrow \bar{\nu}_{ij} & \text{for } j = 1, \dots, c \\ \beta_{ij} &\longrightarrow -\delta_{i,j-c} & \text{for } j = c+1, \dots, s \end{aligned} \quad (42)$$

thereby demonstrating the equivalence of (39) and (39a).

In order to calculate the equilibrium values of $\frac{d\chi_j}{d\kappa}$, $\frac{dT}{d\kappa}$, and $\frac{d \ln p}{d\kappa}$ from Equations (28), (34), (36) and (39) the value of $\frac{d \ln A}{d\kappa}$ must be known. The value of the area ratio at a temperature step is calculated from Equation (13) using the results of the equilibrium calculation for ρ and u , and the equilibrium-flow value of the critical mass flow, m . In the nozzle flow program the area distribution is specified as a polynomial in κ , the distance along the nozzle, taking the origin at the geometric throat. Having determined the area ratio at a given point in the calculation the specified formula for $A(\kappa)$ is inverted to obtain κ at the current computational point. Then, using this value of κ , $d \ln A / d\kappa$ can be calculated from the specified description of the nozzle.

As mentioned in the previous section the nozzle geometry may be specified in either of two ways. When a simple shape, i. e., a wedge, cone or hyperboloid geometry, is used $A(\kappa)$ is a quadratic expression in κ . For the case of a simple geometry then, κ may be obtained from a given area using the relations

$$\kappa = - \frac{A_2 + \sqrt{A_2^2 - 4A_3(A_1 - A)}}{2A_3}, \quad \kappa < 0 \quad (44)$$

$$\kappa = - \frac{B_2 - \sqrt{B_2^2 - 4B_3(B_1 - A)}}{2B_3}, \quad \kappa > 0 \quad (44a)$$

The signs employed in the quadratic formula are determined by the behavior of $A(\kappa)$ in the converging and diverging sections.

The other method for specifying the nozzle geometry is to use a series of polynomial fits to actual nozzle contours. In the first intervals upstream and downstream the polynomials must be quadratics. In quadratic regions Equations (44) or (44a) are used to invert the $A(\kappa)$ expression to find κ . In the intervals employing higher-order polynomials a Newton-Raphson iteration procedure is used to invert the $A(\kappa)$ relation. The value of κ at the previous step is used as an initial estimate in this procedure. Since quadratic expressions are used in the first intervals in both sections, initial estimates for κ which lie in the correct interval are ensured. The correct polynomial to be used for $A(\kappa)$ is found by comparing A with the values at the dividing points between intervals.

Summarizing the discussion of the starting procedure to this point: the equilibrium flow solution is obtained as a function of temperature. Using the equilibrium calculation for ρu and the equilibrium flow value of m , $A(\kappa)$ is calculated at each point; the specified relation for A in terms of κ is then inverted to find κ . In turn, the calculated value of κ is used to evaluate $d \ln A / d \kappa$ at the current step. Having computed the equilibrium composition and flow properties and evaluated $d \ln A / d \kappa$, the equilibrium values of $dx_j / d \kappa$, $dT / d \kappa$, and $d \ln p / d \kappa$ may be found from Equations (28), (34), (36), and (39).

The values of the above derivatives are then used to obtain the perturbations of the composition and flow properties from their infinite-rate equilibrium values. This procedure is continued until the perturbations are large enough to start the numerical integration of the nonequilibrium solution.

The calculation of the perturbations and the size they must attain to start the numerical integration are discussed in ensuing the section.

Once the perturbation calculation indicates that the nonequilibrium solution can be started, the perturbations in the species concentrations and the temperature are added to the equilibrium flow values. Then the static enthalpy and velocity are recomputed using Equations (12) and (15), respectively. The density is obtained from Equation (13) using the equilibrium-flow, critical mass flow and the area ratio computed in the starting procedure. The pressure is then evaluated from the state Equation (11b). Using the thus obtained approximations to the nonequilibrium flow composition and properties at a point, the slopes $\frac{dT_i}{dx}$, $\frac{dT}{dx}$, and $\frac{d \ln \rho}{dx}$ can be calculated from the nonequilibrium flow equations as discussed in Section 3.1. Notice that the nonequilibrium solution then proceeds in steps of x instead of T as in the starting procedure. Also, at each new value of x the area ratio, $A(x)$, and $d \ln A / dx$ can be calculated directly from the specified relations for the nozzle geometry. The rest of the nonequilibrium solution then proceeds as described in Section 3.1.

If the departure of the flow from equilibrium is expected to be small upstream of the nozzle throat then the starting procedure may be initiated at the nozzle throat. Provision is made for taking a variable temperature step from the equilibrium throat conditions. After this initial step the starting procedure continues at the usual temperature interval employed in the frozen and equilibrium computations ($0.01 T_0'$). If the starting procedure is initiated at the reservoir and the solution approaches the nozzle throat without the perturbations becoming large, the calculation is continued in the same manner as if the option for starting at the throat were exercised.

3.3 Modification of Nonequilibrium Calculation when Integration is Started Upstream of Nozzle Throat

In discussing the nonequilibrium calculation and the starting procedure, the critical mass flow was assumed to be the equilibrium-flow value. If the flow is appreciably out of equilibrium upstream of the nozzle throat then the

critical mass flow is not known beforehand. The results of earlier studies⁷ indicated that the nonequilibrium density distribution upstream of the throat and the critical mass flow differed only slightly from the equilibrium flow values. On this basis an inverse procedure is used in the upstream region.

When the perturbation calculation (Section 3.4) indicates that the numerical integration of the nonequilibrium solution should be started upstream, the following procedure is adopted. The equilibrium flow density distribution and critical mass flow are considered to be the prescribed boundary condition instead of the specified nozzle geometry. The equilibrium density is assumed to be related to the specified area distribution by

$$(\rho A)^\alpha (1 - \rho^\alpha) = C \quad (45)$$

This is the form of the relation between ρ and A for an ideal gas where $\alpha = \gamma - 1$. In using Equation (45) to describe the $\rho(A)$ relation, the constants α and C are evaluated from the following conditions at $A = 1$: $\rho = \rho^*$ (computed for equilibrium flow) and $dA/d\rho = 0$. Differentiating (45) and setting $A = 1$, $dA/d\rho = 0$, and $\rho = \rho^*$ yields

$$(\rho^*)^\alpha (\alpha + 2) = 2 \quad (46)$$

This resulting equation for α is solved using a Newton-Raphson-type iteration to satisfy the condition

$$g(\alpha) = (\rho^*)^\alpha (\alpha + 2) - 2 = 0 \quad (47)$$

Since $g(\alpha)$ must be zero, the $n+1$ estimate for α is given by

$$\alpha^{n+1} = \alpha^n - \frac{g(\alpha^n)}{\left. \frac{\partial g}{\partial \alpha} \right|_{\alpha=\alpha^n}} \quad (48)$$

where $g(\alpha^{n+1})$ is obtained from a two-term Taylor series expansion about α^n .

If Equation (46) is rewritten as

$$\alpha \ln \rho^* + \ln(\alpha + 2) = \ln 2$$

and $\ln(\alpha+2)$ is expanded in a Taylor series about $\alpha = 2$, retaining the first three terms, the following approximation is obtained for α :

$$\alpha \approx 4 + 8 \ln \rho^* \quad (49)$$

This result is used as an initial estimate for α in the iterative solution of Equation (46). Once α is evaluated then C may be found by substituting $\rho = \rho^*$ and $A = 1$ in Equation (45).

Having found the constants α and C , the density-area relation may then be employed in the nonequilibrium solution upstream of the throat. At each new value of x in the numerical integration the area ratio is found from the specified geometry. The equilibrium flow density and $d \ln \rho / dx$ are then evaluated as follows. Again a Newton-Raphson-type iteration procedure is employed to find the value of ρ which satisfies Equation (45) for the given values of A , α , and C . In this case the relation to be satisfied is

$$f = (\rho A)^2 (1 - \rho^\alpha) - C = 0 \quad (50)$$

and the $n+1$ value for ρ is obtained from a three-term Taylor series expansion about the n^{th} estimate

$$f(\rho^{n+1}) \approx f(\rho^n) + \left. \frac{\partial f}{\partial \rho} \right|_{\rho=\rho^n} (\rho^{n+1} - \rho^n) + \left. \frac{\partial^2 f}{\partial \rho^2} \right|_{\rho=\rho^n} \frac{(\rho^{n+1} - \rho^n)^2}{2} = 0 \quad (51)$$

This equation is then a quadratic equation for $\Delta \rho = \rho^{n+1} - \rho^n$. The solution is given by

$$\Delta \rho = \frac{-D_1 \pm \sqrt{D_1^2 - 2DD_2}}{D_2} \quad (52)$$

where

$$D = f(\rho^n) \quad D_1 = \left. \frac{\partial f}{\partial \rho} \right|_{\rho=\rho^n} \quad D_2 = \left. \frac{\partial^2 f}{\partial \rho^2} \right|_{\rho=\rho^n}$$

The sign in the quadratic formula is chosen so that the smaller $|\Delta \rho|$ is used. The density from the previous computational step is used as an initial estimate in solving for ρ at the new x .

In order to compute the nonequilibrium solution when $\rho(x)$ is specified $d \ln \rho / dx$ must be calculated. Once the equilibrium flow density has been evaluated, $d \ln \rho / dx$ may be calculated using the values of A and $d \ln A / dx$ corresponding to the actual specified geometry, and the relation

$$\frac{d \ln \rho}{dx} = \frac{2C}{\alpha(\rho A)^2 - (\alpha + 2)C} \frac{d \ln A}{dx} \quad (53)$$

This relation may be derived by logarithmically differentiating Equation (45). The nonequilibrium flow Equations (28), (30), (34) and (36) are then solved for dx_j/dx , dT/dx , and $d \ln \tilde{A} / dx$, where \tilde{A} is the cross-section of the nonequilibrium streamtube flow having the density variation $\rho(x)$, and the numerical solution proceeds. For a converging-diverging nozzle $d \ln A / dx$ passes through zero at the geometric throat. In the governing equations for the flow of a reacting gas through a nozzle, a branch point exists where the flow velocity becomes equal to the "frozen" sound speed. Since the frozen sound speed for a reacting gas is always slightly larger than the velocity at the point of minimum cross section [i. e., $\sqrt{(dp/dx)/(k\rho/dx)}$]³ this branch point will occur slightly downstream of the geometric throat. Hence the solution for the upstream region is continued until the value of the area ratio, $\tilde{A}(x)$, reaches a value which is typically downstream of this singular point in the solution. Then the solution is continued in the usual way, i. e. by specifying $A(x)$ and solving for $\rho(x)$. In the downstream region the specified $A(x)$ is modified to obtain a smooth transition from the $\tilde{A}(x)$ obtained using the inverse procedure in the upstream region.

When the nonequilibrium calculation is switched from the upstream region to the downstream region the calculated value of $d \ln A / dx$ is compared with the value given by the modified area-ratio relation for the downstream section. If these two values differ by greater than a specified amount, the switch from the upstream to downstream region is made at a smaller value of x . Also, once the switch from the upstream region to the downstream region has been effected, the value of $d \ln \rho / dx$ computed at each point in the nonequilibrium solution is monitored. If $d \ln \rho / dx$ becomes positive slightly downstream of the switching point from the upstream to the downstream

region, this switching point is moved further downstream. If $d \ln \rho / dx$ becomes positive at a significant distance from the upstream to downstream switching point the reason cannot be attributed to the branch point in the solution and the calculation is stopped.

As evident in the present discussion, when the solution is started in the upstream region the area-ratio variation of the nonequilibrium solution is slightly different from the specified geometry. Consequently, the area-ratio variation for this case does not become unity at the throat. In principle this area ratio distribution should then be renormalized using the value at the minimum cross-section. In practice, this value differs from unity by less than 1% and renormalization is unnecessary.

3.4 Perturbation Calculation Used in Starting Nonequilibrium Flow Solution

As mentioned earlier the numerical integration cannot be started at the reservoir because there the gradients of the flow properties vanish. The procedure adopted in the present program is to start the numerical integration by considering the nonequilibrium flow solution to be a perturbation about the infinite-rate equilibrium flow in the initial stage of the expansion. Let the species concentrations and flow properties be given by

$$\begin{aligned} \chi_j &= \bar{\chi}_j + \delta \chi_j \\ T &= \bar{T} + \delta T \\ \rho &= \bar{\rho} + \delta \rho \end{aligned} \quad (54)$$

where the bar symbol denotes the infinite rate equilibrium value. The element conservation equation (Eq. (27)) yields

$$\sum_{j=1}^s \alpha_{j^k} \delta \chi_j = 0 \quad k = 1, 2, \dots, c \quad (55)$$

Similarly substituting (54) in the species conservation equations (Eq. (30)) yields, to first order,

$$\frac{d\bar{\chi}_i}{d\bar{x}} + \frac{d(\delta \chi_i)}{d\bar{x}} = \sum_{i=1}^n \beta_{ij} \left[\bar{P}_i \bar{\chi}_i + \bar{\chi}_i \delta P_i + \bar{P}_i \delta \chi_i \right]$$

Now an important point in the perturbation procedure arises. The bar symbol denotes that a quantity is to be evaluated using the equilibrium flow values of the dependent variables. Thus, \bar{P}_i does not denote the value of P_i for the infinite-rate equilibrium flow, but rather P_i evaluated using the actual value of h_{T_i} and $\bar{\rho}$, \bar{T} , and $\bar{\tau}_j$. Since, $\bar{\tau}_i$ is the same as in the equilibrium flow, $\bar{\tau}_i = 0$ and the above equation becomes

$$\frac{d\bar{\tau}_i}{dx} + \frac{d(\delta\tau_i)}{dx} = \sum_{i=1}^n \beta_{ij} \bar{P}_i \delta\tau_i \quad j = c+1, \dots, s \quad (56)$$

The $\delta\tau_i$'s may be written in terms of $\delta\tau_j$, δT , and $\delta\rho$ retaining only first-order terms as

$$\delta\tau_i = \frac{\partial\bar{\tau}_i}{\partial T} \delta T + \frac{\partial\bar{\tau}_i}{\partial\rho} \delta\rho + \sum_{j=1}^s \frac{\partial\bar{\tau}_i}{\partial\tau_j} \delta\tau_j$$

Evaluating the coefficients of the perturbations leads to^{1,9}

$$\delta\tau_i = -\sum_{j=1}^s \frac{\beta_{ij}}{\bar{\tau}_j} \delta\tau_j + \sum_{j=1}^s \frac{\beta_{ij}}{\bar{T}} \left(\frac{h_j}{\bar{T}} - 1 \right) \delta T - \frac{\beta_i}{\bar{\rho}} \delta\rho \quad (57)$$

From the energy Equation (15)

$$\delta H + \bar{u} \delta u = 0$$

Using Equations (12) and (13) this becomes

$$\frac{m_o}{\bar{u}^2} \sum_{j=1}^s \bar{h}_j \delta\tau_j + \frac{m_o}{\bar{u}^2} \sum_{j=1}^s \bar{\tau}_j \frac{dh_j}{dT} \delta T - \frac{\delta\rho}{\bar{\rho}} = 0 \quad (58)$$

The remaining governing equation, the momentum equation, has not as yet been perturbed. The perturbed momentum equation would involve derivatives of the perturbations. The use of the perturbed momentum equation would then make the solution for the perturbation quantities quite difficult. At this point two approximations based on the pure diatomic gas studies⁷ are introduced

$$\delta\rho = 0 \quad (59)$$

and

$$\frac{d(\delta\tau_j)}{dx} \ll \frac{d\bar{\tau}_j}{dx} \quad (60)$$

In Reference 9 it is shown that the series expansion procedure employed to start the solutions obtained in Ref. 7 justifies these assumptions near the reservoir.

Also discussed in Reference 9 are alternative methods which might be used instead of Equations (59) and (60). Rather than using $\delta\rho = 0$ in place of the perturbed momentum equation the condition

$$\delta S' = 0 \quad (61)$$

was employed. Based on numerical computations with the program Equation (61) is known to be accurate to higher order than $\delta\rho = 0$. Equation (61) is used in the program modification discussed in Appendix A. Also, a successive approximation scheme was employed to estimate the terms $d(\delta\chi_j)/dx$ in Equation (56). This improvement offered no significant advantage over the method presented here.

Using Equations (57) and (60) in (56) yields

$$\frac{d\bar{\chi}_j}{dx} = \sum_{i=1}^n \beta_{ij} \bar{P}_i \left[\sum_{k=1}^s \frac{\beta_{ik}}{\bar{T}} \left(\frac{\bar{h}_k}{\bar{T}} - 1 \right) \delta T - \sum_{k=1}^s \frac{\beta_{ik}}{\bar{\chi}_k} \delta \chi_k - \frac{\beta_i}{\bar{\rho}} \delta \rho \right] \quad (62)$$

Now Equations (55), (58), (59), and (62) provide $(s+2)$ algebraic equations for $\delta\chi_j$, δT , and $\delta\rho$ in terms of the equilibrium flow properties at a given nozzle station.

As described in Section 3.2 the nonequilibrium nozzle flow solution is started by obtaining the equilibrium flow solution at successive steps in temperature. At each step the results of the equilibrium calculation are used to obtain the values of $\delta\chi_j$, δT , and $\delta\rho$. Then, using these results, values of $\delta\chi_i$ are computed at each point from Equation (57). When any one of the $\delta\chi_i$'s exceeds a specified value, the values of $\delta\chi_j$, δT , and $\delta\rho$ are added to the respective equilibrium flow values and the numerical integration is begun.

Numerical difficulties arise when trying to integrate the nonequilibrium equations for small values of χ_i . Consequently, the solution should be started for as large values of $\delta\chi_i$, i. e., as far downstream as possible

without the linear perturbation procedure becoming inaccurate. At each computational step in the starting procedure the perturbations are added to the equilibrium values of χ_j , T , and ρ , and values of χ_i are computed from Equation (33). Since $\bar{\chi}_i = 0$, if the linearization procedure is valid

$$\chi_i(\bar{\chi}_j + \delta\chi_j, \bar{T} + \delta T, \bar{\rho} + \delta\rho) \approx \delta\chi_i \quad (63)$$

Experience obtained in the use of the program indicates that Equation (63) holds for values of $\delta\chi_i$ up to the order of 10^{-1} . Thus, the numerical integration is started when the largest $\delta\chi_i$ is typically 0.1.

In the above discussion it is indicated that all of the species gradients are evaluated from the rate equations once any $\delta\chi_i$ exceeds the specified test. In the nonequilibrium flow of a multicomponent mixture it is possible for some reactions to remain much closer to equilibrium than others. In Reference 9, a procedure is described whereby the numerical integration is started at different points for different species. However, if there are more reactions than species there is more than one production term in the species conservation equations and the procedure becomes inconvenient. Furthermore, the method does not help when two competing reactions keep a species concentration near the equilibrium value. As discussed in the ensuing section the numerical-integration scheme employed in the computer program was developed specifically for strongly coupled nonequilibrium processes. The use of this method has alleviated difficulties associated with some species remaining near their equilibrium distributions.

3.5 Numerical Integration Method Employed in Nozzle Flow Program

The solution of the nonequilibrium nozzle flow problem requires the numerical integration of a system of first-order differential equations of the form

$$\frac{dy}{dx} = f(x, y) \quad (64)$$

In the original version of the program a fourth-order Runge-Kutta scheme was employed. For this method, the formula for each Δy in an interval is of form

$$\Delta y = \frac{\Delta x}{6} (f_1 + 2f_2 + 2f_3 + f_4) \quad (65)$$

where

$$\begin{aligned} x_2 &= x_1 + \frac{\Delta x}{2} & y_2 &= y_1 + f_1 \frac{\Delta x}{2} \\ x_3 &= x_1 + \frac{\Delta x}{2} & y_3 &= y_1 + f_2 \frac{\Delta x}{2} \\ x_4 &= x_1 + \Delta x & y_4 &= y_1 + f_3 \Delta x \end{aligned} \quad (66)$$

and

$$f_i = f(x_i, y_i)$$

The 4th order Runge-Kutta formula (Equation (65)) is derived assuming that the slope in any integration interval is given by

$$\frac{dy}{dx} = A + B(x - x_1) + \frac{C}{2}(x - x_1)^2 \quad (67)$$

The Runge-Kutta method is generally quite adequate for the numerical solution of nonequilibrium flows. However, when the flow is near an equilibrium condition this method becomes unstable except for extremely small step sizes. The way in which the instability arises can be explained in the following manner. Near an equilibrium condition the species conservation equations can be written in the form

$$\frac{dy}{dx} \cong -P(y - \bar{y}) \quad (68)$$

where P , an inverse relaxation length, is a large number and $y - \bar{y}$, the departure from equilibrium, is small. Differentiation of Equation (68) shows successive derivatives of y to be P times larger than the previous order, hence the higher order derivatives of y are large.

The 4th order Runge-Kutta method is inadequate for such equations. Recently, Treanor²⁰ has developed a modification of the 4th order Runge-Kutta scheme which alleviates the numerical inaccuracy of the original method for near-equilibrium flows. Instead of Equation (67) the following relation is used for the slope in an interval,

$$\frac{dy}{dx} = -P(y - y_1) + A + B(x - x_1) + \frac{C}{2}(x - x_1)^2 \quad (69)$$

This relation leads to the following integration formula

$$\Delta y = \Delta x \left\{ A F_1 + B(\Delta x) F_2 + C(\Delta x)^2 F_3 \right\} \quad (70)$$

where

$$F_0 = e^{-P(\Delta x)}, \quad F_n = \sum_{k=0}^{\infty} \frac{[-P(\Delta x)]^k}{(n+k)!} = \frac{F_{n-1} - \frac{1}{(n-1)!}}{-P(\Delta x)} \quad (71)$$

and

$$P = -\left(\frac{f_3 - f_2}{y_3 - y_2}\right) = -\frac{2}{\Delta x} \left(\frac{f_3 - f_2}{f_2 - f_1}\right)$$

$$A = f_1$$

$$B = \frac{1}{\Delta x} \left[-3(f_1 + P_{y_1}) + 2(f_2 + P_{y_2}) + 2(f_3 + P_{y_3}) - (f_4 + P_{y_4}) \right] \quad (72)$$

$$C = \left(\frac{2}{\Delta x}\right)^2 \left[(f_1 + P_{y_1}) - (f_2 + P_{y_2}) - (f_3 + P_{y_3}) + (f_4 + P_{y_4}) \right]$$

The f_i and y_i are again given by Equation (66). The modified Runge-Kutta expression is of higher order than the 4th order Runge-Kutta expression but approaches the latter for small values of $P(\Delta x)$.

When $P(\Delta x)$ is large the value obtained for y_4 using the Runge-Kutta relation (Equation (66)) is inaccurate. Since P is evaluated knowing f_1 , f_2 , and f_3 then y_4 can be evaluated using Equation (67) with the quadratic term omitted. The result is

$$y_4 = y_1 + \Delta x \left\{ 2f_3 F_2 + f_1(F_1 - 2F_2) + f_2 F_2 P(\Delta x) \right\} \quad (73)$$

When $P(\Delta x)$ is small, which corresponds to a situation where Equation (68) is not valid, negative values of P are possible. In this case the original Runge-Kutta formula is used. Furthermore, when f_1 , f_2 , and f_3 are nearly equal, P cannot be evaluated accurately using Equation (72). However, when the slopes f_1 , f_2 , and f_3 are very close, the Runge-Kutta formula should be accurate and again it is used to obtain Δy .

In a nozzle flow calculation the numerical integration is stable for a much larger step size in the later stage of the expansion than in the initial stage. The numerical integration is begun with a step size which is known to be small enough to ensure stability. Then if the solution passes certain integration tests the step size is increased. In this way much larger integration steps are taken in the downstream part of the solution and the computing time is not prohibitive.

Two integration tests are used to control the step size in the program: (1) the percentage changes of γ_j and T in an interval must be less than a specified value (2) γ_j and T must be positive at both intermediate points and the final point in the integration. Initially, if these tests are passed on a specified number of successful steps then the interval size is increased by a factor of 1.1. If the interval size has been increased successfully a specified number of times then the factor by which the interval size is changed is increased by 0.1. In the program the number of successful increases required before increasing the rate of increase is taken to be the same as the number of successful steps required before increasing the interval. When any of the integration tests are failed the step size and the rate of increase are reduced.

The use of the modified Runge-Kutta scheme including the latter method for determining γ_4 (Equation (73)) has considerably extended the capability of the nozzle flow computer program. Many solutions have been obtained which could not be obtained using the 4th order Runge-Kutta method. Also, solutions can be obtained with far fewer integration steps and hence for smaller computing times. The results obtained for the species concentrations in a solution for a nozzle expansion of air from reservoir conditions of $T_0 = 10,000^\circ\text{K}$, $p_0 = 4400$ atm. are shown in Figure 1. As discussed in Reference 11 these reservoir conditions fall in the range where the nitric-oxide shuffle reactions keep the nitrogen-atom concentration very near its equilibrium value throughout the expansion. This solution, which was originally obtained using the Runge-Kutta method, was repeated using the modified Runge-Kutta scheme. A comparison between the two results for the nitrogen-atom concentration for a section in the initial part of the

expansion is shown in Figure 2. As can be seen the step size in the modified Runge-Kutta method is larger. Attempts at increasing the step size with the Runge-Kutta method lead to oscillations of the character demonstrated in Figure 2.

In the above comparison of the modified and 4th order Runge-Kutta schemes the integration tests which limit the relative changes in the species concentrations and temperature were set at 1%. The modified Runge-Kutta method can be used successfully with larger integration tests: the integration tests on the species concentrations and the temperature are typically set at .10 and .05 respectively. When these values of the integration tests are used, solutions can be started with integration steps as high as 10^{-2} cm for the modified Runge-Kutta scheme as opposed to 10^{-6} cm for the 4th order method.

4. THERMODYNAMIC AND CHEMICAL-KINETIC MODELS

In this section the methods employed in the computer program for specifying the thermodynamic and chemical character of a gas model are described. As mentioned in Section 2.1 the chemical species which are to be considered in a mixture are specified through the α_{ij} matrix. Further data which must be supplied to compute the thermodynamic properties of the mixture at a given point are thermodynamic properties h_j , μ_j° , and s_j° for each species. In the nonequilibrium computation, data for chemical reactions among the species must be provided in addition to the thermodynamic properties of the species.

As mentioned previously, it is assumed that the expanding gas mixture remains in thermal equilibrium and consequently that there is no coupling between the chemical kinetics and the internal degrees of freedom of the gas. In high temperature expansions vibration-dissociation coupling may become significant. Unfortunately there are not at present any established models available for the assessment of these effects, hence they have not been included in the program.

The data for specific kinetic models are not included in the present discussion. However, the reports and papers describing the applications of the program^{1, 10-17} contain detailed summaries of the models employed. A sample kinetic model for air and the preparation of input data for this model are illustrated in Section 6.2.

4.1 Specification of Thermodynamic Properties of the Species

For a mixture of ideal gases the thermodynamic properties h_j , μ_j° , and s_j° are only functions of temperature. Two methods are employed in the computer program to specify these required functions of temperature (a) a simple-harmonic-oscillator model, (b) polynomial fits to more accurate calculations of species properties. In both methods the species are assumed to be vibrationally and electronically excited, in equilibrium with the local

translational temperature. Both the translational and rotational degrees of freedom are assumed to always be fully excited. In the harmonic-oscillator description the electronic excitation is assumed to be given by the first few terms in the partition function sum. In the thermo-fit method, as the polynomial fit method is called, the computations of the vibrational and electronic contributions are typically more accurate than the simple harmonic oscillator calculation since account is usually made of anharmonic vibrations, vibration-rotation coupling, and more terms in the electronic partition function.

Using the simple harmonic-oscillator model the specific enthalpy for a monatomic or diatomic species may be written

$$\frac{h_j - h_{j_0}^\circ}{T} = \frac{5+2(\pi_j-1)}{2} + (\pi_j-1) \frac{\theta_{v_j}}{T} \frac{1}{e^{\theta_{v_j}/T} - 1} \frac{\sum_{l=1}^{L_j} \epsilon_{l_j} g_{l_j} e^{-\epsilon_{l_j}/T}}{T \sum_{l=1}^{L_j} g_{l_j} e^{-\epsilon_{l_j}/T}} \quad (74)$$

where π_j = no. of atoms per molecule of j th species,

θ_{v_j} = characteristic vibrational temperature of j th species,

g_{l_j}, ϵ_{l_j} = degeneracy and energy of l th electronic state of j th species,

and $h_{j_0}^\circ$ is the formation enthalpy of each species at standard conditions (usually zero temperature). The maximum value of L_j , the number of terms in the electronic contribution to h_j , allowed for in the program is 10.

For the oscillator model the chemical potential at standard pressure (1 atm.) is given by

$$\frac{\mu_j^\circ - h_{j_0}^\circ}{T} = - \left\{ a_j + \frac{5+2(\pi_j-1)}{2} \ln T + (\pi_j-1) \ln \left(\frac{e^{\theta_{v_j}/T}}{e^{\theta_{v_j}/T} - 1} \right) + \ln \sum_{l=1}^{L_j} g_{l_j} e^{-\epsilon_{l_j}/T} \right\} \quad (75)$$

where

$$a_j = h_j + \frac{5+2(\pi_j-1)}{2} \ln T_0' \quad (76)$$

and

$$h_j = \frac{3}{2} \ln \frac{2\pi m_j' k}{h^2} + \ln \frac{k}{p^{o'}} - (n_j - 1) \ln \theta_{v_j}' \quad (77)$$

In Equation (75) m_j' , k , h , $p^{o'}$ are respectively the mass of the j th particle, Boltzmann's constant, Planck's constant, and the standard pressure, all in c.g.s. units. Also θ_{v_j}' is the characteristic rotational temperature in °K.

In the nozzle flow computations the quantities s_j^o and C_{p_j} are also needed. Using Equation (17) s_j^o may be found once h_j and μ_j^o are known,

$$s_j^o = \frac{h_j - \mu_j^o}{T} \quad (17)$$

Differentiating Equation (74)

$$C_{p_j} = \frac{dh_j}{dT} = \frac{5+2(n_j-1)}{2} + (n_j-1) \left(\frac{\theta_{v_j}'}{T}\right)^2 \frac{e^{\theta_{v_j}'/T}}{(e^{\theta_{v_j}'/T} - 1)^2} + \left[\sum_{l=1}^{L_j} g_{l_j} \left(\frac{\epsilon_{l_j}}{T}\right)^2 e^{-\epsilon_{l_j}/T} - \sum_{l=1}^{L_j} g_{l_j} \frac{\epsilon_{l_j}}{T} e^{-\epsilon_{l_j}/T} \right] / \sum_{l=1}^{L_j} g_{l_j} \left(\frac{\epsilon_{l_j}}{T}\right) e^{-\epsilon_{l_j}/T} \quad (78)$$

Thus, in the harmonic-oscillator description of the species properties the following constants must be specified for each species: n_j , θ_{v_j}' , h_j , L_j , $h_{j_0}^o$, g_{l_j} and ϵ_{l_j} .

The thermo-fit method of specifying h_j or μ_j^o is to fit a fourth-order polynomial in temperature to calculated data for the individual species. Thus

$$\frac{\mu_j^o - h_{j_0}^o}{T} = a_j (1 - \ln T') - b_j T' - \frac{c_j}{2} (T')^2 - \frac{d_j}{3} (T')^3 - \frac{e_j}{4} (T')^4 - k_j \quad (79)$$

h_j is obtained by differentiation

$$\frac{h_j - h_{j_0}^o}{T} = a_j + b_j T' + c_j (T')^2 + d_j (T')^3 + e_j (T')^4 \quad (80)$$

Again s_j° is computed from Equation (17) and $C_{p,j}$ is obtained by differentiating Equation (80). Thus, in order to use the thermo-fit method the polynomial coefficients a_j , b_j , c_j , d_j , e_j , and k_j together with h_j° must be specified for each species.

In the computer program provision is made for using the harmonic-oscillator description for some species and the thermo-fit method for others, in a given calculation. The use of this option is discussed in Section 6. This option is useful, for example, for a mixture containing triatomic or more complex species since the above harmonic-oscillator description can only be used for monatomic and diatomic species.

Another option incorporated in the program allows the use of a thermo-fit description over the initial part of the expansion and a harmonic-oscillator description downstream. This additional feature is useful for high-expansion nozzle flows at high reservoir temperatures. In general the harmonic-oscillator model becomes inaccurate at high temperatures. Thus a polynomial fit to more accurate data can be used in the initial, high-temperature portion of the expansion. However, the temperature variation in such an expansion is large and hence may decrease below the lower limit of the range over which the polynomial coefficients are valid. In this case, the harmonic-oscillator description which is accurate at moderate and low temperatures (up to about 5000°K in air) can be used to extend the thermodynamic description to cover the entire expansion. The use of this latter option is illustrated for the air flow example presented in Section 6.

4.2 Chemical Kinetic Model

The chemical reactions among the species in the gas model are specified through the ν_{ij} and ν'_{ij} matrices. As seen from Equation (26) these matrix elements represent the stoichiometric coefficients of the j th species on the reactants and products side, respectively, of the i th reaction. In addition, the reaction rate constants must be specified for the forward direction of each reaction. Thus each reaction should be written so that the rate constant is known for the forward direction. The reverse rate constant is then computed through the equilibrium constant.

In the computer program forward rate constants are written in the form

$$k_{f_i} \sim A_i T'^{\eta_i} \exp \left[E_{act_i} / R_o T' \right] \quad (81)$$

which is the usual form in which experimental data are given. If third-bodies appear in dissociation-recombination reactions and the rate-constants are the same for some of the third bodies the following simplification is possible. For reactions having the same rate constant but different third bodies only one reaction is written, omitting the third bodies in the ν_{ij} and ν'_{ij} matrices. Then the forward rate constant for this reaction is written

$$k_{f_i} = A_i T'^{\eta_i} e^{-E_{act_i}/R_o T'} \left[\rho' \sum_{j=1}^s U_{ij} \nu_j \right]^{g_i} \quad (82)$$

where $U_{ij} = 1$ for all species which are third bodies in the i th reaction and zero otherwise. As can be seen from Equations (30)-(33) when $g_i = 1$, this procedure for reducing the number of reactions in the kinetic model is simply a regrouping of the chemical production terms in the species conservation equations. If there are no third bodies in a given reaction then $g_i = 0$ and no entry is necessary in the corresponding row of the U_{ij} matrix.

When the numerical solution is begun at a point where the flow is out of equilibrium and hence all the flow properties and the composition are specified, there is no requirement for a minimum number of reactions in the kinetic model. However, when the perturbation method is employed to start from an equilibrium state, there must be as many linearly independent reactions in the chemical kinetic model as there are formation reactions in the equilibrium calculation. In other words, a sufficient number of linearly independent reactions must be included so that the rank of the β_{ij} matrix is $(s-c)$. If the rank of β_{ij} is less than $(s-c)$, the perturbations in species concentrations are not uniquely determined by the perturbed rate equations. In each nozzle flow calculation the rank of β_{ij} is tested using a standard diagonalization procedure. If the reactions thought to be important in a calculation do not have a β_{ij} of rank $(s-c)$, appropriate formation reactions with fictitiously low rate constants should be included in the model.

5. ADDITIONAL CAPABILITIES OF NOZZLE FLOW PROGRAM

The nozzle flow computer program contains options which permit including ionized species and nonequilibrium ionization reactions, vibrational excitation frozen at the reservoir value, and effects of moderate gas imperfections on the initial, near-equilibrium portion of the expansion. The analysis underlying these options and the procedure for exercising them are discussed in this section.

5.1 Nozzle Flow Calculation for Ionized Flows

The procedure for computing the flow of a reacting mixture through a converging-diverging nozzle can be extended to ionized mixtures by treating electrons as a separate chemical element¹⁵. Each of the positively ionized species would then be formed by subtracting electrons from the corresponding neutral species; negatively, by adding. The conservation of elements equation (Eq. (27)) for the electrons then enforces conservation of charge. The formation enthalpy of each of the ions is the sum of the formation enthalpy and the ionization potential of the corresponding neutral species. Accordingly the electrons are referenced to the same zero level of energy as the molecular species. The sample calculation described in Section 6 includes ionized species.

In the reservoir and equilibrium-flow computations the electrons are an independent species or component. Hence, the concentrations of the ions in the mixture are found in terms of the electron concentration. In an equilibrium expansion to low temperature the electron concentration and thus the ion concentrations approach zero. Thus, when the electron concentration decreases below a specified value, the ionized species are dropped from the computation. In order to perform this truncation of the model the electrons and ions must be listed in a certain order in the α_{ij} matrix. The instructions for ionized flows are included in the description of the input-data format in Section 6. At present the ionized species are dropped from the computation when the electron concentration becomes less than 10^{-30} moles per gram of mixture. However, the electron concentration cannot be

expected to be calculated accurately at these very low levels. The accuracy of the equilibrium solution for an ionized flow is further discussed in Section 7 under the description of the subroutine used for solving the set of linear algebraic equations arising in the Newton-Raphson iteration.

If the electrons are treated as a separate chemical species the procedure for specifying reactions between ions and neutrals or electrons, ions, and neutrals is the same as for chemical reactions of neutral species. Solutions for nozzle flows of high-temperature air have been obtained including the effects of nonequilibrium ionization¹⁵. The estimates for the rate constants of three-body deionization paths included in the computational model led to values of A_i (Eq. (82)) which exceed the digital capacity of the machine ($> 10^{38}$). Since the product $k_{fi}l$ appears as a multiplying factor in each term of the species production terms (Eq. (30)) the following remedy was adopted. The constant factors in all of the rate constants were lowered by a factor such that the largest value would be $< 10^{38}$. Then the characteristic length, l , was increased by this factor. When this procedure is employed the coefficients in the $A(x)$ relation must be compensated so that the correct value of A'/A^* is given at each $x' = xl$.

In previous experience with this option of the program it was found that when several positive ions were included in the calculation, charge was not conserved in the nonequilibrium solution. This discrepancy has been attributed to integration error arising from using the differentiated form of the element conservation equations (Eq. (28)). This problem does not arise in conserving the neutral elements, element conservation being obtained to within four-decimal places in existing solutions. The lack of charge conservation has been remedied by equating the electron concentration to the algebraic sum of the ion concentrations after each numerical integration step in the nonequilibrium solution.

Using the above procedure for solving ionized flows is valid only for weakly ionized flows in the absence of applied fields. At very high temperature and low pressures gases become highly ionized and the assumption of a mixture of perfect gases breaks down. Attractive forces between the charged particles become important and Debye shielding effects must be considered in the state equation. Also the present analysis neglects

diffusion and nonequilibrium electron temperatures, assumptions which are not valid for highly ionized nozzle flows.

5.2 Nozzle Flow Calculation for Frozen Vibrational Excitation

In describing the nozzle-flow computation for frozen, equilibrium and nonequilibrium chemistry the vibrational degree of freedom was said to remain in equilibrium with translation during the expansion. The other limiting assumption for the degree of vibrational excitation, i. e. frozen at the reservoir value, is also allowed for in the nozzle-flow program. This option may only be exercised when the harmonic-oscillator model is used for the thermodynamic data because that model explicitly displays the vibrational contribution to the internal energy.

If the vibrational excitation is assumed to remain frozen at the reservoir value, the equation for the specific enthalpy of the j th species becomes

$$\frac{h_j - h_{j0}^{\circ}}{T} = \frac{5+2(n_j-1)}{2} + (n_j-1) \frac{\theta_{vj}}{T} \frac{1}{e^{\theta_{vj}-1}} + \frac{\sum_{l=1}^{L_j} (\epsilon_{lj}/T) g_{lj} e^{-\epsilon_{lj}/T}}{\sum_{l=1}^{L_j} g_{lj} e^{-\epsilon_{lj}/T}} \quad (74a)$$

Accordingly, the chemical potential of each species is given by

$$\frac{\mu_j^{\circ} - h_{j0}^{\circ}}{T} = - \left\{ a_j + \frac{5+2(n_j-1)}{2} \ln T + (n_j-1) \ln \left(\frac{e^{\theta_{vj}}}{e^{\theta_{vj}-1}} \right) + \ln \left(\sum_{l=1}^{L_j} g_{lj} e^{-\epsilon_{lj}/T} \right) \right\} \quad (75a)$$

The derivative dh_j/dT now contains no vibrational contribution and hence is given by Equation (78) with the vibrational term omitted. s_j° is obtained

$$\begin{aligned} s_j^{\circ} = & a_j + \frac{+2(n_j-1)}{2} (1 + \ln T) + (n_j-1) \left\{ \frac{\theta_{vj}}{e^{\theta_{vj}-1}} + \ln \left(\frac{e^{\theta_{vj}}}{e^{\theta_{vj}-1}} \right) \right\} \\ & + \frac{\sum_{l=1}^{L_j} \left(\frac{\epsilon_{lj}}{T} \right) g_{lj} e^{-\epsilon_{lj}/T}}{\sum_{l=1}^{L_j} g_{lj} e^{-\epsilon_{lj}/T}} + \ln \left(\sum_{l=1}^{L_j} g_{lj} e^{-\epsilon_{lj}/T} \right) \end{aligned} \quad (76a)$$

5.3 Correction for Moderate Gas Imperfections

At very high densities, the assumption that the molecules of a gas are noninteracting, point particles is no longer valid. At high temperatures and high densities, if ionization is negligible, the dominant intermolecular forces in a gas mixture are the repulsive forces between particles. Thus, in this situation the gas imperfections essentially stem from the finite volume of the particles.

When these effects are moderate, i. e. when the volume of the particles is 10% or less of the volume occupied by the gas, they can be approximated by assuming the mixture to be composed of fictitious hard-sphere particles. The equation of state for such a mixture is ²¹

$$p' = \frac{\rho'}{1 - \frac{\rho' b_0}{m^0}} \frac{R_0 T'}{m} \quad (11c)$$

where b_0 is four times the volume of the particles, m^0 is the molecular weight of the undissociated mixture, and m is the molecular weight of the mixture. The so-called "co-volume" of the particles, b_0 , is given by

$$b_0 = \frac{2}{3} \pi N_0 \sigma^3 \quad (83)$$

where N_0 is Avogadro's number and σ is the diameter of the particles. The state equation may be written

$$p' = \tilde{\rho}' R_0 T' / m \quad (84)$$

where $\tilde{\rho}'$ is an effective density defined by Equations (11c) and (84).

When a hard-sphere model is employed to account for gas imperfections there is no correction to the ideal-gas internal energy. However the enthalpy is given by

$$H' = E' + p'/\rho' = E' + \frac{\tilde{\rho}'}{\rho'} \frac{R_0 T'}{m} \quad (85)$$

or

$$H' = H'_{ideal} - \left(1 - \frac{\tilde{\rho}'}{\rho'}\right) \frac{R_o T'}{m} \quad (85a)$$

If the temperature and pressure of a gas mixture are specified and the diameter of a hard sphere representing the mixture is used, then the gas density is given by (11c) and the enthalpy is given by (85).

Using the above approximation the effect of gas imperfections on the nonequilibrium nozzle flow calculations can be accounted for in the following manner. The reservoir computation is carried out for a specified temperature and pressure. The composition is the same as for an ideal gas mixture but the enthalpy and density are computed using (85) and (11c). The computation for the equilibrium portion of the expansion proceeds in the same fashion as before. However, now the thermal and caloric state equations are written

$$p = \tilde{\rho} T \frac{m_o}{m} = \frac{\rho \rho_o'}{\tilde{\rho}_o' \left(1 - \rho' \frac{t_o}{m_o}\right)} T \frac{m_o}{m} \quad (11d)$$

$$H = H_{ideal} + \frac{p}{\tilde{\rho}} \left(\frac{\tilde{\rho} \tilde{\rho}_o'}{\rho \rho_o'} - 1 \right) \quad (85b)$$

The solutions available for nonequilibrium nozzle flows indicate that high reservoir densities delay the departure from equilibrium. At densities sufficiently high for gas imperfections to be significant, the flow will remain near equilibrium over an appreciable portion of the expansion. Thus, in the nozzle-flow program the corrections for gas imperfections are included in the state equations only for the near-equilibrium portion of the flow. The flow will most likely have expanded to the point where the ideal-gas equations apply before departing from equilibrium.

The above procedure for accounting for gas imperfections has been applied to nozzle flows of air for reservoir temperatures of 8000, 10,000, 12,000 and 15,000°K and reservoir densities of 10 and 100 times sea level density.¹¹ Hilsenrath²² has computed the thermodynamic properties and composition of equilibrium air including second virial corrections for temperatures up to 15000°K densities up to $\log(\rho/\rho^0) = 2.2$. Considering air to be composed of fictitious "air molecules", a value of σ of 2.6Å in Equation (11c) was found to fit Hilsenrath's calculations for the compressibility factor Z very well in the range of interest. For given temperature and pressure, the correction to the density at an ideal gas value of $100 \rho^0$ is about 10% in this temperature range. Also, at this density level Hilsenrath's results indicate the corrections to the internal energy and enthalpy to be about 1% and 3% respectively. While the model used in the nozzle flow program assumes no correction to the internal energy, the correction to the enthalpy given by Equation (85) is about 3%. In the nozzle flow solutions obtained in Reference 11, the gas had expanded to the point where it could be considered ideal before significantly departing from equilibrium. Further details on the application of this method to high density airflows and the results of such calculations are presented in Reference 11.

Thus, the computer program is capable of including the effects of moderate gas imperfections on nozzle expansions for high reservoir densities. In order to use this option an empirical value of σ , the diameter of a "molecule" of the mixture, must be chosen for the conditions of interest. As discussed in Section 6, this option can be excluded from the calculation by simply setting $b_0 = 0$. Then the equations in the program reduce to those for a mixture of ideal gases.

6. INPUT-OUTPUT PROCEDURES

This section describes the input-output procedures for the nozzle-flow program. The preparation of input cards is discussed, including a description of various options available in the program. This is followed by sample input data for an ionized air calculation. The output format is then described, illustrated by sample output data for the ionized air example.

6.1 Preparation of Input Cards

The input cards necessary to initiate a nozzle flow computation are listed below. The cards are listed in the order they appear in the data deck and an explanation of the information required is given for each card type. The definitions of the FORTRAN symbols used to indicate the information on each card type are given in Section 7.3; sample input cards are presented in Section 6.2.

<u>Card Type 1</u>	<u>Format (16I4)</u>
ISW1A	1 if solution with frozen chemistry is required 0 otherwise
ISW2A	1 if solution with nonequilibrium chemistry is required 0 otherwise
ISW3A	1 if solution with equilibrium chemistry is required 0 otherwise
ISW4A	1 if another run follows 0 otherwise
ISW5A	0 this indicator is not currently used

ISW6A	1 if reservoir calculation only is required 0 otherwise
ISW1B	Six extra indicators are available for additional
ISW2B	options as required. Storage is allotted in COMMON
ISW3B	for those indicators. If not used, the remainder of
ISW4B	the card may be left blank.
ISW5B	
ISW6B	

Card Type 2

Format (12A6)

ACOM(I)	up to 120 alpha-numeric characters describing run, printed as heading on first page of output. (There will be 2 cards.)
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Card Type 3

Format (16I4)

IRUN	run number
ISC	number of chemical elements (maximum of 10, including the electron)
ISS	number of chemical species (maximum of 20)
ISR	number of reactions (maximum of 64)
IC	number of ions (do not count the electron)
NQS	number of successful integration steps before increasing step size (normally 4)
IUPD	1 if starting upstream of throat 0 if starting downstream of throat

The nonequilibrium solution may be started either upstream or downstream of the nozzle throat. For upstream starts, the solution is begun by stepping off in temperature an amount DELT3 from the reservoir. For downstream starts the

program computes the equilibrium conditions at the throat and then steps off in temperature DELT2 to begin the nonequilibrium solution. The downstream start may be used for cases in which nonequilibrium effects are negligible upstream. However, if any question exists the solution should be started upstream.

NFIT	1 if any thermo-fit cards are to be used 0 otherwise
KHO	1 if any harmonic-oscillator cards are to be used 0 otherwise
KKUR	1 if third body matrix is used (see Card Type 8, QQ(I)) 0 otherwise
NAFIT	1 if fitted nozzle geometry is used 0 if standard nozzle geometry is used (see Card Type 13a, b)
INEQV	1 if frozen vibration 0 if equilibrium vibration
IROBAR	1 if effective density, RHOBAR, is printed (see Section 6.3) 0 otherwise

Card Type 4

Format (7F10.0)

CTAP	reservoir temperature in °K
PRESA	reservoir pressure in atm
CTMXX	temperature at which switch is made from thermo-fit to harmonic-oscillator data (in °K) (see Card Types 14-18)

CXMAX Maximum value of α

The nonequilibrium calculation may be terminated either by an upper limit on α or a lower limit on temperature (TSTOP). Both values must be read in, the one not being used set to a large (small) number. The frozen and equilibrium solutions use only the temperature stop. For these calculations TSTOP must be greater than the size of the temperature step used (DELTA1, which is set equal to $.01 T_0'$ in the program) otherwise a calculation will be attempted at nearly zero temperature.

SL Characteristic length used for nondimensionalizing α (cm.). When a standard geometry is used the nozzle scale may be changed by simply changing l . The equations for a wedge, cone, or hyperbolic nozzle become $A = 1 + \alpha$, $A = 1 + 2\alpha + \alpha^2$, and $A = 1 + \alpha^2$ if l is $h/\tan\theta$, $r^*/\tan\theta$, and $r^*/\tan\psi$, respectively. In these expressions for l , h is the half-height of the wedge throat, r^* the throat radius of the conical or hyperbolic nozzle, θ is the half-angle of the wedge or cone, and ψ is the half-angle of the asymptote cone for the hyperbolic, axisymmetric nozzle. For fitted geometries l is usually set at 1 cm so that the coefficients in the area-ratio expression are the same as for α measured in cm.

BZERO Constant b_0/M_0^0 used in imperfect gas correction. (Section 5.3) (cm^3/mole) set at zero if ideal gas equation of state is used.

TSTOP temperature stop in $^{\circ}\text{K}$

Card Type 5

Format (7F10.0)

TPRINT	Temperature interval between printouts (nondimensional) if TPRINT = 0, every step is printed.
DELTA X	Initial integration step size (nondimensional), usually 0.01.
DELT2	Temperature step from throat for starting the nonequilibrium solution downstream (nondimensional), usually 0.01. DELT2 must be small enough so that departures from equilibrium are still small at the starting point.
DELT3	Temperature step from reservoir for upstream start, usually .001.
TTEST	Integration test: maximum size of $\left \frac{\Delta T}{T} \right $ in one Runge-Kutta step, usually .05.
GTEST	Integration test: maximum size of $\left \frac{\Delta \chi_i}{\chi_i} \right $ in one step, usually 0.1.

Card Type 6

Format (7F10.0)

CECHII(I)	The switch from equilibrium to nonequilibrium is made when $\delta \chi_i$ lies in the range $CECHII(I) \leq \delta \chi_i \leq PCTEST (CECHII(I))$. If $\delta \chi_i$ crosses this interval in one step, the step size is reduced until a value of $\delta \chi_i$ is found in the correct range. The switch is made when any one of the $\delta \chi_i$'s reaches the test value. Usually $CECHII(I) = 0.1$, $PCTEST = 1.2$. There will be ISR of the $CECHII(I)$, 7 to a card. Use as many cards as necessary.
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Card Type 7

Format (A6, 2F10.0)

ELMENT (K)	Chemical symbol for element
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CAPQ(K) Atoms of element k per molecule of mixture
(atom fractions of elements).

CMW(K) Molecular weight of element k .
(There will be ISC of these cards.)

Card Type 8 Format (4E14.8)

CAI(I) A_i , $\text{cm}^3/\text{mole sec}(\text{°K})^{\eta_i}$ or $\text{cm}^6/\text{mole}^2 \text{ sec}(\text{°K})^{\eta_i}$

ETAI(I) η_i , power of temperature dependence in k_{fi}

CEACT(I) E_{act_i} , cal/mole °K

QQ(I) 1 if reaction involves a third body
0 otherwise

For reactions involving a nonreacting third body,



it is convenient to be able to treat all third bodies having the same reaction-rate constant as a single molecule, rather than including a separate reaction for each. This is made possible by setting QQ(I) = 1. The species which are to serve as third bodies are specified on Card Type 12. (Section 4.2).

(There will be ISR of these cards.)

Card Type 9 Format (24F3.0)

ALPIJ(I, J) Number of atoms of element J in species I,
J = 1, ---ISC. The independent species or components must be listed in the first ISC rows. Any set of species may be chosen as components as long as the resulting α_{ij} matrix is of rank ISC. However, a species whose concentration

may go to zero during the expansion should not be chosen. Thus, it is sometimes better to choose diatomic molecules (N_2 , O_2) than atoms. If ionization is considered, the electron should be chosen as one of the components. Provision has been made to truncate the α_{ij} matrix if the concentration of electrons becomes $< 10^{-30}$. Consequently, the electrons should be listed in the first row and all ions in the last rows of α_{ij} (see Section 5.1).
(There will be ISS of these cards.)

Card Type 10

Format (24F3.0)

XNUIJP(I, J)

Number of molecules of species J on product side of reaction I. $J = 1, \dots, ISS$.
(There will be ISR of these cards.)

Card Type 11

Format (24F3.0)

XNUIJ(I, J)

Number of molecules of species J on reactant side of reaction I. $J = 1, \dots, ISS$.
(There will be ISR of these cards.)

Card Type 12

Format (30I1)

KUR(I, J)

1 if species J serves as a third body in reaction I
0 otherwise

(There will be one card for each reaction which involves a third body.)

Card Type 13 a

Format (5E14.8)

ASUB(I)

upstream area coefficients, $I = 1, \dots, 10$

BSUB(I)

downstream area coefficients. $I = 1, \dots, 31$

ATP(I) area transfer points. I = 1, . . . , 5
 (These cards are used only if fitted geometry is desired. There are 10 cards.)

Card Type 13 b

Format (5E14.8)

ASUB(I) upstream area coefficients. I = 1, 2, 3

BSUB(I) downstream area coefficients. I = 1, 2, 3

(These cards are used only if standard nozzle geometry is desired. There are 2 cards.) Standard geometries are wedge, cone or hyperbolic, axisymmetric nozzles and have area distributions of the form $A = A_1 + A_2x + A_3x^2$ upstream of the throat, and $A = B_1 + B_2x + B_3x^2$ downstream where x is nondimensional (x is measured from the throat and is negative upstream). Use of the fitted geometry permits the specification of seven different polynomials, two upstream of the throat and five downstream. The transition points must also be specified. For example

$$x < \text{ATP}(1), \quad A = A_1 + A_2x + A_3x^2$$

$$\text{ATP}(1) \leq x \leq 0, \quad A = A_4 + A_5x + A_6x^2 + A_7x^3 + A_8x^4 + A_9x^5 + A_{10}x^6$$

$$0 < x < \text{ATP}(2), \quad A = B_1 + B_2x + B_3x^2$$

$$\text{ATP}(2) \leq x \leq \text{ATP}(3), \quad A = B_4 + B_5x + B_6x^2 + B_7x^3 + B_8x^4 + B_9x^5 + B_{10}x^6$$

$$\text{ATP}(3) \leq x < \text{ATP}(4), \quad A = B_{11} + B_{12}x \text{ -----} + B_{17}x^6$$

$$\text{ATP}(4) \leq x \leq \text{ATP}(5), \quad A = B_{18} + B_{19}x \text{-----}$$

$$+ B_{24}x^6$$

$$\text{ATP}(5) \leq x, \quad A = B_{25} + B_{26}x \text{-----}$$

$$+ B_{31}x^6$$

Quadratic fits must be used for the first and third segments, since the program requires an explicit solution for x in these regions. However, these segments may be made very small, one or two integration steps. If a fitted geometry is used, all 10 upstream and 31 downstream coefficients must be read in. If fewer segments or lower order polynomials are required, zeros should be read in for the additional coefficients. The area distributions should be chosen to match as closely as possible at the transfer points. Slight discontinuities can be tolerated as long as the area distributions remains monotonic in both converging and diverging sections. (Also see SL on Card Type 4)

Typical nozzle expansions span a wide range of temperature. This presents difficulty in accurately prescribing thermodynamic data. Simple-harmonic-oscillator formulas which are accurate at low temperatures may not be sufficiently precise at the higher temperatures. Polynomial fits of tabulated data (thermo-fits) may be used at higher temperatures. Considerable flexibility has been built into the program and several options are available.

1. All harmonic oscillator (HO) data. Set CTMXX = 0, NFIT = 0, KHO = 1. IGJ(J) need not be read in (Card Type 14). Only harmonic oscillator data need be read in.

2. All thermo-fit (TF) data. Set CTMXX = 0, NFIT = 1, KHO = 0, IGJ(J) = 1 for all species. Only thermo-fit data need be read in.
3. Harmonic oscillator data for some species, thermo-fit and harmonic oscillator data for the rest, with a switch from TF to HO data at T = CTMXX. Set KHO = 1, IGJ(J) = 0 for HO species, IGJ(J) = 1 for the others. Set CTMXX equal to the desired switching temperature, which must be the same for all species. Set NFIT = 1. Only HO data need be read in for the HO species, while both sets of data are required for the rest. If the TF data is to be used for the entire temperature range, set CTMXX = 0 and do not read in HO data for these species.

It is essential that the two sets of data agree very closely at the switching temperature, otherwise oscillations may occur in the nonequilibrium solution.

Card Type 14

Format (30I1)

IGJ(J)

1 if thermo-fit data is used for species J,
J = 1, . . . , ISS

0 otherwise

This card is used only if thermo-fit data are employed.

The reading sequence for cards 15-18 is as follows: All thermodynamic data for species 1 is read in; Cards 15, 16, 17, 18 as required. Next, data for species 2, etc. Species are numbered in the order they appear in the α_{ij} matrix.

Card Type 15

Format (4E15.7)

TFA(J)

a_j

TFB(J)

b_j

TFC(J)

c_j

TFD(J)

d_j

(There will be 1 card for each species for which IGJ = 1.)

Card Type 16Format (3E15.7, A15)

TFE(J)

 e_j

TFK(J)

 k_j

SHJAP(J)

 h_{j0}'

HP(J)

species symbol

(There will be 1 card for each species for which IGJ = 1.)

Card Type 17Format (A6, 4E14.8, I2)

HP(J)

species symbol

ETAJ(J)

 η_j

SBJ(J)

 b_j

THEVP(J)

 θ_{j0}'

SHJAP(J)

 h_{j0}''

IGM(J)

number of electronic levels

(There will be 1 card for each species. If CTMXX = 0 there will be one card for each species for which IGJ = 0.)

Card Type 18Format (4(F3.0, E15.8))GELJ(L, J),
ELJ(L, J)

If no electronic excitation is considered, one card must still be included, with GELJ (1, J) = ground state degeneracy, ELJ(1, J) = 0.

For each card of type 17, there will be enough cards of type 18 to describe the electronic levels, 4 to a card, a maximum of 10 levels permitted.

6.2 Sample Calculation

The sample case chosen to illustrate the use of the nozzle flow program is an expansion of ionized air through a contoured nozzle. It has been established¹⁵ that at the selected reservoir conditions, $T_o' = 6500^\circ\text{K}$ and $p_o' = 1000$ atm, the dominant source of electrons is NO. Thus NO^+ is the only ion included in the calculation. An 8 species, 11 reaction chemical model is used with thermodynamic data in both harmonic-oscillator and thermo-fit form. The description of the necessary input data is summarized below and the corresponding input data cards are shown in Fig. 3. Sample pages of the output data are shown in the ensuing section to illustrate the printout formats.

Summary of Input Specifications for Sample Calculation

Run No. 1000

Upstream start, vibrational equilibrium

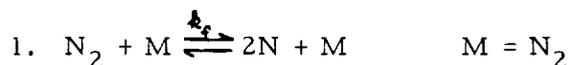
Do frozen, equilibrium, and nonequilibrium solutions

$T_o' = 6500^\circ\text{K}$ $p_o' = 1000$ atm.

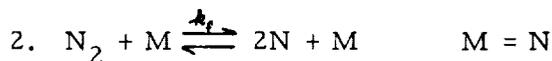
Species: e^- , N_2 , O_2 , A, N, O, NO, NO^+

Elements: N, O, A, e^-

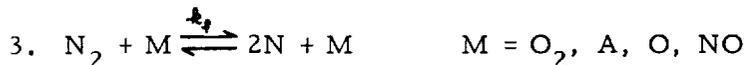
Reactions:



$$k_f = 3 \times 10^{21} T'^{-1.5} \exp \left[-2.2499 \times 10^5 / R_o T' \right]$$



$$k_f = 1.5 \times 10^{22} T'^{-1.5} \exp \left[-2.2499 \times 10^5 / R_o T' \right]$$



$$k_f = 9.9 \times 10^{20} T'^{-1.5} \exp \left[-2.2499 \times 10^5 / R_o T' \right]$$

4. $O_2 + M \xrightleftharpoons{k_f} 2O + M \quad M = O_2$
 $k_f = 3.6 \times 10^{21} T'^{-1.5} \exp \left[-1.1796 \times 10^5 / R_o T' \right]$
5. $O_2 + M \xrightleftharpoons{k_f} 2O + M \quad M = O$
 $k_f = 2.1 \times 10^{18} T'^{-0.5} \exp \left[-1.1796 \times 10^5 / R_o T' \right]$
6. $O_2 + M \xrightleftharpoons{k_f} 2O + M \quad M = N_2, A, N, NO$
 $k_f = 1.2 \times 10^{21} T'^{-1.5} \exp \left[-1.1796 \times 10^5 / R_o T' \right]$
7. $NO + M \xrightleftharpoons{k_f} N + O + M \quad M = N_2, O_2, A, N, O, NO$
 $k_f = 5.2 \times 10^{21} T'^{-1.5} \exp \left[-1.4996 \times 10^5 / R_o T' \right]$
8. $O_2 + N \xrightleftharpoons{k_f} O + NO$
 $k_f = 10^{12} T'^{0.5} \exp \left[-6.2 \times 10^3 / R_o T' \right]$
9. $N_2 + O \xrightleftharpoons{k_f} NO + N$
 $k_f = 5 \times 10^{13} \exp \left[-7.552 \times 10^4 / R_o T' \right]$
10. $N_2 + O_2 \xrightleftharpoons{k_f} NO + NO$
 $k_f = 9.1 \times 10^{24} T'^{-2.5} \exp \left[-1.2912 \times 10^5 / R_o T' \right]$
11. $NO^+ + e^- \xrightleftharpoons{k_f} N + O$
 $k_f = 1.8 \times 10^{21} T'^{-1.5}$

Nozzle Geometry

$l = 1 \text{ cm.}$

Upstream: $A = 1 + \alpha^2$

Downstream: $0 < \alpha < 1.25, A = 1 + .6141903\alpha^2$

$1.25 < \alpha < 3.25, A = .6000286 + .6399541\alpha + .3582086\alpha^2$

$$\begin{aligned}
3.25 < \kappa < 5.08, \quad A = 20.39065 - 15.40933\kappa + \\
& \quad 4.613686\kappa^2 - .3664322\kappa^3 \\
5.08 < \kappa, \quad A = .006603241 + 1.607688\kappa + \\
& \quad .3041264\kappa^2 - .02642175\kappa^3 + .000948788\kappa^4 - \\
& \quad .001619982\kappa^5 + .00001077302\kappa^6
\end{aligned}$$

Since the upstream fitted geometry involves only one polynomial the same coefficients are read in for both of the available upstream regions. An arbitrary transfer point, $\kappa = -1$, is selected. Only 4 of the 5 downstream regions are utilized. The last transfer point is chosen beyond the range of the calculations.

Thermodynamic Data

Both thermo-fit and harmonic-oscillator data are to be used for each species, with the switch from the former to the latter description taking place at $T' = 5000^\circ\text{K}$. The numerical values of the constants in the thermodynamic data may be seen from the input data cards in Fig. 3 or, in more compact form, in the program listing of the input data given in Fig. 4 in Section 6.3. The constants in the harmonic-oscillator data were taken from Reference 2. The coefficients in the thermofit data were taken from Reference 23. It has been established¹¹ that the two thermodynamic descriptions are nearly the same at 5000°K . References 2 and 23 also contain the necessary harmonic-oscillator and thermo-fit data for the other ionized species present in high-temperature air (N^+ , O^+ , N_2^+ , O_2^+ , Ar^+ , O^-).

Constants and Test Values

BZERO = 0 (no real gas correction)

Maximum value of $\kappa = 320$

Minimum value of temperature = 3250°K (The solution was stopped at this point only for the purposes of the example. Usually the frozen-flow and equilibrium flow solutions are stopped at .01 of T_o')

Initial $\Delta x = 0.01$	TTEST = .05
DELT2 = .01	GTEST = .10
DELT3 = .001	Interval Size Control = 4

6.3 Output Formats

In this section the formats for printing the results of the machine computations are described. The results of the sample calculation, for which the input data were described in Section 6.2, are used to illustrate the printout procedure. Then the diagnostic messages which may occur in the printout are listed and are used to indicate some of the experience which has been gained in using the program.

For each computational case or run, the program lists the input data. The program listing of the input data for the sample calculation is shown in Figure 4. The format for this printout is evident from the figure. The specified values of the indicators IUPD and INEQV are denoted by printing UPSTREAM RUN or DOWNSTREAM RUN and VIBRATION EQUIL. or FROZEN VIBRATION on the input data listing. The program listing of the input data also includes the format for displaying the frozen, equilibrium and nonequilibrium solutions. If a given solution is not to be computed then the format for that solution is not printed.

The results of the reservoir computation are printed after the program listing of the input data. The results of the reservoir computation for the sample air case are shown in Figure 5. The reservoir temperature, pressure, and density are in units of °K, atm, and gm/cc, respectively. The enthalpy is normalized by $m_0/R_0 T_0'$ and the entropy is in cal/gm°K. The species concentrations are in moles/gm.

The frozen flow solution, if computed, is printed after the reservoir values using the format given in Figure 4. The first page of the frozen-flow solution for the sample case is shown in Figure 6. The gasdynamic variables are all printed in dimensionless form. The entropy is always given in cal/gm°K. Notice that the printout of the composition is not repeated at each step in the frozen flow solution.

The throat conditions for frozen and equilibrium flow are shown in Figures 7 and 8 for the sample calculation. The first page of the equilibrium solution for the sample case is shown in Figure 9. The printout of the density-fit constants used in the starting procedure for the sample nonequilibrium solution are shown in Figure 10. If the solution is to be started in the downstream region then the conditions at the initial computational point downstream of the throat would be printed in place of the density-fit constants. The format for printing the starting values for a "downstream run" is the same as that for printing the equilibrium throat conditions.

The printing procedure for the nonequilibrium flow results is illustrated in Figure 11. The first three pages of the printout for the sample calculation are shown in the figure and the format is that given in Figure 4. Again all of the flow properties are given in dimensionless form with the exception of the entropy which is given in units of cal/gm°K. The species concentrations are in moles/gm of mixture. In the nonequilibrium solution the current value of the indicator INEQ, which denotes when the numerical integration has begun, is printed at each step.

The values of the nonequilibrium flow quantities which are printed for the steps where $INEQ = 0$ are actually the equilibrium flow variables plus the appropriate perturbations (see Figure 11). Also, when $INEQ = 0$, the equilibrium-flow temperature and species concentrations are printed at each step according to the format presented with the input-data listing in Figure 4. The above printout procedure permits the values of the perturbation quantities calculated in the starting procedure to be examined.

After the first step on which the value of INEQ changes from 0 to 1 the values of the nonequilibrium flow properties printed are those obtained from numerical integration. The starting values for the numerical integration are the quantities on the step where INEQ is first equal to unity. Notice that after INEQ becomes 1 the printout of the nonequilibrium solution no longer follows the format shown in Figure 4, in that the equilibrium-flow temperature and species concentrations are not printed at each point.

All of the above output data are written on the system output-tape unit. For the nonequilibrium solution additional information is written on an auxiliary tape unit. The present program uses a tape unit designated logical tape unit 2. A page of these additional output data which was generated in the sample calculation is shown in Figure 12. For the steps corresponding to values of INEQ = 0 the quantities χ_i , P_i , $\delta\chi_i$, $(\chi_i)_b$, $i = 1, 2, \dots, n$, are printed. When INEQ = 0, the quantities χ_i , P_i , and $\delta\chi_i$ are evaluated using the equilibrium values of τ_j , T , ρ , and $(\chi_i)_b$ is χ_i evaluated using $\tau_j = \bar{\tau}_j + \delta\tau_j$ and $T = \bar{T} + \delta T$. At each step the run number and equilibrium-flow temperature are included in order to relate this additional printout to the printout of the flow properties and composition. The format for printing each step is as follows

Run No. T

χ_1	P_1	$(\chi_1)_b$	$\delta\chi_1$	χ_2	P_2	$(\chi_2)_b$	$\delta\chi_2$	χ_3	P_3	$(\chi_3)_b$	$\delta\chi_3$
χ_4	P_4	$(\chi_4)_b$	$\delta\chi_4$
.	χ_n	P_n	$(\chi_n)_b$	$\delta\chi_n$				

The quantity χ_i evaluated using the infinite-rate equilibrium values τ_j , T , and ρ gives an indication of how closely the results of the Newton-Raphson procedure satisfy the condition of chemical equilibrium. As pointed out in Section 3.4 a comparison of $(\chi_i)_b$ and $\delta\chi_i$ is a check on the accuracy of the linearized perturbation calculation.

The additional output which corresponds to steps where INEQ = 1 contains the quantities χ_i , P_i , $P_i \chi_i$, and $d\tau_j/dx$. Here, of course, χ_i , P_i and $P_i \chi_i$ are the values evaluated in performing the numerical integration of the nonequilibrium solution. Since there may be more reactions than species in a chemical model the fourth entry in each group of 4 quantities is meaningful only for the first s groups. The format for printing these quantities when INEQ = 1 is

Run No. T

χ_1	P_1	$P_1 \chi_1$	$d\chi_1/dx$	χ_2	P_2	$P_2 \chi_2$	$d\chi_2/dx$	χ_3	P_3	$P_3 \chi_3$	$d\chi_3/dx$
χ_4	P_4	$P_4 \chi_4$	$d\chi_4/dx$
...	χ_5	P_5	$P_5 \chi_5$	$d\chi_5/dx$	χ_{s+1}	P_{s+1}	$P_{s+1} \chi_{s+1}$	—
...	χ_n	P_n	$P_n \chi_n$	—				

These quantities are useful in checking the progress of the non-equilibrium solution and in determining which reactions in the kinetic model are the dominant ones.

In Section 5.3 an option for including the effects of moderate gas imperfections on the nozzle flow solutions was described. If this option is used and if the indicator IROBAR is read in as unity then the effective density, $\tilde{\rho}$, defined in Section 5.3 is printed with the output data. In the frozen and equilibrium-flow solutions $\tilde{\rho}$ is printed in place of the entropy, which does not change in either case. In the nonequilibrium solution the correction is applied over the near-equilibrium portion of the flow and $\tilde{\rho}$ is printed in place of the Mach number. Notice that $\tilde{\rho}$ need not be printed even though this option is exercised.

Diagnostic messages may appear interspersed with the output data obtained from the systems output tape. The diagnostic messages are of two types. The first includes error messages which are written by the FORTRAN IV library system;²⁴ the second includes diagnostic messages written by the program.

The error messages generated by the FORTRAN IV system²⁴ are typically encountered when attempting operations such as taking the square root or logarithm of a negative number, taking the logarithm of zero, or taking the antilogarithm of a number greater than 88. The most frequent sources of these error messages have been eliminated as discussed below.

In the nonequilibrium calculation a Mach number is computed from Equation (38). As can be seen from this equation M varies from 1 to ∞ as $d \ln A/dx / d \ln \rho/dx$ varies from 0 to -1. Since M is sensitive to small variations in this ratio of derivatives, an oscillation in the solution which

led to a value of $\left| \frac{d \ln \rho}{dx} \right| < \left| \frac{d \ln A}{dx} \right|$ would in turn result in taking the square root of a negative number. In the program this situation is avoided by calculating M from

$$M = \frac{1.0}{\gamma \left| 1 + \left(\frac{d \ln A}{dx} / \frac{d \ln \rho}{dx} \right) \right|}$$

The occurrence of this condition will be evidenced in the output by an oscillation in the Mach number.

The program has been modified to eliminate FORTRAN IV error message printout in the calculation of the quantities χ_i and $P_i \chi_i$. If one of the species concentrations on the reactant side of a reaction approaches zero and the reverse rate of a reaction becomes much larger than the forward rate, then operations such as $\ln(0)$ and e^{288} are attempted. This situation is avoided for the current computational step by computing the reverse reaction-rate constant from the forward rate constant and the equilibrium constant, and changing the direction in which the reaction is written.

The messages which may appear in the second type of diagnostic printout, i. e. that written by the program, are listed below. The significance and probable cause of each of the messages are described.

(i) DISCRIMINANT NEGATIVE IN MAIN PROGRAM - This diagnostic refers to the calculation of α from the quadratic formula (Eq. (44)). The sign used in the quadratic formula has been chosen based on the expected behavior of $A(\alpha)$ and hence this diagnostic message is seldom encountered. If encountered this diagnostic probably indicates an error in the input data.

(ii) TOO MANY NEWTON-RAPHSON ITERATIONS - This diagnostic indicates that more than the allowed number of iterations have been performed in the Newton-Raphson procedure for calculation of the equilibrium composition and pressure. It is obvious from the output data whether the failure occurred in computing the reservoir or a point in the equilibrium flow. Apart from inconsistencies in the input data this failure can occur when the various species concentrations have widely different values. One possible remedy would be to relax the test on ΔX_j ; which, as described in Section 2.1,

defines convergence. See also the discussion given under subroutine SIMSOL in Section 7.1.

(iii) IN NEWRAP, CAPX(K) = 0, IN NEWRAP, P = 0. - These diagnostics are printed when the correction to the guess made for one of the unknowns in the Newton-Raphson iteration procedure would yield a value of zero for the next guess. This diagnostic usually occurs when the iteration procedure diverges and hence is usually accompanied by (ii).

(iv) BETA MATRIX OF INSUFFICIENT RANK - As discussed in Section 4.2, the β_{ij} matrix must be of rank (s-c) in order for the perturbation quantities used in the starting procedure to be uniquely determined. Before performing the nonequilibrium flow calculation the rank of β_{ij} is checked and if it is not (s-c) the computation is stopped.

(v) DATEST AND DBTEST INCONSISTENT - This diagnostic refers to a failure in joining a nonequilibrium solution started in the upstream region to the desired solution in the downstream region. The failure referred to is that the test (DBTEST) on the percentage difference between the value of $d \ln A / dx$ calculated from the upstream region solution and that calculated from the specified $A(x)$ for the downstream region cannot be satisfied for the specified switching point (DATEST). If this diagnostic is encountered without (vi) then there is considerable nonequilibrium effect on the flow density upstream of the nozzle throat. This diagnostic usually indicates incorrect specified input data. See (vi)-(b) below.

(vi) DLOGR IS POSITIVE - As discussed in Section 3.3, a branch point exists slightly downstream of the geometric throat in the solution for a nonequilibrium nozzle flow. The primary purpose of inserting this diagnostic into the program was to indicate whether an upstream solution had been joined to the subsonic branch of a downstream solution. However, testing for points in the calculation where $\frac{d \ln \rho}{dx}$ becomes positive has additional diagnostic value. The probable causes of failing this test at various points in the nozzle flow calculation are listed below.

- (a) Downstream run - If this diagnostic occurs in a calculation which is started downstream of the nozzle throat there are two possible causes. First, if the diagnostic occurs at a point away from the nozzle throat, then either an oscillation in the solution or decrease in the nozzle-cross-sectional area is responsible for $d\ln\rho/dx$ becoming positive. An oscillation in the solution is accompanied by small integration step sizes. A discontinuity in dA/dx will usually occur at a transfer point in the $A(x)$ relation.

If this diagnostic occurs for a value of A very near 1 (say ≤ 1.005) then the numerical integration has been started too close to the nozzle throat. This situation is easily remedied by either halving the specified values of CECHII(I) and restarting the calculation as an upstream run or by doubling the values of CECHII(I) and restarting the downstream run.

- (b) Upstream run - Again there are two probable causes of this diagnostic. The first of these, which occurs away from the nozzle throat, is the same as the first type of difficulty listed above for the downstream run. If the diagnostic is encountered very near the throat and the numerical integration has begun, then the switch from the upstream region to the downstream region has been attempted too close to the nozzle throat. This situation is remedied by moving this switching point downstream, i. e. by increasing DATEST. (DATEST is initialized in Subroutine (INIT.)

(vii) TEMPERATURE GREATER THAN RESERVOIR VALUE - At each point in the nonequilibrium solution the value of the flow temperature is compared with the reservoir value. The test is intended as an over-all check on the progress of the calculation. This diagnostic indicates a radically incorrect computational result, most probably caused by an error in input data.

(viii) DISCRIMINANT NEGATIVE IN AXFIT (see i).

(ix) MATRIX SINGULAR or INDEXING OR STORAGE FAILURE -

These diagnostics are encountered in subroutine MATINV (see Section 7.1), which is used to invert the α_{ij} matrix. The first diagnostic will occur if the rank of α_{ij} is not equal to c , i. e. if α_{ij} is improperly specified. The second diagnostic will occur if the dimension statements of BTA and ALPIJ are not consistent, and will only be encountered when recompiling the program.

7. SUBROUTINES AND VARIABLES USED IN FORTRAN- LANGUAGE NOZZLE FLOW PROGRAM

In this section the function performed by each subroutine in the program is explained. Flow charts are provided for the more complicated subroutines. Also, a list of all the FORTRAN variables is given, indicating their definitions and the subroutines in which they are used.

7.1 FORTRAN Subroutines and Their Functions

Subroutines for which flow charts appear in Section 7.2 are marked with an asterisk. After each description, the calling subroutines are written in parentheses.

MAIN PROGRAM* The routine which directs the computation is designated as the main program. This routine contains the logic for selecting which of the reservoir, frozen-flow, equilibrium-flow or nonequilibrium-flow computations are to be done on a given run.

READ This subroutine performs the reading in of the input data.
(MAIN PROGRAM).

LIST This subroutine writes the input data on the system output tape. The format in which the input data are listed is given in Section 6.
(READ).

INIT Performs initialization and nondimensionalization of data.
(MAIN PROGRAM).

INTA* First the specification of the chemical composition of the gas model is rewritten in terms of the designated independent species. Then the computation of the reservoir composition and thermodynamic properties is performed. (INIT).

THERM* This subroutine computes the thermodynamic properties, h_j , μ_j° , C_{p_j} , and s_j° , for each species at a given temperature.
(INTA, FROZEN, NEWRAP, NONEQ, PERT, RNKT).

FROZEN* This is the subroutine which controls the calculation of the throat conditions for frozen flow and the frozen-flow solution. (MAIN PROGRAM).

PROP At each computational step in the frozen-flow calculation this subroutine calculates the pressure from Equation (25), the enthalpy from Equations (12) and (84b), the density from Equation (11d) and the velocity from Equation (15). (FROZEN).

PRTA This subroutine controls the printing of the output data for the nonequilibrium flow solution. The output format is discussed in Section 6. (NONEQ).

NRMAX* This subroutine controls the computation of the equilibrium-flow throat conditions. (MAIN PROGRAM).

NEWRAP* The Newton-Raphson iteration procedure for finding the equilibrium-flow conditions at a given temperature, entropy, and reservoir condition is contained in this subroutine. (NRMAX, EQUIL, NONEQ, AXFIT).

EQUIL* This subroutine controls the calculation of the equilibrium-flow solution (MAIN PROGRAM).

NONEQ* This is the controlling subroutine for the nonequilibrium solution. It also contains the logic for the starting procedure and for switching from an upstream to downstream region. (MAIN PROGRAM).

COMM* This subroutine computes the production terms in the species conservation equations (Eq. (29)). If the nonequilibrium integration has been started the pressure and entropy are also computed using Eqs. (11b) and (16), respectively. (NONEQ, RNKT).

GEOM* In this subroutine the area ratio at a given nozzle station is computed from the specified polynomial relation. If the nonequilibrium integration is started upstream of the nozzle throat the density is computed from the density-fit relation and the area ratio is obtained from the continuity equation. (COMM).

- EXACT* In this subroutine the derivatives of $\frac{dy_i}{dx}$ and $\frac{dT}{dx}$ are computed for use either in the numerical integration of the nonequilibrium equations or for use in the perturbation calculations. (NONEQ, RNKT).
- PERT* This subroutine computes the perturbation quantities used in the starting procedure for the numerical integration of the nonequilibrium equations. (NONEQ).
- AXFIT* The function of this subroutine is to invert the $A(x)$ relation to obtain the value of x corresponding to a given area ratio in the starting procedure of the nonequilibrium flow calculation. (NONEQ).
- THROAT* When the nonequilibrium solution is started upstream of the nozzle throat it is obtained as a function of the equilibrium flow density. This subroutine modifies the specified geometry to match that computed for the nonequilibrium flow upstream of the nozzle throat. (NONEQ).
- RNKT* This subroutine performs the numerical integration of the nonequilibrium flow solution. (NONEQ).
- MATINV This subroutine transposes the α_{ij} matrix for the purpose of specifying the chemical composition of the mixture in terms of the independent species. The calling sequence for this subroutine is CALL MATINV (BTA, ISC, 64) where BTA is the matrix to be transposed, ISC is the size of the square matrix, and 64 is the 2nd dimension of this matrix according to the dimension statement. (INTA).
- SIMSOL In both the equilibrium and nonequilibrium flow calculations it is necessary to solve a set of linear, simultaneous algebraic equations. This subroutine is one which is available for such a function in the program library at CAL. This subroutine is written in MAP language and hence is peculiar to the IBM 7044 version machine in use at CAL, i. e. one including double precision hardware. The calling sequence for the subroutine used in the nozzle flow program is CALL SIMSOL (AA, ISSP2, 22). The array denoted by AA consists of the matrix of coefficients and the right hand sides of the simultaneous equations to be solved. The right hand sides of the equations are listed in the

last column of AA. The second number, here ISSP2, in the calling sequence denotes the size of the matrix of coefficients. The third number, here 22, is the number of rows allowed for in the dimension statement for AA.

One of the computations in the program which uses this subroutine is the Newton-Raphson procedure for finding the composition at a point in an equilibrium flow. In an equilibrium nozzle expansion, the concentrations of some species, for example atomic species, become quite small. As discussed in the section on input data, species which are expected to vanish in an equilibrium expansion to low temperature should not be chosen as independent species. In early work with the program the Newton-Raphson iteration was found to diverge even when the concentrations of the dependent species became vanishingly small. This situation was remedied by using a SIMSOL subroutine which employs double precision arithmetic. While this accuracy is not consistent with the single precision arithmetic used throughout the program this procedure permits continuing the computation even when dependent species concentrations underflow the digital limit of the machine and hence are set to zero. This subroutine included in the program is one using double precision arithmetic. If such a subroutine cannot be used, some provision must be made to set to zero the concentrations of dependent species when they become less than a given small number. Otherwise the equilibrium solution cannot be continued to temperatures where species become vanishingly small.

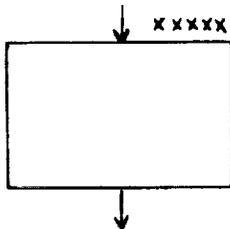
As discussed in Section 5.1, in considering ionized flows in equilibrium, the electrons, which are an independent species, may vanish. The electron concentration cannot be allowed to underflow and hence in this case the gas model is truncated and all ionized species are dropped from the calculation when the electron concentration becomes less than 10^{-30} . When the concentration of the electrons becomes less than about 10^{-15} moles per gram the accuracy of the results for the ionized species is questionable. If desired the electrons could be dropped from the calculation at a larger concentration. (INTA, NEWRAP, EXACT, PERT).

SAVE Frequently it is necessary to terminate program execution for considerations of time and/or to check the progress of the solution. This can be done by storing the contents of the computer memory on magnetic tape. Since the subroutine used for this purpose is peculiar to the CAL system, a dummy subroutine has been inserted in the deck. Users may wish to insert their own subroutine for this purpose. (NONEQ).

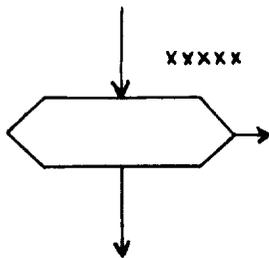
SSWTCH, PDUMP, EXIT These are standard subroutines available in systems utilizing FORTRAN IV language programming.²⁵

7.2 Flow Charts of FORTRAN Subroutines

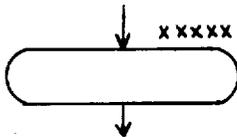
This section contains flow charts of the more complicated subroutines in the nozzle flow program. These flow charts do not depict every statement in the FORTRAN Source deck but rather connect the description in the text to the actual program. The following symbols are used in these charts:



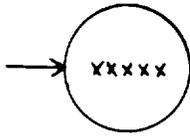
Operational block. This symbol refers to computational instructions. When appropriate the description in an operational block contains references to equations in the text. The numbers above the upper right-hand corner refer to the numbers of the cards in the FORTRAN source deck to which the block refers.



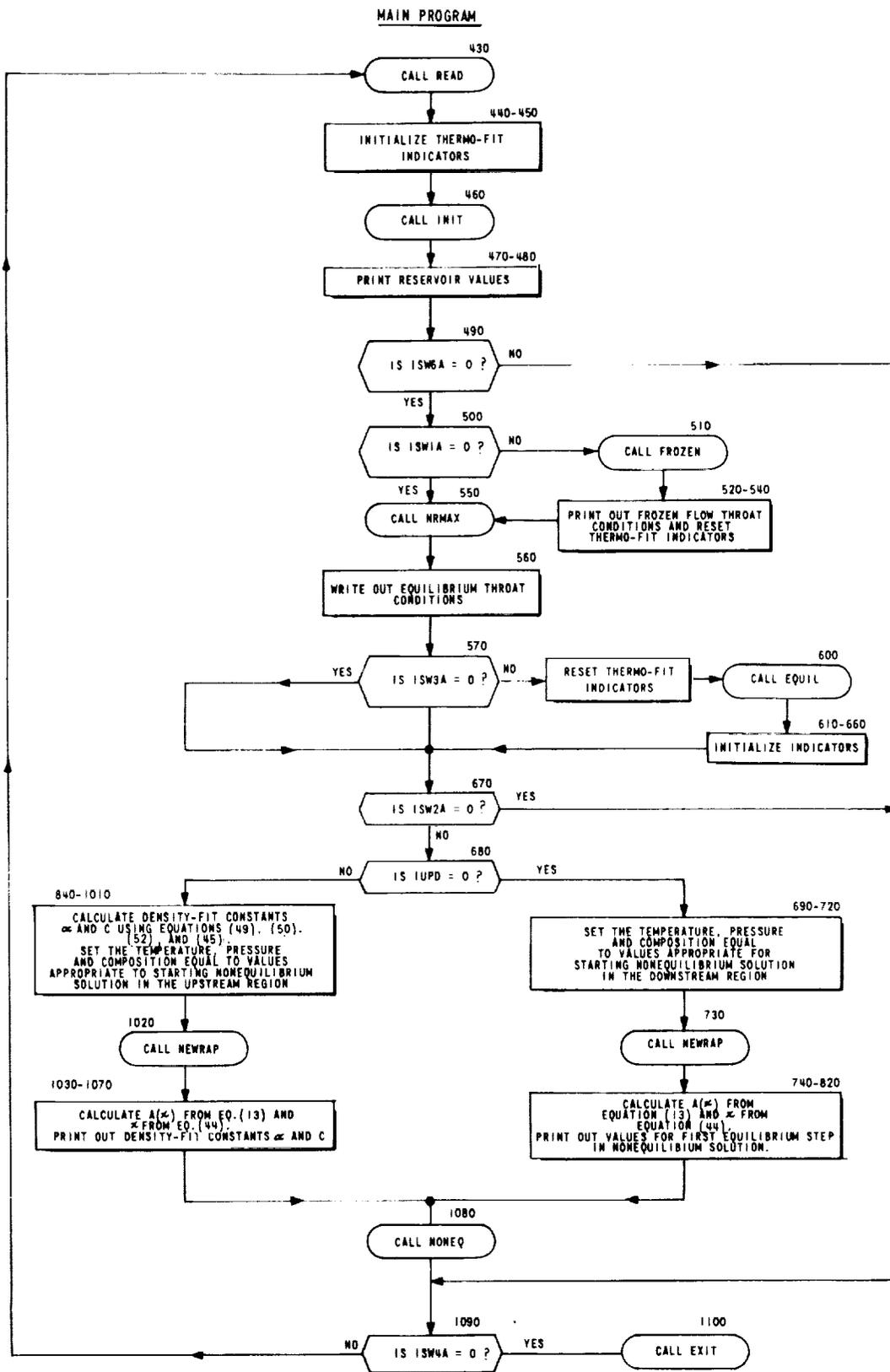
Decision block. This symbol denotes points in the program beyond which two or more paths are possible. The information in the block questions the value of some indicator. Again the number outside the block refers to the card in the FORTRAN program.



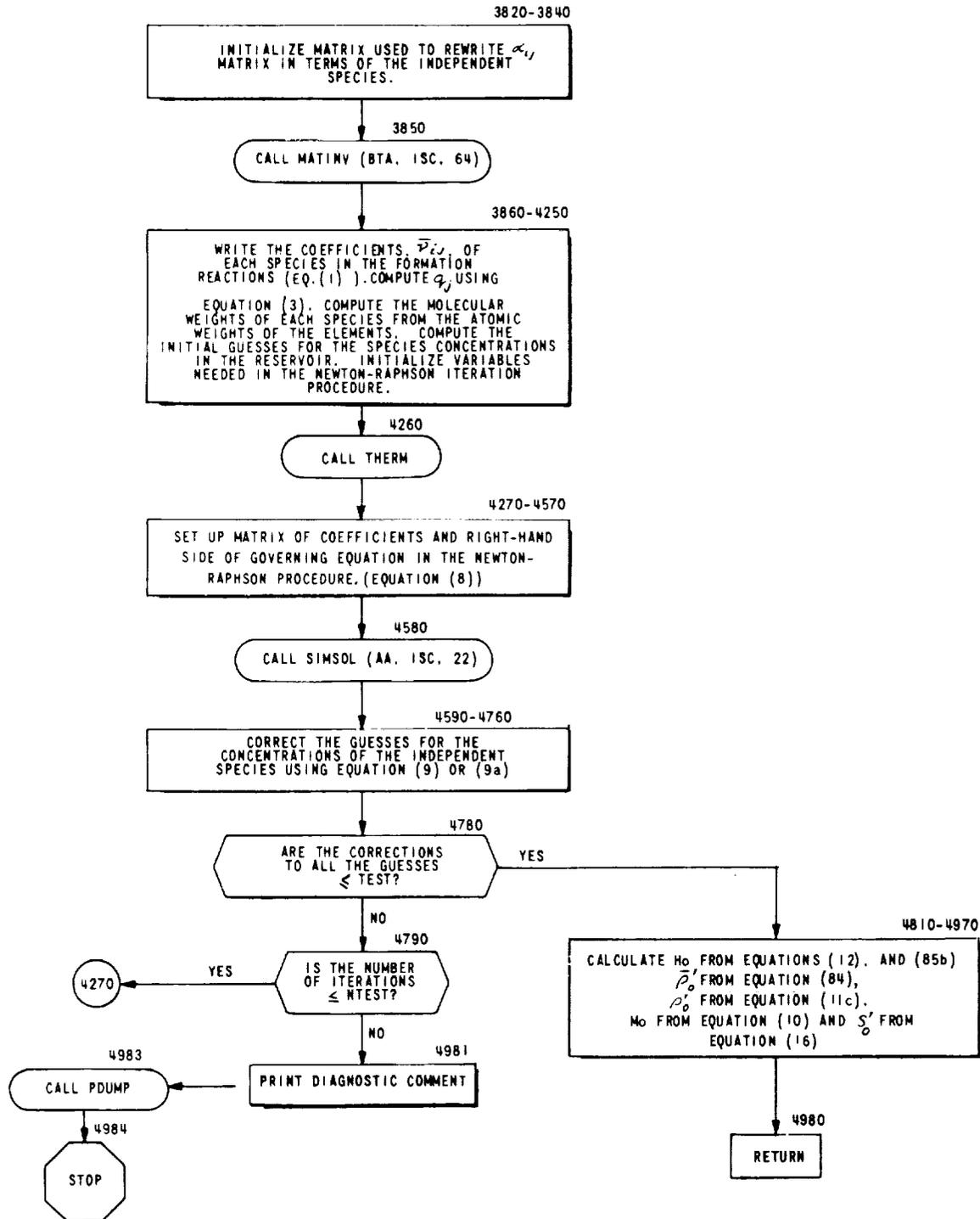
Calling block. This symbol indicates a call statement for a FORTRAN subroutine.

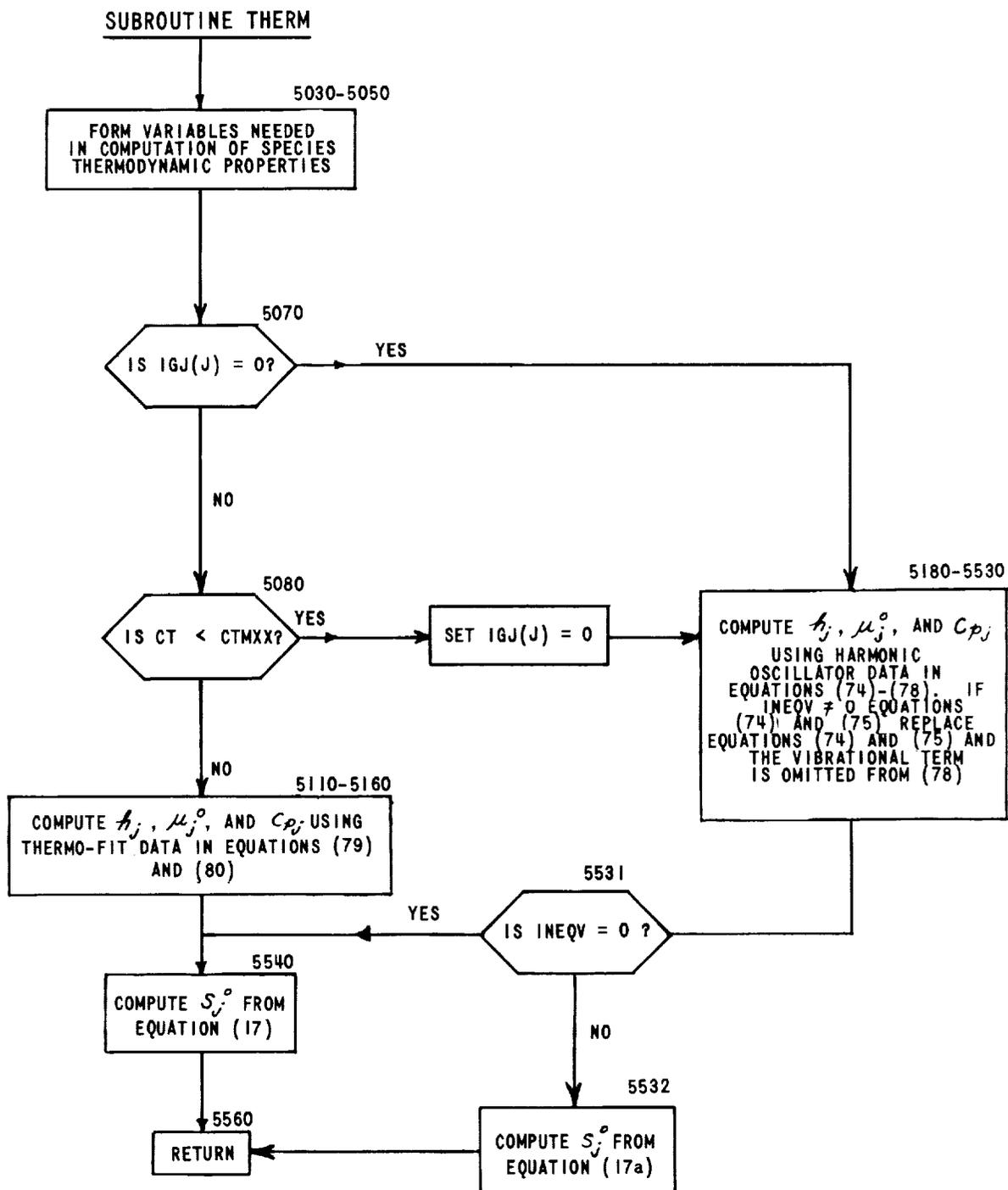


Connector. This symbol is used to display a connection for a case where arrows cannot be used conveniently. The number in the circle refers to the number of the card in the FORTRAN deck corresponding to the instruction to which the connection is made.

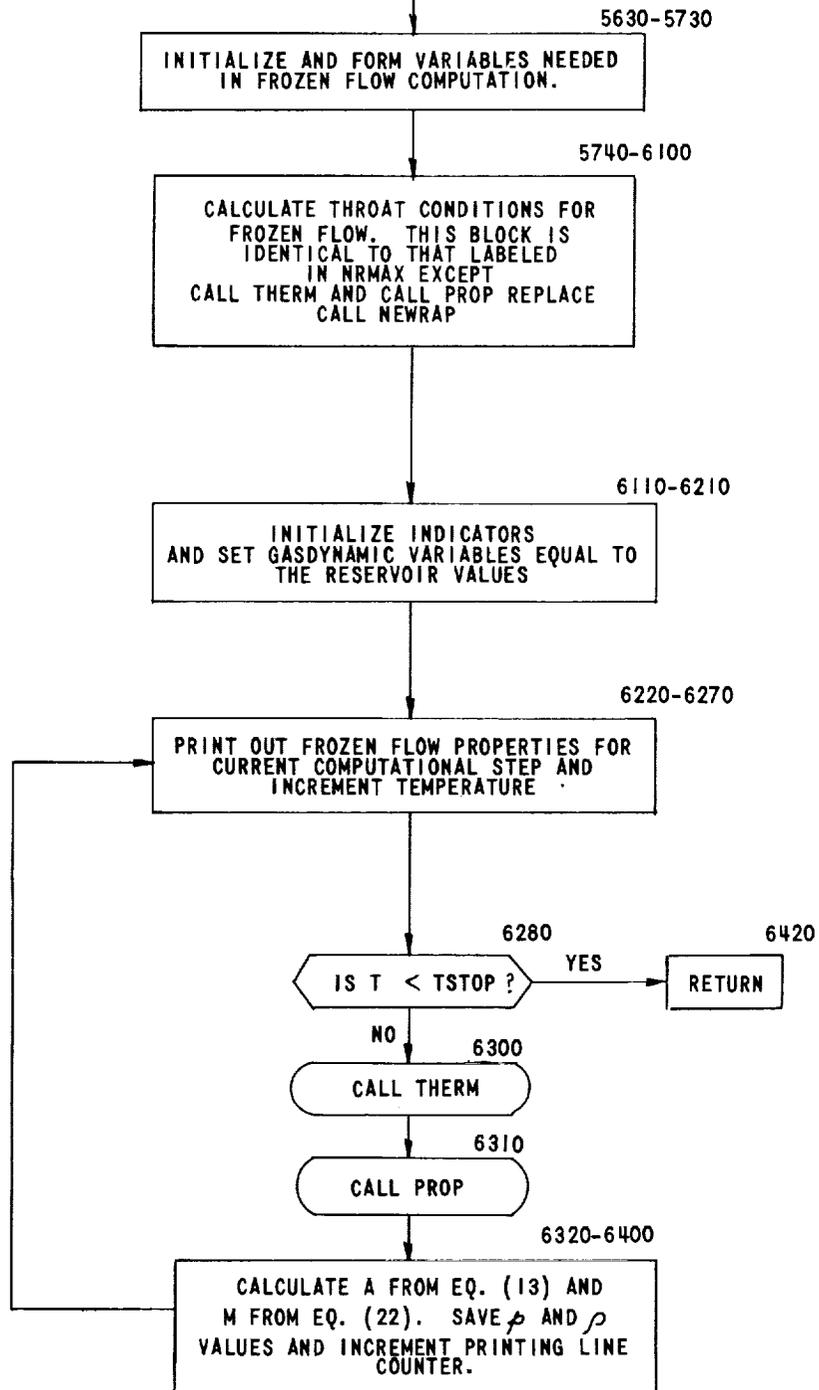


SUBROUTINE INTA

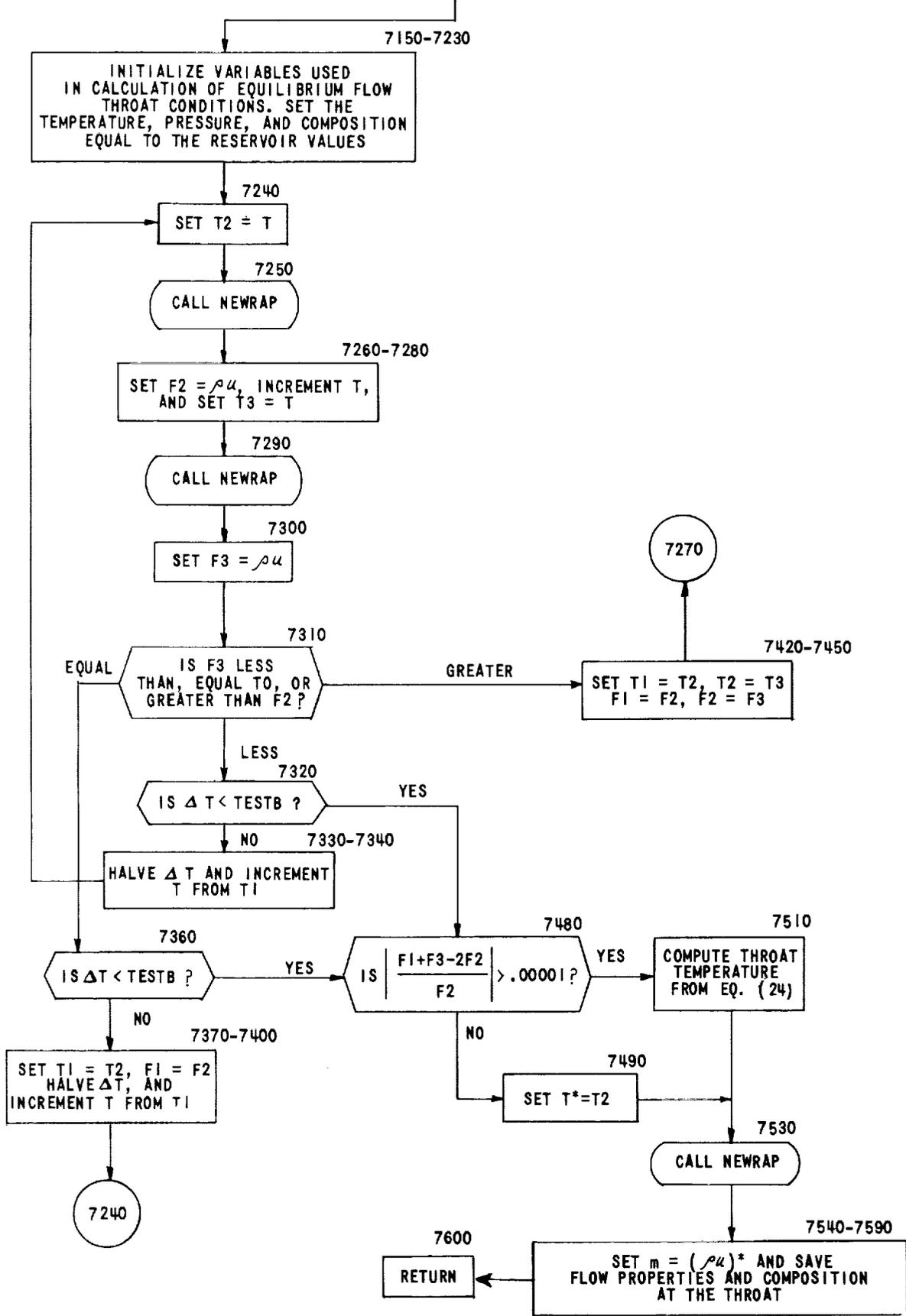




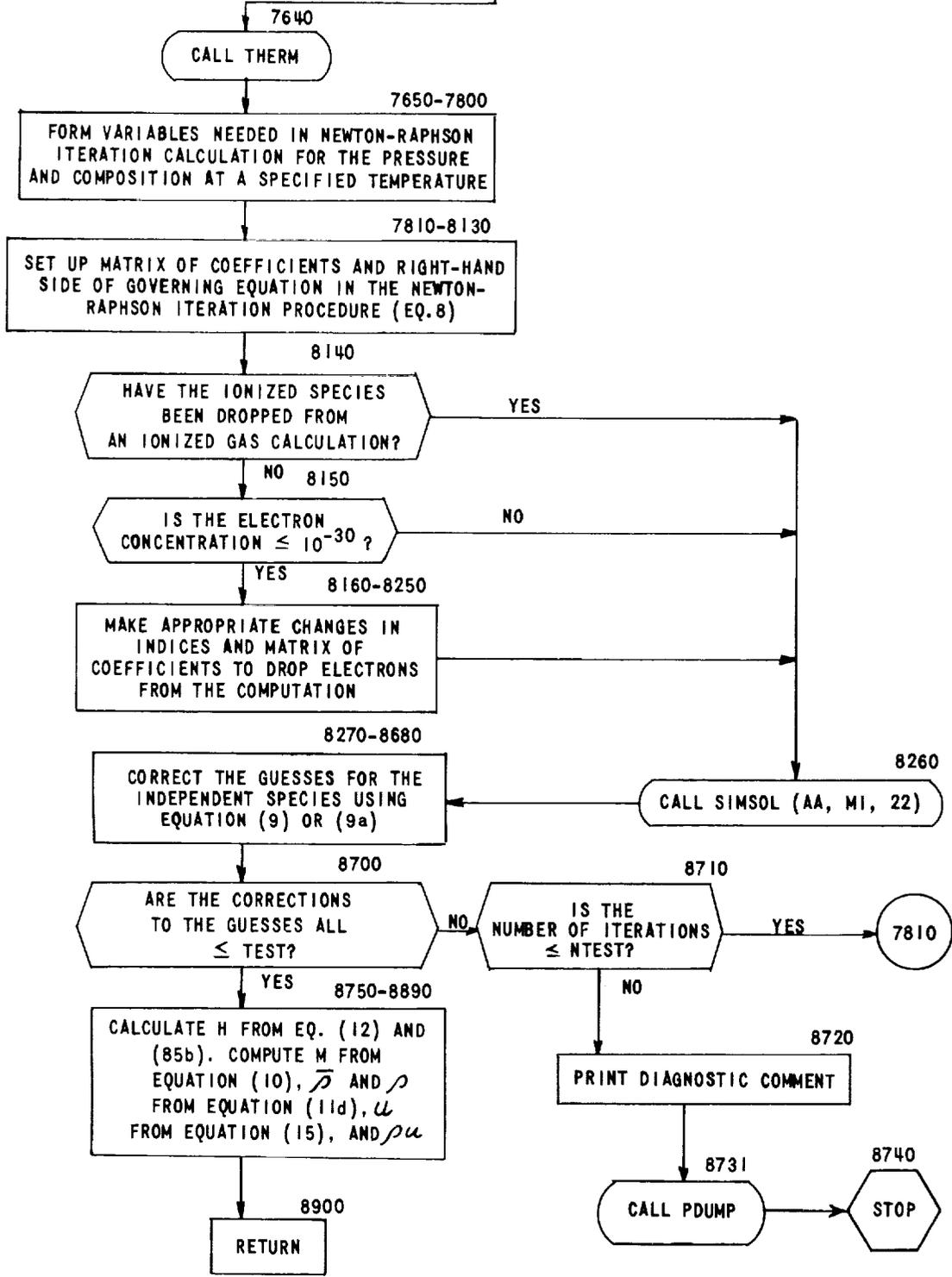
SUBROUTINE FROZEN

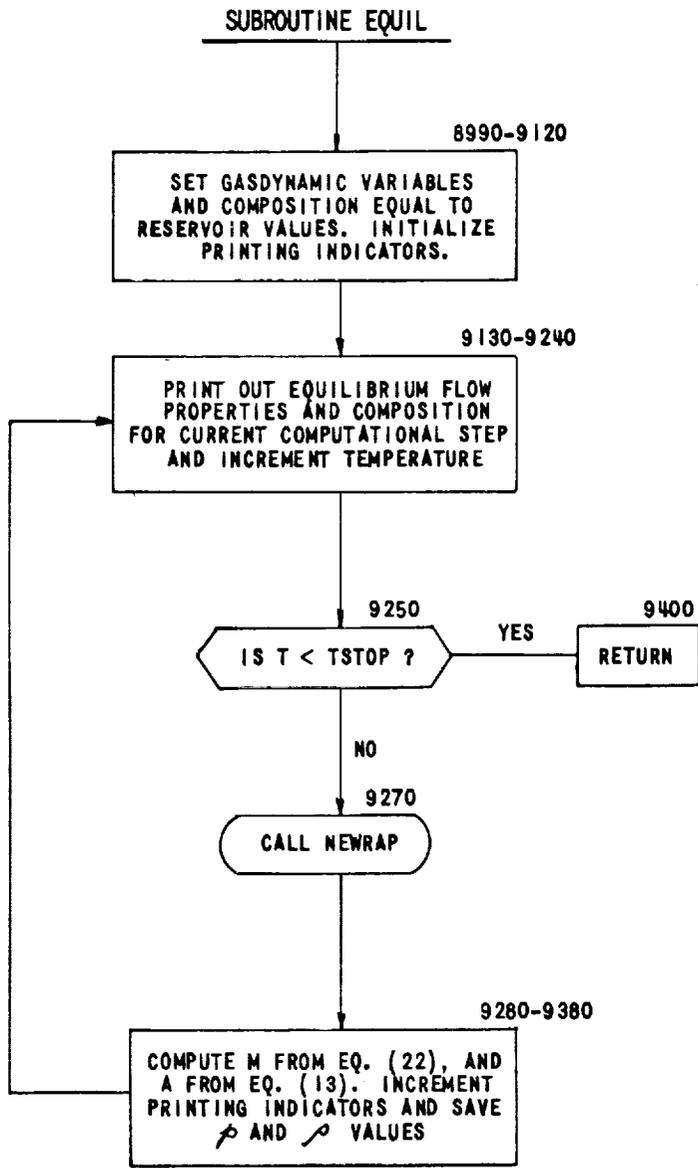


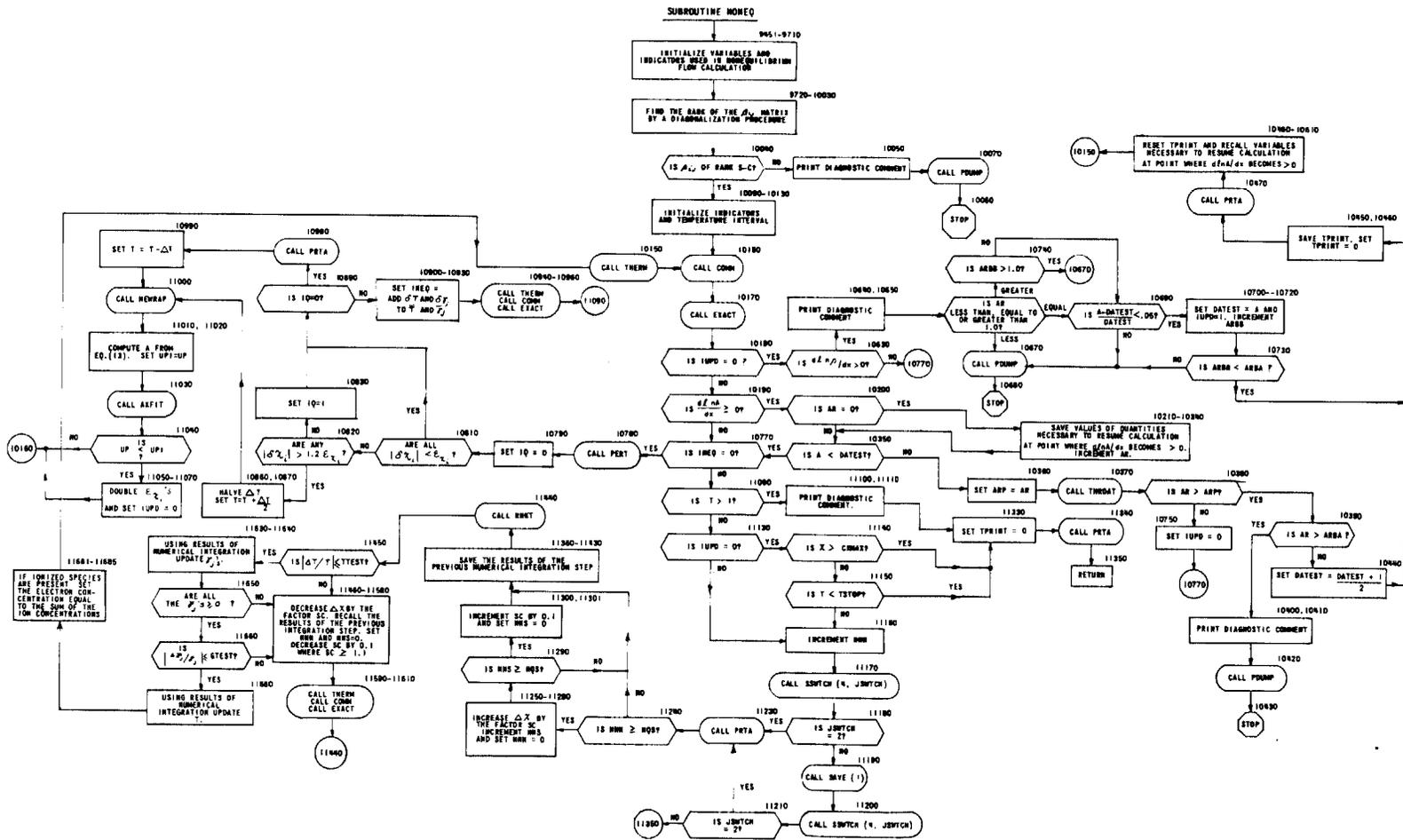
SUBROUTINE NRMAX

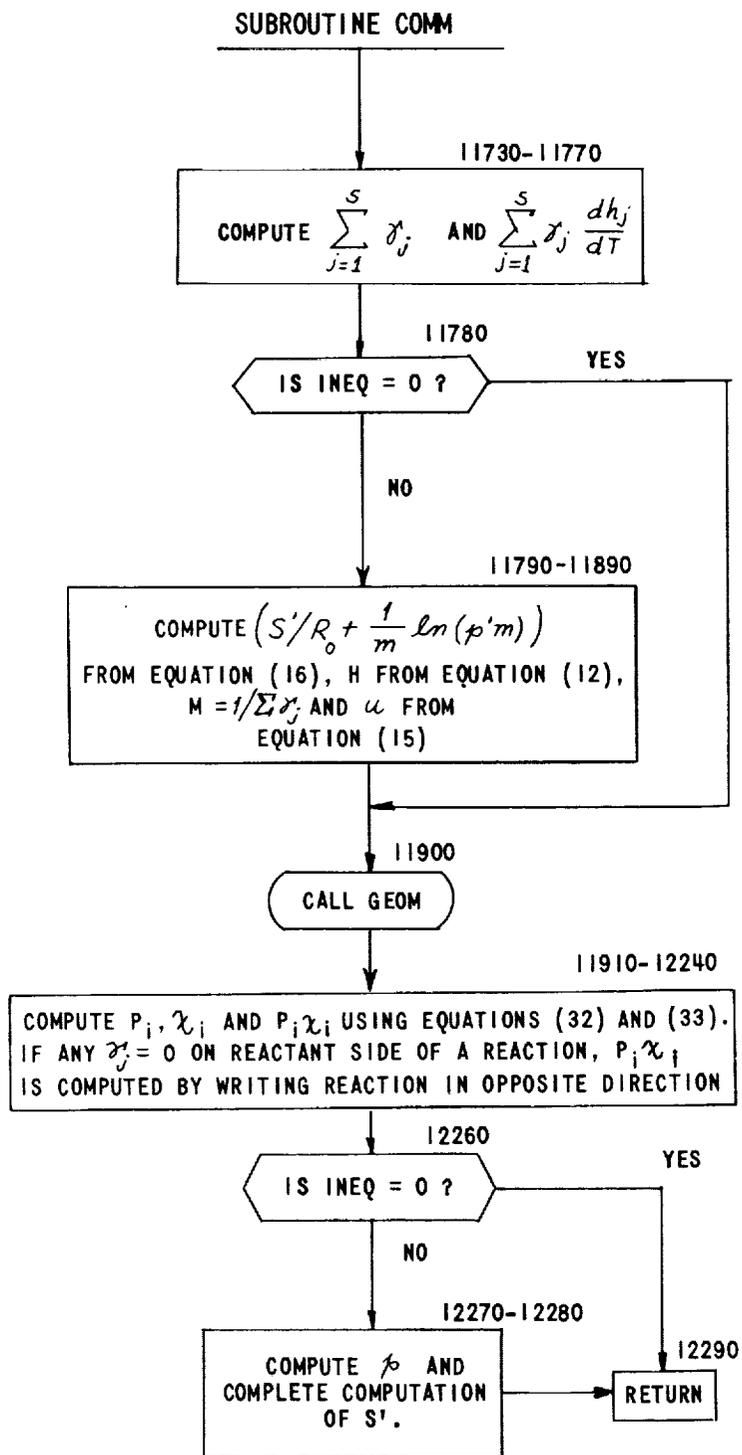


SUBROUTINE NEWRAP

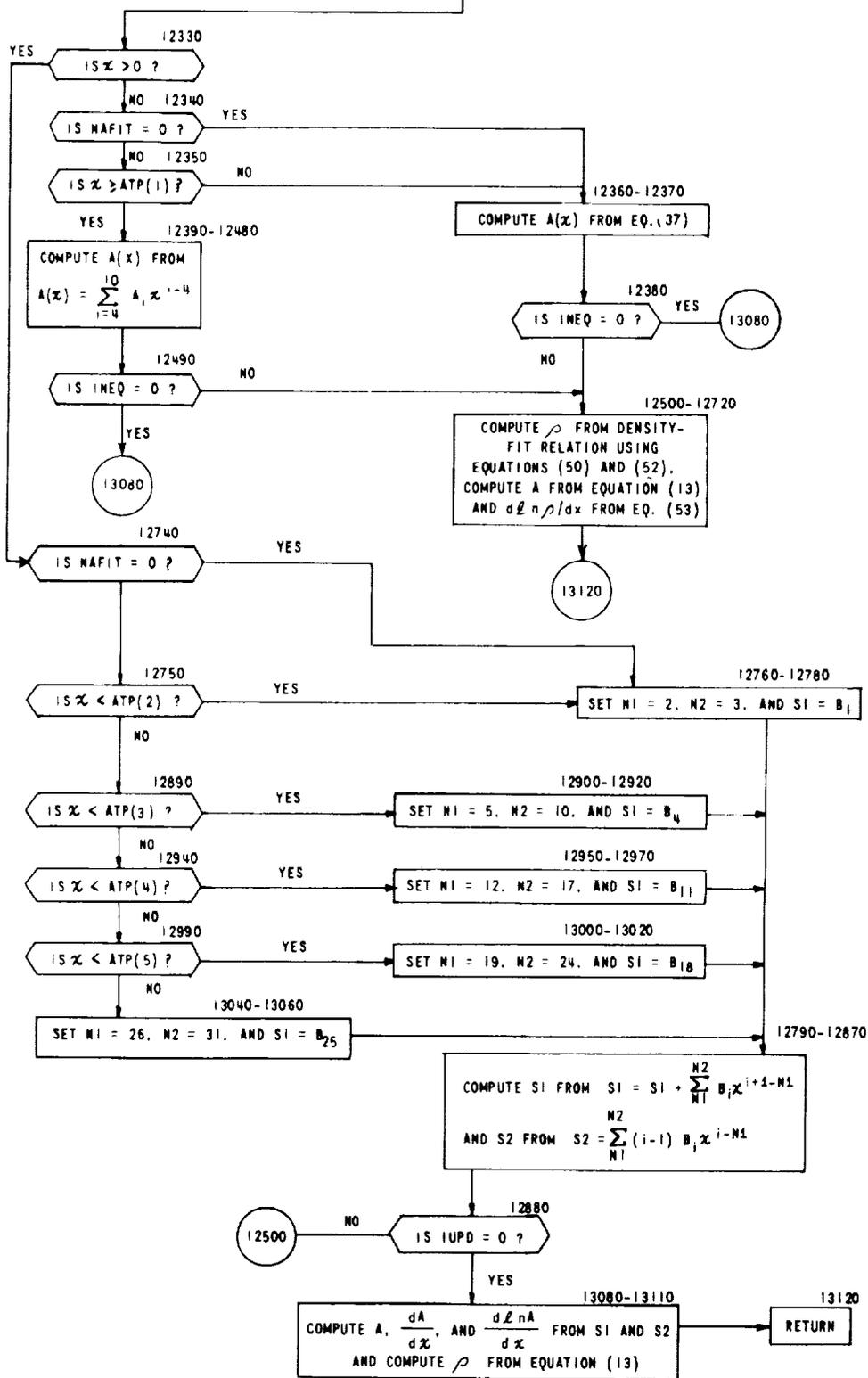








SUBROUTINE GEOM



SUBROUTINE EXACT

13160-13600

SET UP THE MATRIX OF COEFFICIENTS AND THE RIGHT-HAND SIDES OF THE GOVERNING EQUATIONS FOR $d\delta_j/dx$, dT/dx AND $d \ln \rho/dx$ OR $d \ln A/dx$. IF $INEQ=1$ THESE EQUATIONS ARE (28), (30), (34), AND (36) IF $INEQ=0$ EQUATION (39) REPLACES (29) IF $IUPD=1$ AND $INEQ=1$ THEN $d \ln \rho/dx$ IS SPECIFIED AND $d \ln A/dx$ IS UNKNOWN

13610

CALL SIMSOL
(AAA, ISSP2, 22)

13620-13690

SET THE QUANTITIES $d\delta_j/dx$ AND dT/dx EQUAL TO THE FIRST (S+1) ROWS OF THE SOLUTION VECTOR IF $IUPD=1$ AND $INEQ=1$ THEN $d \ln A/dx$ IS THE (S+2) ROW OF THE SOLUTION VECTOR. OTHERWISE $d \ln \rho/dx$ IS COMPUTED.

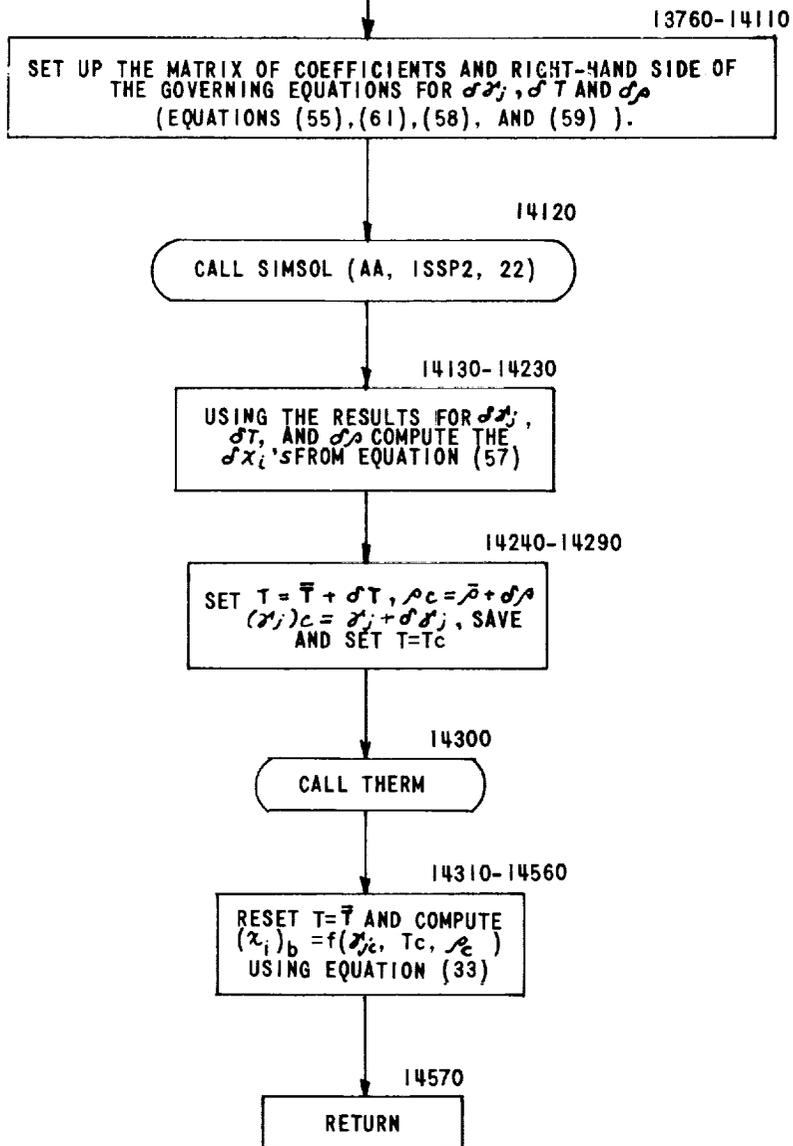
13700

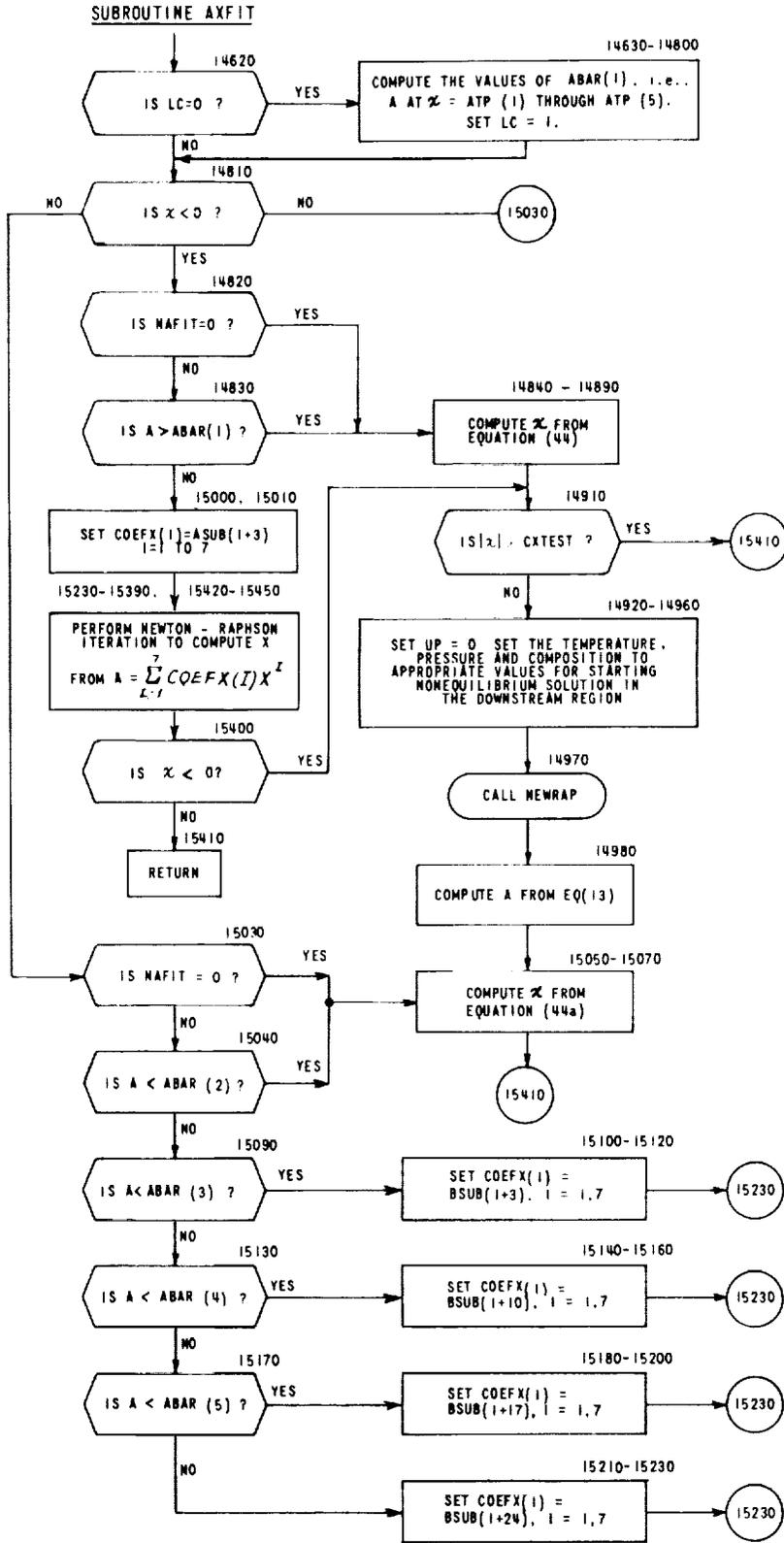
COMPUTE M FROM EQ. (38)

13710

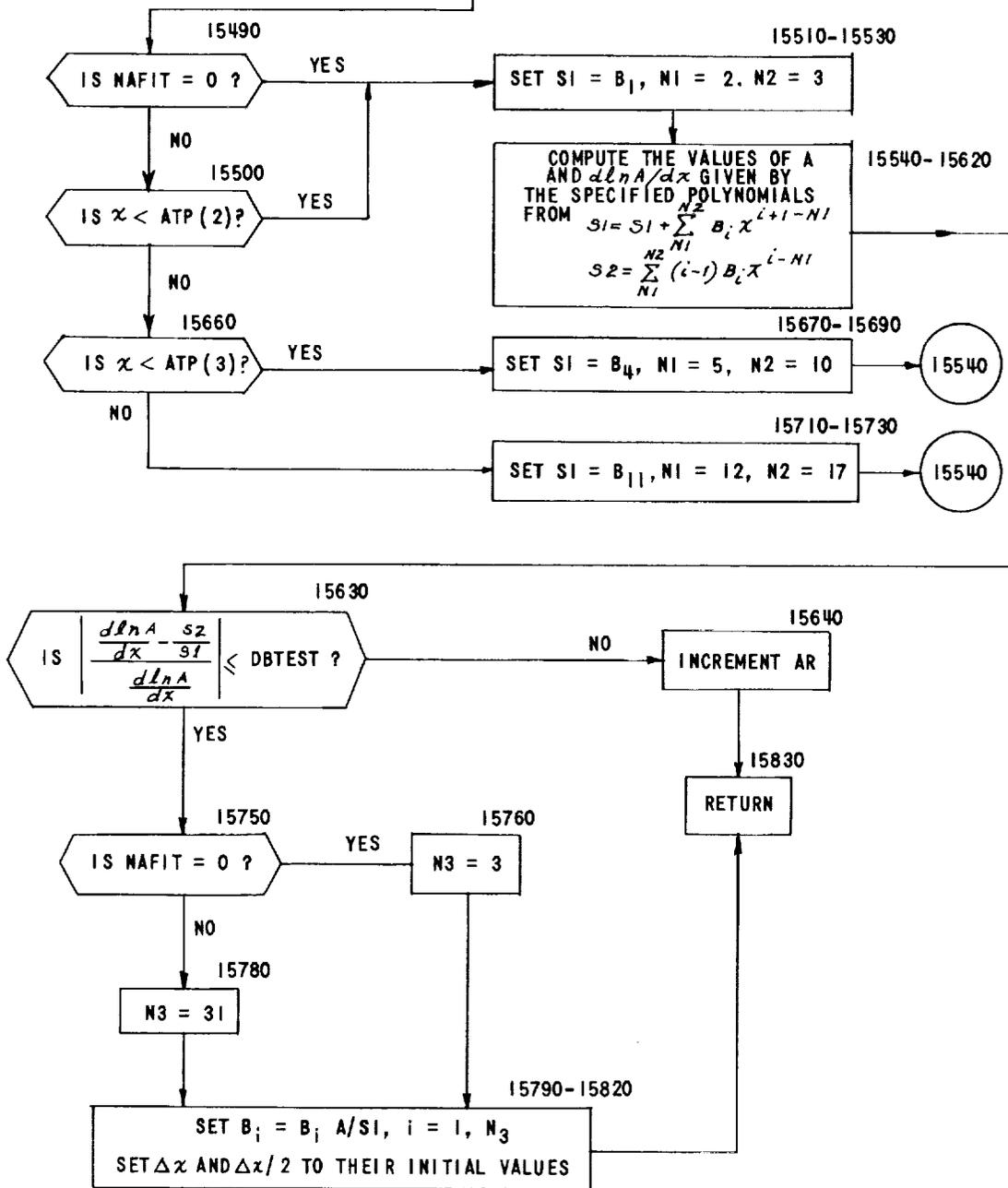
RETURN

SUBROUTINE PERT



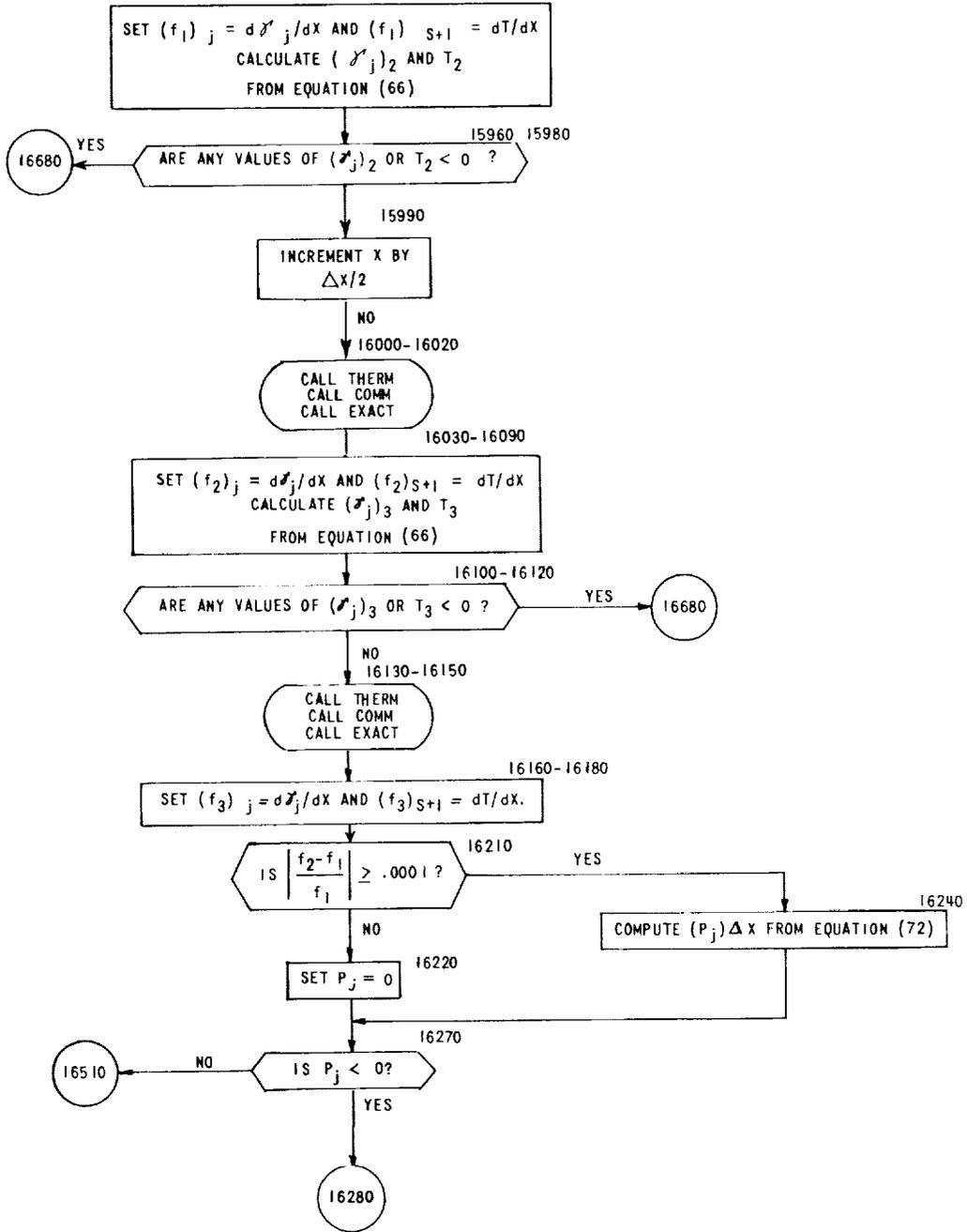


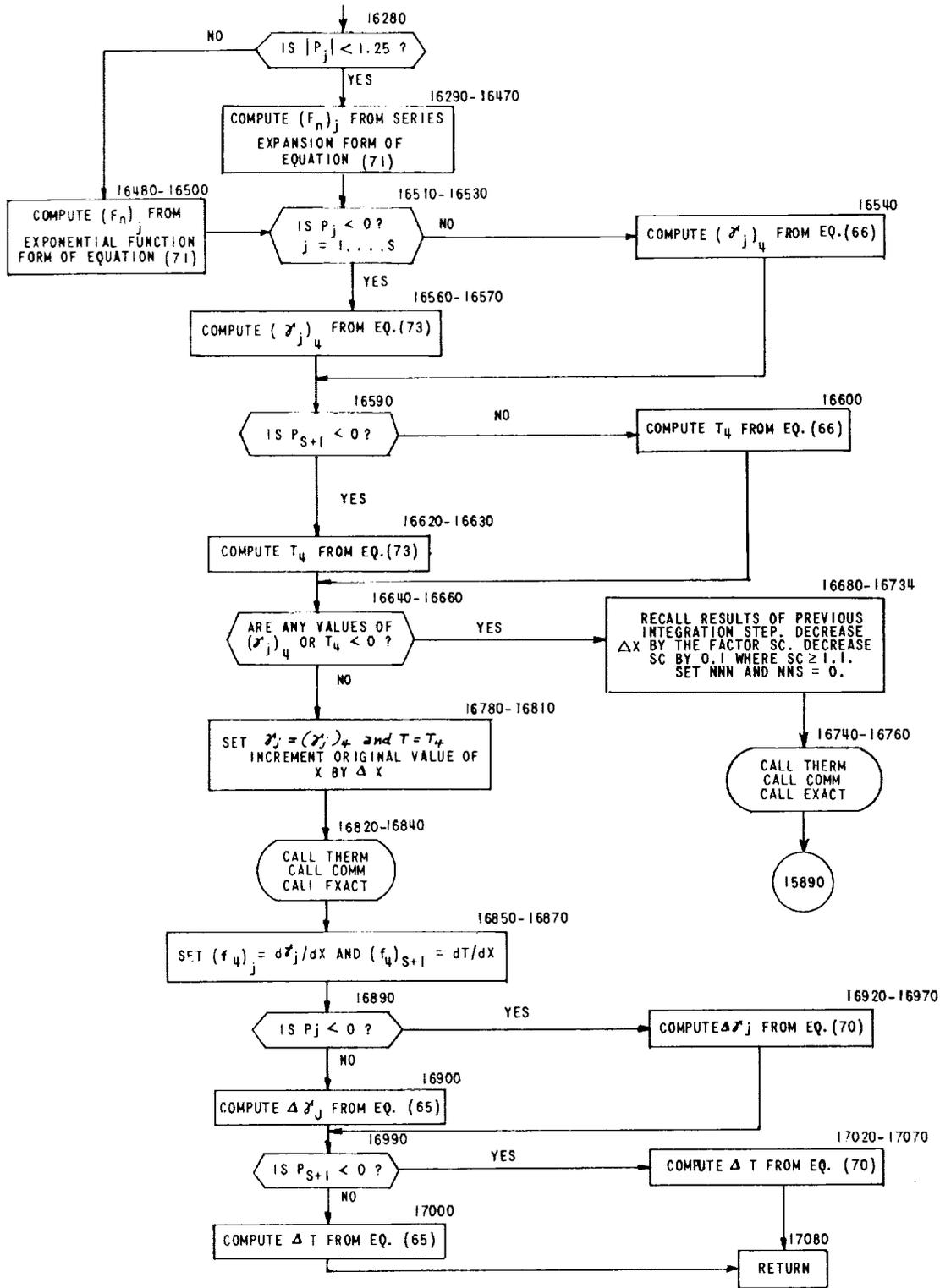
SUBROUTINE THROAT



SUBROUTINE RNKT

15890-15950





7.3 FORTRAN Variables Used in Nozzle Flow Program

The variables which appear in the COMMON statement of the nozzle flow program are listed in this section. The FORTRAN symbols, their definitions, and the subroutines in which they are used are given. The numbers used to denote the subroutines in which a FORTRAN variable is used refer to the following list. Where possible the corresponding algebraic symbol is used to define a FORTRAN variable.

- | | |
|------------|------------|
| 1. MAIN | 12. EQUIL |
| 2. READ | 13. NONEQ |
| 3. LIST | 14. COMM |
| 4. INIT | 15. GEOM |
| 5. INTA | 16. EXACT |
| 6. THERM | 17. PERT |
| 7. FROZEN | 18. AXFIT |
| 8. PROP | 19. THROAT |
| 9. PRTA | 20. RNKT |
| 10. NRMAX | 21. MATINV |
| 11. NEWRAP | |

<u>FORTRAN Variable</u>	<u>Subroutine</u>	<u>Definition</u>
A	1, 15	α , constant in density-fit relation
AA(I, J)	5, 11, 17	matrix element
AAA(I, J)	16	matrix element
ACOM(I)	2	comment which appears in list of input data
AFNTS	1, 13, 18	used to denote area ratio calculated for equilibrium flow in starting procedure for nonequilibrium solution
AFNX	7, 9, 12, 13, 15, 19	A , area ratio ($A = A'/A^*$)

<u>FORTTRAN Variable</u>	<u>Subroutine</u>	<u>Definition</u>
ALPIJ(I, J)	2, 3, 5, 16, 17	α_{ij} , number of atoms of j^{th} element per molecule of the i^{th} species
AMACH	7, 9, 12, 16	M , Mach number
AR	13, 19	indicator which denotes where $d \ln A / dx$ becomes positive and number of times switch from upstream to downstream region has been attempted
ARBA	4, 13	maximum number of tries at switching from upstream to downstream region
ARBB	4, 13	counter for number of times upstream-downstream switching point is moved downstream
ASUB(I)	1-3, 15, 18	A_i , coefficients in area-ratio expression for upstream region
ATP(I)	2, 3, 15, 18, 19	transfer points in area-ratio expression
B(I, J)	13	dummy variable used in ranking β_{ij}
BCHI(I)	9, 17	τ_i evaluated for $\bar{v}_j + \delta \tau_j, \bar{T} + \delta T, \bar{p} + \delta p$
BE(I)	13, 17	$\beta_i, \beta_i = \sum_j \beta_{ij}$
BET(I)	5, 11, 16	$\bar{v}_i - 1$ where $\bar{v}_i = \sum_j \bar{v}_{ij}$
BETA(I, J)	13, 14, 16, 17	$\beta'_{ij}, \beta_{ij} = v'_{ij} - v_{ij}$
BLBK(I)	13	dummy variables for downstream area coefficients
BSUB(I)	1-3, 13, 15, 18, 19	B_i , coefficients in area-ratio expression in downstream region
BTA(I, J)	5	dummy variable used in transposing α_{ij}

<u>FORTTRAN Variable</u>	<u>Subroutine</u>	<u>Definition</u>
BZERO	2, 3, 5, 8, 11	h_o/η^o (see Eq. (11c))
C	1, 15	C , constant used in density-fit relation
CAI(I)	2, 3, 13, 14	A_i , constant factor in (Eq. (82))
CAPQ(K)	2, 3, 5	Q_k , number of gram-atoms of element k
CAPX(J)	1, 5, 10, 11, 18	X_j , mole fraction of j^{th} species
CAPXTH(J)	1, 10, 18	X_j^* , mole fraction at throat
CARB	13	dummy variable for $A(x)$
CCI(I)	5	intermediate variable for computing molecular weights of species from molecular weights of elements
CCPJ(J)	6, 14, 17	C_{p_j} , $C_{p_j} = dh_j/dT$
CDIJ(I, J)	5, 11, 16	$\bar{\nu}_{ij}$, stoichiometric coefficients in equilibrium formation reactions
CEACT(I)	2, 3, 14	E_{act_i} , activation energy
CECHII(I)	2, 3, 13	ϵ_{χ_i} , test on $\delta\chi_i$ which determines where numerical integration is begun
CGI(I)	5, 11	molecular weights of species
CGMU(I)	5, 11	$\ln X_i$
CH	1, 5, 8, 11, 14	H , enthalpy
CHA	1, 5, 8, 11, 14	H_o , reservoir or stagnation enthalpy
CHI(I)	9, 14	χ_i defined by Eq. (31)
CHII(I)	5, 11	intermediate variable in computation of equilibrium constant based on mole-fractions
CLN1MC(I)	14	$\ln(1-\chi_i)$

<u>FORTTRAN Variable</u>	<u>Subroutine</u>	<u>Definition</u>
CLNPI(I)	14	$\ln P_i$
CLNT	6, 14	$\ln T'$
CM	5, 11, 14	M , molecular weight
CMA	1, 5, 7, 8, 11, 13, 14, 16, 17	M_o , reservoir molecular weight
CMW(I)	2, 3, 5	M_i , atomic weights of elements
CRA	4, 5, 14	R_o , universal gas constant (=1.98647 cal/mole °K)
CRP	4, 13, 14, 17	$R_o T_o'$
CRRB	5, 7, 11	intermediate variable in calculation of entropy
CRS	13	dummy variable for entropy
CSTA	13, 14	$0.5 \ln (M_o / R_o T_o')$
CT	1, 4, 6-14, 16-18, 20	T , temperature ($T = T' / T_o'$)
CTAP	1-6	T_o' , reservoir temperature in °K
CTB	13, 20	dummy variable for T
CTC	17	dummy variable for T
CTMAX	1, 7, 10, 18	T^* , throat temperature
CTMXX	2-4, 6	temperature for switching from thermo-fit to harmonic-oscillator model for species properties
CTP	6	T' , temperature in °K
CTPL	4	$\ln T_o'$
CTT	9, 13	temperature at previous step in nonequilibrium calculation
CX	1, 9, 13, 15, 18-20	x , distance along streamtube ($x = x'/l$)

<u>FORTTRAN Variable</u>	<u>Subroutine</u>	<u>Definition</u>
CXB	13, 20	dummy variable for κ
CXMAX	2, 3, 13	maximum value of κ desired in nonequilibrium solution
DATEST	4, 13	value of A at which non-equilibrium solution is switched from upstream to downstream region
DBTEST	4, 19	percentage difference allowed between calculated and specified $d \ln A / dx$ at switching point from upstream to downstream region
DELTA1	1, 4, 7, 10, 12, 13	temperature increment used in frozen flow and equilibrium flow calculations
DELTA2	1-3, 18	temperature increment used to start nonequilibrium solution in the downstream region
DELTA3	2, 3	temperature increment used to start nonequilibrium solution in upstream region
DELTAX	2, 3, 13, 19, 20	$\Delta \kappa$
DGJ(J)	9, 16, 17, 20	$d\gamma_j / dx$
DLOGA	13, 15, 16, 19	$d \ln A / dx$
DLOGR	13, 15, 16	$d \ln p / dx$
DT	16, 20	dT / dx
ELJ(L, J)	2-4, 6	ϵ_{lj} , energy of l^{th} electronic level of j^{th} species ($\epsilon_{lj} = \epsilon'_{lj} / R_0 T_0$)
ELMENT(K)	2, 3	chemical symbols for elements in mixture
ENT	7, 8	intermediate variable used in frozen flow calculation
ETAI(I)	2, 3, 14	η_i , temperature exponent in k_{fi}

<u>FORTTRAN Variable</u>	<u>Subroutine</u>	<u>Definition</u>
ETAJ(J)	2-4, 6	η_j : number of atoms in j^{th} species
FLUX	7, 8, 10-13, 18	ρu
GELJ(L, J)	2, 3, 6	g_{lj} : degeneracy of l^{th} electronic level of j^{th} species
GJ(J)	1, 9-14, 16, 17, 20	γ_j : species concentration in moles/gm
GJA(J)	1, 5, 7, 8, 10, 12	$(\gamma_j)_0$: species concentration in reservoir
GJB(J)	13, 20	dummy variable for γ_j
GJC(J)	17	dummy variable for γ_j
GTEST	2, 3, 13	allowed value of $\Delta \gamma_j / \gamma_j$ in Runge-Kutta integration step
HDELX	13, 19, 20	$\Delta x / 2$
HP(J)	1-3	chemical symbol for species in mixture
IC	2, 3, 5, 11	number of ions included in chemical model
IGJ(J)	1-3, 6	indicates whether thermo-fit data is to be used for the j^{th} species
IGM(J)	2-4, 6	number of electronic levels for j^{th} species
IM	1, 4, 11	index which is incremented when electrons are dropped from calculation
INEQ	9, 13-16	indicates when numerical integration of nonequilibrium solution has begun
INEQV	2, 3, 6	indicator for selecting whether equilibrium or frozen vibrational model is to be used

<u>FORTTRAN Variable</u>	<u>Subroutine</u>	<u>Definition</u>
IP	7, 9, 12, 13	printout line-counter
IROBAR	2, 3, 7, 9, 12	indicates that effective density is to be printed out
IRUN	1-3, 9	run number
ISC	2-5, 10, 11, 13, 16, 17	c , number of elements in mixture
ISCP1	13, 16, 17	$c + 1$
ISMC	1, 4, 5, 13	$s - c$
ISMCNR	1, 4, 11	current value of $(s - c)$ in equilibrium flow calculation (decreased by IC when electrons are dropped from calculation)
ISR	2, 3, 9, 13, 14, 16, 17	r , number of reactions
ISS	1-14, 16-18, 20	s , number of species in mixture
ISSNR	1, 4, 11	current value of s in equilibrium flow calculation (decreased by IC when electrons are dropped from calculation)
ISSP1	13, 16, 17, 20	$s + 1$
ISSP2	13, 16, 17	$s + 2$
ISSP3	13, 16, 17	$s + 3$
ISSP4	13, 16	$s + 4$
ISW1A	1-3	indicates whether frozen flow solution is desired
ISW2A	1-3	indicates whether nonequilibrium flow solution is desired
ISW3A	1-3	indicates whether equilibrium flow solution is desired

<u>FORTRAN Variable</u>	<u>Subroutine</u>	<u>Definition</u>
ISW4A	1, 2	indicates whether another calculation is to be done after completion of one case
ISW6A	1, 2	indicates when only reservoir calculation is to be done
ISW5A, ISW1B ISW2B, ISW3B ISW4B, ISW5B ISW6B	2	additional indicators not currently used in program
ITB(I)	13	dummy variable for indicators
IUPD	1-3, 13, 15, 16	indicates whether calculation is in upstream or downstream region
IZERO	1-3, 5, 6, 13	logical variable used to denote zero
JJK	1, 4, 11	indicates when electrons are dropped in equilibrium calculation
KHO	2-4	indicates whether any harmonic-oscillator data are used
KKUR	2	indicates whether the third body matrix is used in the chemical model
KUR(I, J)	2, 3, 14	U_{ij} , third body matrix
LC	13, 18	indicates the first time subroutine AXFIT is called
M1	5, 10, 11	index equal to $c+1$
NAFIT	2, 3, 15, 18, 19	indicator for selecting standard or fitted geometry
NFIT	2-4	indicates whether any thermo-fit data is to be used
NIT	11	counter for number of iterations in Newton-Raphson procedure
NNN	13, 20	integration step counter

<u>FORTTRAN Variable</u>	<u>Subroutine</u>	<u>Definition</u>
NNS	13, 20	number of times $\Delta \kappa$ has been increased by current value of SC
NQS	2, 3, 13	number of successful steps before $\Delta \kappa$ is increased
NTEST	4, 5, 11	number of iterations allowed in Newton-Raphson procedure
PCT	9, 13, 17	δT , perturbation in temperature
PCTEST	4, 13	tolerance on ϵ_{τ_i} when testing size of $\delta \tau_i$
PERTGJ(J)	9, 13, 17	$\delta \tau_j$, perturbation in species concentrations
PGJ(J)	11	intermediate variable in Newton-Raphson calculation of equilibrium composition
PI(I)	9, 13, 14, 17	P_i defined by Eq. (32)
PICHI(I)	9, 14, 16	$P_i \tau_i$
PRES	1, 7-12, 14, 18	p , pressure ($p = p'/p_o'$)
PRESA	1-3, 5, 14	p_o' , reservoir pressure in atm
PRESB	7, 12	dummy variable for p
PRESTH	1, 7, 10, 18	p^* pressure of throat
PRHO	17	$\delta \rho$ perturbation in density
QM(I)	5, 11	q_j number of moles of j^{th} components in one mole of mixture
QQ(I)	2, 3, 14	q_i
RHAP	1, 5, 14, 17	ρ_o' reservoir density (gms/cc)
RHO	1, 7-15, 17	ρ , density ($\rho = \rho'/\rho_o'$)
RHOB	7, 12, 13	dummy variable for ρ

<u>FORTTRAN Variable</u>	<u>Subroutine</u>	<u>Definition</u>
RHOBAR	7-9, 11, 12	$\bar{\rho}$, effective density defined by Eq. (84)
RHOC	17	dummy variable for ρ
RHOP	14	ρ' density in gms/cc
RHPL	14	$\ln \rho'$
RHTH	1, 7, 10, 15	ρ^* density at throat
ROBARA	5, 7, 8, 11, 12, 14	$\bar{\rho}'_0 / \rho'_0$
ROBARP	5, 8, 11	$\bar{\rho}'_0$ effective density in reservoir
SAJ(J)	4, 6	a_j constant in harmonic - oscillator expression for μ_j
SBJ(J)	2-4	b_j constant defined by Eq.(76)
SC	13, 20	factor by which integration interval is changed
SCPG	14, 16	$\sum_j \tau_j C_{p_j}$
SDCHI(I)	9, 13, 17	$\delta \tau_i$ perturbation in τ_i
SDELTX	13, 19	initial value of $\Delta \tau$
SDGJ(J)	13, 20	$\Delta \tau_j$, change of τ_j in integration interval
SDT	13, 20	ΔT , change of T in integration interval
SEN	1, 5, 7, 9, 12-14	S' , entropy in cal/gm °K
SENT(J)	5, 6, 8, 11, 14	s_j° , species entropy, $s_j^\circ = s_j' / R_0$
SHDELX	13, 19	initial value of $\Delta \tau / 2$
SHJ(J)	5, 6, 8, 11, 14, 16, 17	h_j , species enthalpy ($h_j = h_j' / R_0 T_0'$)
SHJA(J)	4, 6	h , formation enthalpy ($h_{j_0}^\circ = h_{j_0}' / R_0 T_0'$)
SHJAP(J)	2-4	h_{j_0}' , formation enthalpy in cal/mole

<u>FORTTRAN Variable</u>	<u>Subroutine</u>	<u>Definition</u>
SHPG	8, 14	$\sum \tau_j h_j$
SKIL(I)	5, 11	intermediate variable in calculation of dependent species concentrations from concentrations of components
SL	2, 3, 13, 18	l characteristic length
SL64	13, 14	$l/6, 470$
SM	1, 7, 10, 12, 13, 15, 18	m critical mass flow rate
SS	7	$\ln(\tau_j)_0$
SU	1, 7-9, 11, 12, 14, 15	u , velocity $u = u' \sqrt{M_0 / R_0 T_0'}$
SU2	8, 11, 14, 16, 17	u^2
SUMG	14, 16	$\sum \tau_j$
TB(J)	13	dummy variable for quantities necessary to return to previous step in nonequilibrium calculation
TEMP1	1, 18	discriminant in calculation of x from quadratic formula
TEST	4, 5, 11	size of correction to guesses used to define convergence of Newton-Raphson procedure
TESTB	4, 7, 10	tolerance allowed in locating temperature at throat for frozen and equilibrium flow
TFA(J)	2, 3, 6	a_j , coefficient in thermo-fit expression for h_j and μ_j^0/T
TFB(J)	2-4, 6	b_j , coefficient in thermo-fit expression for h_j and μ_j^0/T
TFC(J)	2-4, 6	c_j , coefficient in thermo-fit expression for h_j and μ_j^0/T
TFD(J)	2-4, 6	d_j , coefficient in thermo-fit expression for h_j and μ_j^0/T
TFE(J)	2-4, 6	e_j , coefficient in thermo-fit expression for h_j and μ_j^0/T

<u>FORTTRAN Variable</u>	<u>Subroutine</u>	<u>Definition</u>
TFK(J)	2, 3, 6	k_j , coefficient in thermo-fit expression for h_j and μ_j^0/T
THEV(J)	4, 6	θ_{v_j} characteristic vibrational temperature ($\theta_{v_j} = \theta'_{v_j} / T_0'$)
THEVP(J)	2-4	θ'_{v_j} characteristic vibrational temperature in °K
TPRINT	2, 3, 9, 13	temperature interval at which results of nonequilibrium calculation are to be printed
TSTOP	2-4, 7, 12, 13	minimum value of temperature desired in solution
TTEST	2, 3, 13	allowed value of $\Delta T/T$ in Runge-Kutta integration step
UP	13, 18	indicates when nonequilibrium solution which has been started upstream is restarted downstream of nozzle throat
XMJAT(J)	5, 6, 11, 14, 17	μ_j^0/T where μ_j^0 is species chemical potential ($\mu_j^0 = \mu_j^0 / R_0 T_0'$)
XNUI(I)	13, 14	ν_i , $\nu_i = \sum_j \nu_{ij}$
XNUIJ(I, J)	2, 3, 13, 14	ν_{ij} stoichiometric coefficient of j^{th} species on reactant side of i^{th} reaction
XNUIJP(I, J)	2, 3, 13	ν'_{ij} stoichiometric coefficient of j^{th} species on products side of i^{th} reaction
ZP	8, 11	$\ln p$
ZPA	5, 7, 11	$\ln p_0'$

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APPENDICES

MODIFICATIONS OF THE BASIC NOZZLE FLOW PROGRAM FOR ALTERNATIVE APPLICATIONS

The basic computer program calculates the expansion from an equilibrium reservoir through a specified converging-diverging nozzle. Modifications of the program to extend its applicability are described in this section. The changes in the governing equations and in the specification of the input data are given. As for the basic program, the copies of the FORTRAN source cards are available for these modified versions. The modifications were carried out with an emphasis on convenience rather than programming efficiency. Consequently these modified versions contain unnecessary variables and logic which could be removed if desired.

APPENDIX A

NONEQUILIBRIUM EXPANSION FROM ZERO VELOCITY THROUGH A SPECIFIED PRESSURE DISTRIBUTION

In the first modification of the program the pressure distribution rather than the streamtube geometry is specified. The program is then capable of computing the flow along a streamline for a given pressure variation. Typical applications of this program include the design of a nozzle with a specified pressure distribution and the computation of the nonequilibrium flow around the surface of a blunt body with an assumed surface pressure distribution.

Since the frozen and equilibrium flows are independent of the rate of expansion they are computed in the same way as when the nozzle geometry is specified. The properties of a frozen or equilibrium flow at a given point are then determined by the pressure at that point. For programming convenience the procedure for locating the maximum in ρu when the streamtube cross section is specified is not altered. The area ratio calculated at each point in the frozen or equilibrium flow then gives the spreading of the streamtube relative to its minimum cross-section.

In Section 3.1, the governing equations for a nonequilibrium expansion through a converging-diverging nozzle were presented. In the computer program these equations are reduced to $(s+2)$ first-order differential equations, or in finite-difference form to $(s+2)$ algebraic equations for the derivatives dx_j/dx , dT/dx , and $d \ln p/dx$. The equations for the slopes are in terms of the flow properties at a given station and the value of $d \ln A/dx$ for the specified geometry. For the expansion through a specified pressure distribution these equations are written in terms of dx_j/dx , dT/dx , $d \ln A/dx$, and $d \ln p/dx$.

The equations for the conservation of elements (28) and conservation of species (30) are written in the same form for a specified pressure distribution. In addition, du/dx is eliminated from the momentum equation using the energy equation. Also introducing the equation for the enthalpy, (12), yields

$$\sum_{j=1}^s h_j \frac{dx_j}{dx} + \sum_{j=1}^s r_j C_{p_j} \frac{dT}{dx} = \frac{T}{m} \frac{d \ln p}{dx} \quad (86)$$

Then, using the energy equation together with (12) to eliminate the velocity in the continuity equation and combining the result with the logarithmically-differentiated state equation yields

$$\left(\frac{u^2}{m_0 T} + \sum_{j=1}^s r_j C_{p_j} \right) \frac{dT}{dx} + \sum_{j=1}^s \left(\frac{u^2 m}{m_0} + h_j \right) \frac{dx_j}{dx} - \frac{u^2}{m_0} \frac{d \ln A}{dx} = \frac{u^2}{m_0} \frac{d \ln p}{dx} \quad (87)$$

Equation (87) may be simplified using Equation (86). The result is

$$\sum_{j=1}^s \frac{dx_j}{dx} + \frac{1}{mT} \frac{dT}{dx} - \frac{1}{m} \frac{d \ln A}{dx} = \frac{1}{m} \left(1 - \frac{T m_0}{m u^2} \right) \frac{d \ln p}{dx} \quad (88)$$

which together with Equations (28), (30), and (86) comprises the necessary set of $(s+2)$ equations.

Once the flow properties and composition are known at a given point, the derivatives $\frac{dx_j}{dx}$ and $\frac{dT}{dx}$ can be calculated. Then these values are numerically integrated to obtain the temperature and composition at a new station. Having determined T and the r_j 's the density may be obtained from the state equation using these values and the specified pressure at the new x . Also, the enthalpy may be computed from Equation (12), the velocity from Equation (15), and, using the equilibrium critical mass flow, the streamtube cross-sectional area is found from Equation (13). The area ratio of the nonequilibrium streamtube flow will not be unity at the point of minimum cross-section. However, this calculation again is only intended to indicate the relative spreading of the streamtube and is not a necessary part of the computation.

When the nonequilibrium nozzle-flow equations are written in terms of a specified pressure distribution there is no branch point associated with the solution. Consequently, it is not necessary to modify the present computation upstream of the point where the velocity is equal to $\left(\frac{dp}{dx} / \frac{d\rho}{dx} \right)^{1/2}$. Thus, $\frac{d \ln A}{dx}$ could be eliminated from Equations (86) and (88) since there is no good reason

for carrying it along (as there was for retaining $\frac{d \ln \rho}{dx}$ in the equations for a specified geometry). However, retaining $\frac{d \ln A}{dx}$ in Equation (88) greatly simplifies the modification of the program to take a specified pressure distribution. Also, computing $\frac{d \ln A}{dx}$ at each point permits a simple calculation for a Mach number based on the "speed of sound," $a^2 = \frac{dp/dx}{d\rho/dx}$.

$$M = \gamma \sqrt{1 - \frac{\rho u^2}{p} \frac{d \ln A/dx}{d \ln p/dx}} \quad (89)$$

In addition to the Mach number the entropy is also computed at each step using Equation (16).

The nonequilibrium calculation for a specified pressure variation is started in the same manner as that for a nozzle flow. The nonequilibrium solution is considered to be a perturbation about the infinite-rate equilibrium solution and the numerical integration is started when the perturbation calculation indicates significant departure from equilibrium.

The perturbation calculation must be modified for the case of a specified pressure distribution. The perturbed form of the element conservation equations remains valid.

$$\sum_{j=1}^s \alpha_{jk} \delta \chi_j = 0 \quad k = 1, 2, \dots, c \quad (55)$$

In order to obtain the perturbed form of the species conservation equations the χ_i 's should be written as $\chi_i = \chi_i(T, p, \chi_j)$. Then

$$\frac{d \bar{\chi}_i}{dx} = \sum_{i=1}^n \beta_{ij} \bar{P}_i \delta \chi_i$$

where again it is assumed

$$\frac{d(\delta \chi_j)}{dx} \ll \frac{d \bar{\chi}_j}{dx} \quad (60)$$

and

$$\delta \chi_i = \frac{\partial \bar{\chi}_i}{\partial T} \delta T + \frac{\partial \bar{\chi}_i}{\partial p} \delta p + \sum_{j=1}^s \frac{\partial \bar{\chi}_i}{\partial \chi_j} \delta \chi_j \quad (90)$$

Since $p(x)$ is prescribed, $\delta p = 0$. Evaluating the other partial derivatives in (90) leads to

$$\frac{d\bar{\tau}_i}{dx} = \sum_{i=1}^n \beta_{ij} \bar{P}_i \left[\sum_{k=1}^s \frac{\beta_{ik} \bar{h}_k}{\bar{T}^2} \delta T + \sum_{k=1}^s \left(\beta_{ik} \bar{m} - \frac{\beta_{ik}}{\bar{\tau}_k} \right) \delta \tau_k \right] \quad (91)$$

Since the density is not necessarily very near the equilibrium value, the condition $\delta S' = 0$ rather than $\delta \rho = 0$ is used to replace the perturbed momentum equation. From the definition of the Gibbs free energy

$$F' \equiv H' - T' S'$$

the perturbation in F to first order is seen to be

$$\delta F = \delta H - \bar{S} \delta T - \bar{T} (\delta S') \frac{\bar{m}_o}{R_o} \quad (92)$$

Also, since $F = F(T, p, \tau_j)$, then also to first order,

$$\delta F = \left(\frac{\partial F}{\partial T} \right)_{p, \tau_j} \delta T + \left(\frac{\partial F}{\partial p} \right)_{T, \tau_j} \delta p + \sum_{j=1}^s \left(\frac{\partial F}{\partial \tau_j} \right)_{p, T, \tau_i, i \neq j} \delta \tau_j$$

or, using $\delta p = 0$ this equation becomes

$$\delta F = -\bar{S} \delta T + \bar{m}_o \sum_{j=1}^s \mu_j \delta \tau_j \quad (93)$$

Now combining (92), (93), and the first-order perturbation of (12) gives, in the case of $\delta S' = 0$,

$$\sum_{j=1}^s (\bar{h}_j - \bar{\mu}_j) \delta \tau_j + \left(\sum_{j=1}^s \bar{\tau}_j C_{p_j} \right) \delta T = 0 \quad (94)$$

In rewriting the nonequilibrium flow equations the term $\frac{d \ln A}{dx}$ was retained to simplify reprogramming. The perturbation in the streamtube cross-section is retained here for the same reason. Using the perturbed forms of the continuity, energy, and state equations together with $\delta p = 0$ leads to

$$\frac{\delta A}{\bar{A}} = \sum_{j=1}^s \left(\frac{\bar{m}_o \bar{h}_j}{\bar{u}^2} + \bar{m} \right) \delta \tau_j + \left(\frac{\bar{m}_o}{\bar{u}^2} \sum_{j=1}^s \bar{\tau}_j C_{p_j} + \frac{1}{\bar{T}} \right) \delta T \quad (95)$$

Equation (94) may be used to simplify Equation (95) to

$$\frac{\delta A}{\bar{A}} = \sum_{j=1}^s \left(\bar{m} + \frac{\bar{m}_o \bar{\mu}_j}{\bar{u}^2} \right) \delta \tau_j + \frac{\delta T}{\bar{T}} \quad (96)$$

In the program the equation

$$s_j = \frac{h_j - \mu_j}{T} = s_j^\circ - \ln p_j' \quad (97)$$

is employed to write μ_j in terms of s_j° and h_j . Then Equations (94) and (96) become

$$\sum_{j=1}^s \bar{T} \left[\bar{s}_j^\circ - \ln(\bar{r}_j \bar{m} p p_o') \right] \delta r_j + \sum_{j=1}^s \bar{r}_j C_{p_j} \delta T = 0 \quad (98)$$

$$\frac{\delta A}{A} = \frac{\delta T}{\bar{T}} + \sum_{j=1}^s \left\{ \bar{m} + \frac{\bar{m}_o}{\bar{u}^2} \left[\bar{h}_j - \bar{T} (\bar{s}_j^\circ - \ln(\bar{r}_j \bar{m} p p_o')) \right] \right\} \delta r_j \quad (99)$$

Now Equations (55), (91), (98), and (99) are a set of $(s+2)$ algebraic equations for δr_j , δT , and δA .

The procedure described in Section 3.2 for starting the nozzle-flow computation is directly applicable here. The equilibrium solution is obtained at successive temperature steps from the reservoir. At each point the equilibrium slopes are computed and used to determine the perturbations in T and the r_j . When the perturbations are sufficiently large the numerical integration of the nonequilibrium solution is begun. In the computation of the equilibrium slopes the $(s-c)$ equations obtained by differentiating the condition of chemical equilibrium (see Section 3.2) should be written in terms of $\frac{dr_j}{dx}$, $\frac{dT}{dx}$, $\frac{d \ln A}{dx}$, and $\frac{d \ln p}{dx}$. This can be accomplished by using the differentiated form of the continuity equation and the momentum equation whereupon Equation (85) becomes

$$\sum_{k=1}^c \frac{\bar{v}_{j,k}}{\bar{r}_k} \frac{dr_k}{dx} - \frac{1}{\bar{r}_j} \frac{dr_j}{dx} - \left(\sum_{k=1}^c \frac{\bar{v}_{j,k}}{T^2} h_k - \frac{h_j}{T^2} \right) \frac{dT}{dx} + \frac{(\bar{v}_j - 1)}{T} \frac{dT}{dx} - (\bar{v}_j - 1) \frac{d \ln A}{dx} + \frac{(\bar{v}_j - 1) p}{\rho u^2} \frac{d \ln p}{dx} = 0 \quad (100)$$

In the starting procedure for the nozzle flow computation the value of $A(x)$ for the equilibrium solution is used to find the corresponding x from the specified area distribution. In the starting procedure for the streamtube flow the equilibrium flow pressure is used to find x from the specified pressure distribution. The method employed to invert $p(x)$ is the same as that described in Section 3.2 for inverting $A(x)$.

As mentioned above, the modification of the computer program to permit a specified pressure distribution was carried out with a minimum of revision. As a result, the specification of the input data for this case is identical to that described in Section 6 with the following exceptions. The absence of a singularity at the throat of the streamtube excludes the "upstream" region distinction made in the nozzle flow case. Consequently the logic in the specified-pressure-distribution program is that for the "downstream" nozzle-flow region. Accordingly, the indicator IUPD is always read in as 0 for this case. Furthermore, the coefficients in the specified $p(x)$ relation are read in using the locations for the area-relation coefficients, but starting with the first downstream region. That is, x is measured from the stagnation point rather than from the nozzle throat. The storage locations available for specifying the upstream area distribution have been used to provide an additional interval for specifying a pressure distribution. Thus, the polynomial relations given in Section 6 for a fitted geometry become for a specified pressure distribution

$$\begin{aligned}
 p(x) &= B_1 + B_2 x + B_3 x^2 & 0 \leq x < \text{ATP}(2) \\
 p(x) &= \sum_{i=4}^{10} B_i x^{(i-4)} & \text{ATP}(2) \leq x < \text{ATP}(3) \\
 p(x) &= \sum_{i=11}^{17} B_i x^{(i-11)} & \text{ATP}(3) \leq x < \text{ATP}(4) \\
 p(x) &= \sum_{i=18}^{24} B_i x^{(i-18)} & \text{ATP}(4) \leq x < \text{ATP}(5) \\
 p(x) &= \sum_{i=25}^{31} B_i x^{(i-25)} & \text{ATP}(5) \leq x < \text{ATP}(1) \\
 p(x) &= \sum_{i=1}^{10} A_i x^{(i-1)} & x \geq \text{ATP}(1)
 \end{aligned}$$

In the starting procedure the quadratic formula is used to invert $p(x)$ in the first interval, $0 \leq x < \text{ATP}(2)$. Since $p(x)$ behaves differently than $A(x)$ the opposite sign must be used in the quadratic formula when inverting $p(x)$. Thus, in this case Equation (44a) must be written as

$$x = - \frac{B_2 + \sqrt{B_2^2 - 4B_3(B_1 - p)}}{2B_3} \quad (44b)$$

in the program.

The program changes to effect the calculation for a streamtube flow with a specified pressure distribution involved the following changes in the FORTRAN variables listed in Section 7.

AFNTS \rightarrow p calculated from equilibrium solution
 DLOGA \rightarrow $d \ln p / dx$
 DLOGR \rightarrow $d \ln A / dx$

The subroutines in this modified version of the program are the same as described in Section 7 except for those in which the changes discussed in this section are made. The changes in these subroutines are briefly summarized below.

MAIN PROGRAM The computation of the first point in the nonequilibrium solution uses the logic for starting the calculation at the reservoir. The option of starting the nozzle flow computation at the throat is eliminated. Also, the density fit computation is omitted.

NONEQ All of the logic associated with switching the calculation from an upstream region to a downstream region is eliminated.

COMM The computation of the pressure from the state equation is eliminated.

GEOM The computation of A and $d \ln A / dx$ for the intervals in the upstream region are eliminated. The computation of the density from the density-fit relation is also eliminated. The computation of A and $d \ln A / dx$ is modified to calculate p and $d \ln p / dx$. The computation of the density from the state equation is added.

:
.
EXACT The changes discussed above for the governing equations for the derivatives dx_i/dx , dT/dx , and $d \ln A/dx$ are made. The changes incorporate the FORTRAN notation change given above. The formula for the Mach number computation is changed to that given in Equation (89).

PERT The modifications of the perturbation computation to account for a specified pressure distribution are effected in accordance with Equations (91), (98), and (99). The perturbed state equation is used to relate $\delta \rho$ to δT and the δx_i 's. The computation for the δx_i 's in terms of δx_j , δT , and $\delta \rho$ is then kept the same as in the nozzle flow calculation.

AXFIT The logic for determining the proper set of coefficients for inverting $p(x)$ is changed to account for the difference in the behavior of $p(x)$ and $A(x)$.

Since there are no upstream and downstream regions in the nonequilibrium calculation for a specified pressure distribution, subroutine THROAT is eliminated.

APPENDIX B
NONEQUILIBRIUM FLOW FROM A NONEQUILIBRIUM
INITIAL CONDITION THROUGH EITHER A SPECIFIED
PRESSURE OR AREA DISTRIBUTION

The basic nozzle-flow program and the modification described in Appendix A both deal with flows which start from an equilibrium stagnation region. The modification described here is designed to compute a quasi-one-dimensional, nonequilibrium flow from a finite-velocity, nonequilibrium, initial condition. Either a given pressure distribution or a given streamtube area distribution may be the specified boundary condition. This version of the program is applicable, for example, to streamtubes in a body flow field for which the pressure distribution is known from either measurements or an equilibrium flow-field calculation. Also, the chemical-relaxation zone behind a strong shock wave can be solved by specifying the conditions behind a translational-rotational-vibrational equilibrium shock and a constant streamtube cross-section. Furthermore, this modification can be used to continue a calculation originally started from a stagnation point with either boundary condition.

When the nonequilibrium solution is started from a nonequilibrium initial condition the starting procedure discussed in Section 3.2 becomes unnecessary. If the flow properties and composition are given at an initial point the derivatives may be computed and the numerical integration begun immediately. The governing equations for the nonequilibrium flow through a streamtube of given cross-section are Equations (28), (30), (34), and (36) of Section 3.2. As discussed in Appendix A, if the streamtube pressure distribution is specified Equations (86) and (88) replace (34) and (36). The numerical integration of these equations proceeds as discussed in Section 3.1 for the specified area distribution and in Appendix A for the specified pressure distribution.

The modified version of the computer program described here was also obtained with a minimum of reprogramming. Consequently, the input format

is again essentially the same as described in Section 6 for the nozzle-flow program. The values of T_0' and p_0' to be specified are respectively the temperature and pressure at the given initial condition. In addition to the input data described in Section 6 the local values of all the species concentrations in units of moles per gram, the local temperature nondimensionalized by T_0' , the nondimensional axial distance, the total enthalpy in cal/gm. and the molecular weight at the given initial condition must be specified. It is important when using this version of the program to continue a calculation that the original values of T_0' , and p_0' , and the corresponding molecular weight are specified. Otherwise the computed values in the continued solution will be normalized by different factors from those used in the first part of the solution.

This version of the program uses the logic for the downstream region of the basic program. Thus, the indicator IUPD should be read in as zero. Five intervals are available for specifying $A(x)$ and $p(x)$; if more are needed they can be obtained by repeated starting of this version of the program. One of the available indicators, ISWIB, is used in the program to select either the governing equations for a specified $A(x)$ or a specified $p(x)$. If $A(x)$ is specified this indicator should be read in as zero. If $p(x)$ is specified it should be read in as unity. When $p(x)$ is specified the indicator ISWIB is also used to effect the changes in the FORTRAN variable notation listed in Appendix A.

The number of gram-atoms and the molecular weight of each element need not be given because all the concentrations are specified at the initial point. These cards should be eliminated from the input data deck. Also, the input cards for the upstream area coefficients should not be included. The variables and tests which must be specified for the frozen and equilibrium calculations may be left blank on the appropriate cards (see Section 6).

When this version of the program is applied to computing the flow behind a shock wave, for either a specified $A(x)$ or $p(x)$, the initial value of $\Delta x'$ should be reduced to 10^{-6} cm. Also, the integration tests, GTEST and TTEST should be relaxed to about 0.2 and 0.1, respectively.

Due to the elimination of the computations for the reservoir, frozen flow, and equilibrium flow, and the procedure to starting in equilibrium the following subroutines are eliminated in this version of the program:

INTA	NRMAX	PERT
FROZEN	NEWRAP	AXFIT
PROP	EQUIL	MATINV

Also, the logic from the nonequilibrium calculation for a downstream region is removed from NONEQ and incorporated in a modified MAIN PROGRAM peculiar to the present version. Since the logic associated with starting from equilibrium and with switching from an upstream to a downstream region are unnecessary, the remainder of subroutine NONEQ and subroutine THROAT are eliminated. This modification of the program also involved changes in the following subroutines:

READ The instructions for reading in the number of gram-atoms and molecular weights of the elements and the $A(x)$ or $p(x)$ coefficients for an upstream region are eliminated. The instructions for reading in the initial species concentrations, temperature, axial location, and H_0' are added. The procedure for preparing the additional input data is as follows:

First the τ_j' are read in according to the format used on card type 13 of Section 6. Since there may be as many as 20 species there may be 4 cards to read in the initial τ_j' . The values of H_0' (in cal/gm), x , T , and M_0 are read in after the τ_j' , again using card type 13. As mentioned above, when using this version of the program to continue a solution, the specified value of M_0 should be the molecular weight of the mixture at the conditions p_0' and T_0' .

LIST Changes appropriate to the differences in input data are made.

COMM The changes indicated for subroutine COMM in Appendix A are included as an additional option when $p(x)$ is prescribed.

GEOM The computation $A(x)$ or $p(x)$ is allowed for and the logic for an upstream region is eliminated.

:
.
EXACT The computation of the derivatives needed in the nonequilibrium solution for either a specified $A(x)$ and $p(x)$ are included. If $p(x)$ is prescribed, Equations (86) and (88) are used rather than (34) and (36). The calculation of the equilibrium values of the derivatives is eliminated. The Mach number is computed from the formula appropriate to either a specified $A(x)$ (Eq. (38)) or a specified $p(x)$ (Eq. (89)).

APPENDIX C

NONEQUILIBRIUM EXPANSION FROM AN EQUILIBRIUM, FINITE-VELOCITY INITIAL CONDITION

The modification of the program discussed in this section also treats the case where the initial flow velocity is nonzero. The problem treated here is the expansion of a flow assumed to be initially in equilibrium, but moving at supersonic speed, through a divergent channel. This version of the program is applicable to the flow in non-reflected type shock tunnels where the flow behind the incident shock is assumed quasi-steady. Exercising the option of including ionized species also allows the program to be applied to the flow downstream of an MHD accelerator.

As for the nozzle expansion from an equilibrium reservoir state, the initial equilibrium state is found for a specified temperature and pressure. Since the initial state is not a stagnation point the total enthalpy of the flow must also be specified in order to evaluate the velocity. The frozen and equilibrium expansions from this initial point can also be obtained following the same procedure as discussed in Sections 2.2 and 2.3. In this case, however, the mass flow is known at the initial point. The cross-sectional area is referred to that at the initial point and the origin for x is taken where $A(x) = 1$, i. e. the initial point.

Since the computation using this program assumes the flow to be in equilibrium at a finite velocity, the nonequilibrium solution must be started differently than the nozzle expansion from a stagnation point. The perturbation starting procedure discussed in Sections 3.2 and 3.4 is valid only when the flow starts from an equilibrium stagnation point where the non-equilibrium flow actually approaches the infinite-rate equilibrium flow. The assumption made in this section that the flow is in equilibrium at a finite velocity is a physical idealization and the starting procedure is also artificial. The starting procedure adopted here is similar to that described in Reference 4 to start the numerical integration of a nonequilibrium nozzle flow.

Starting values for the integration for the nonequilibrium solution are obtained by assuming that over the first interval, Δx_1 , the species gradients are all zero. In other words, the flow is assumed frozen. Then at $x = \Delta x_1$, the flow will be at some nonequilibrium state which approximates the actual flow. The numerical integration from then on proceeds exactly as discussed in Section 3.1.

The selection of an initial value of Δx is influenced by the numerical difficulties of the type discussed in Section 3.5. In the present application the best initial value must be determined by trial and error. Experience with the use of this program for airflows indicates that an initial Δx of 10^{-3} cm is a satisfactory value.

The input data for the version of the program discussed herein is identical to that described in Section 6 for the nozzle flow calculation. In addition the total enthalpy of the flow must be specified in cal/gm°K. Since there is no nozzle throat and hence no upstream and downstream regions the indicator IUPD should be specified as 0. Although the coefficients of $A(x)$ in the upstream region are not used in this calculation, the appropriate number of blank cards must be included in the input data deck. Also, notice that ATP(2) is the first dividing point between the first and second intervals in the specification of $A(x)$.

As for the other two modifications of the basic nozzle-flow program the present version was obtained with emphasis on minimizing the amount of reprogramming. Consequently the subroutines in this program are the same as described in Section 7 for the basic program with the following necessary exceptions.

MAIN PROGRAM The instructions for calculating the equilibrium throat and the density-fit constants are eliminated.

READ The instruction for reading in the total enthalpy H'_0 in cal/gm°K is added. H'_0 is read in after all the input data discussed in Section 6 and using the same format as card type 13.

INTA The computations of the velocity at the initial point and of the total mass flow are added.

FROZEN The logic for locating the maximum in ρu and hence the throat for frozen flow is eliminated.

EQUIL The procedure for starting the equilibrium calculation from a finite-velocity initial state is incorporated.

NONEQ The logic associated with the perturbation starting procedure and the switch from an upstream to a downstream region are eliminated.

COMM The calculation of the rates for the individual reactions is eliminated on the first step, since $dr_j/dx = 0$ for this interval. The indicator LC is used to determine the first step. In the basic nozzle-flow program LC is used to indicate the first step in subroutine AXFIT, which is unnecessary in this program.

GEOM The calculations of the $\rho(x)$, $A(x)$, and $d \ln A / dx$ for the upstream region are eliminated.

The following subroutines are eliminated in this version of the program.

NRMAX
PERT
AXFIT
THROAT

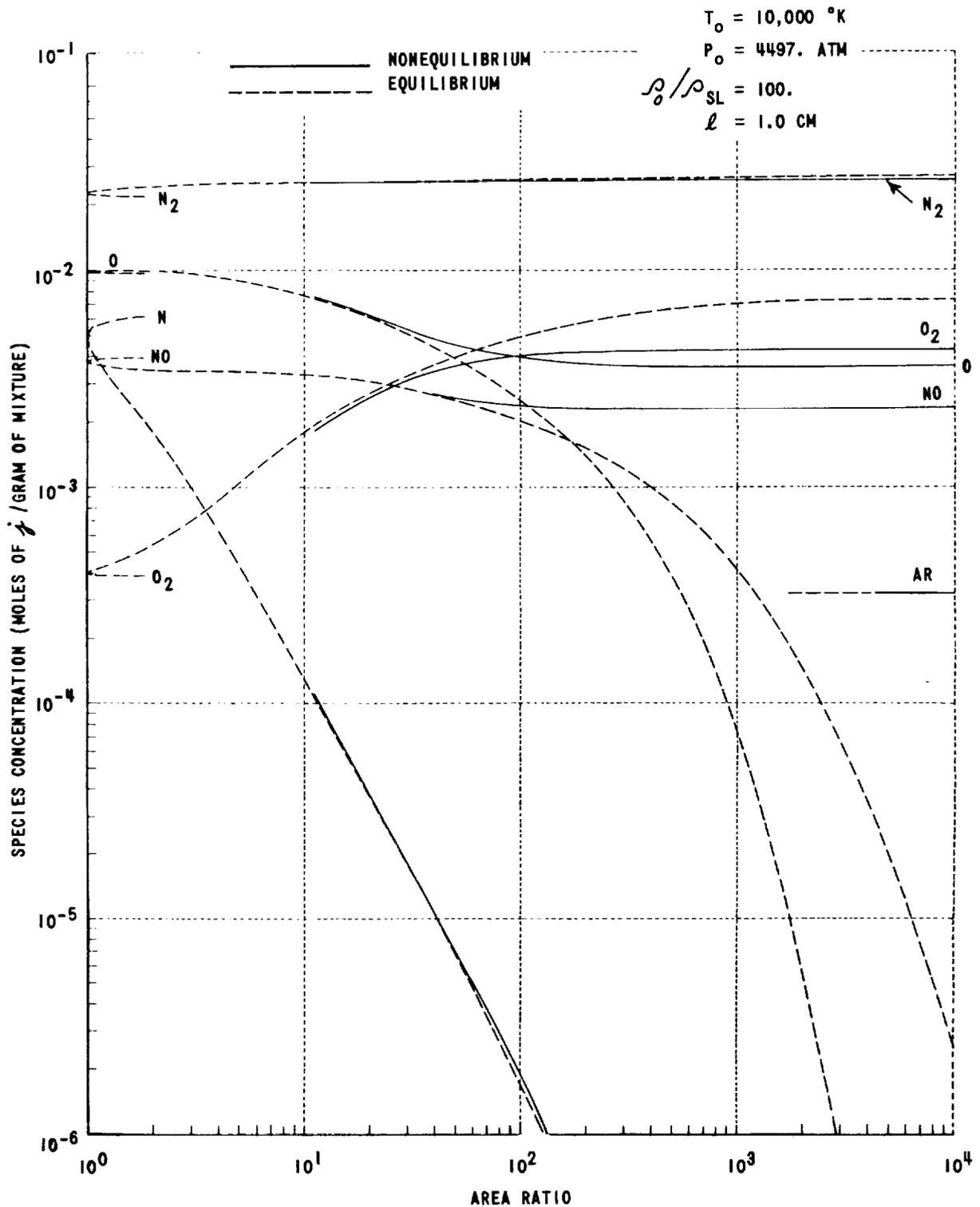


Figure 1 EXAMPLE OF SPECIES DISTRIBUTIONS ALONG A HIGH-TEMPERATURE NOZZLE EXPANSION OF AIR (TAKEN FROM REFERENCE 11)

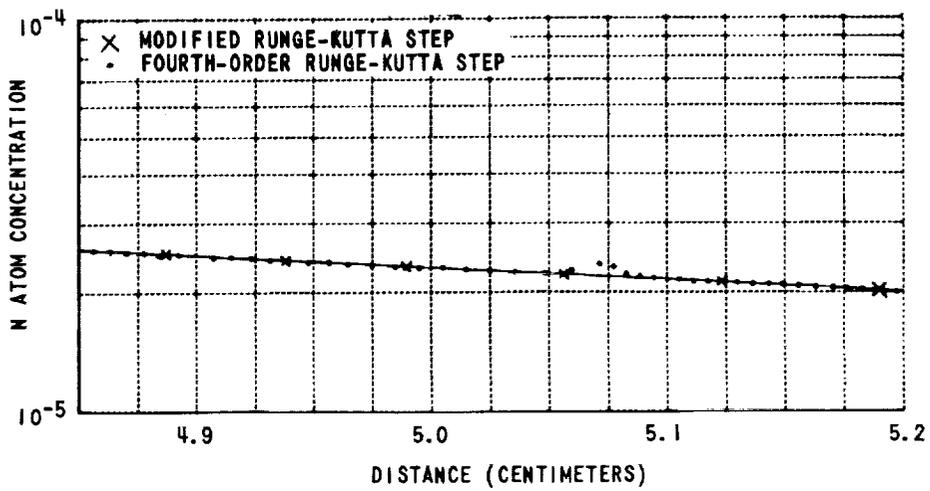
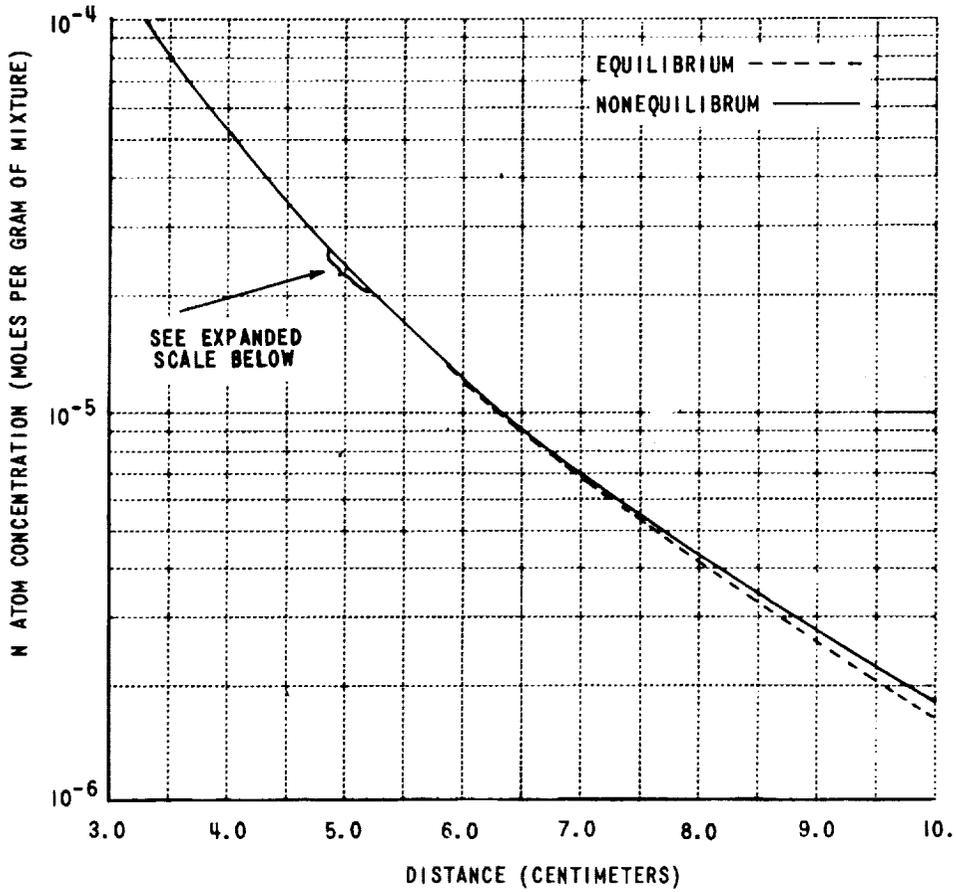


Figure 2 COMPARISON OF RESULTS OBTAINED FOR NITROGEN - ATOM CONCENTRATION USING FOURTH-ORDER RUNGE-KUTTA AND MODIFIED RUNGE-KUTTA INTEGRATION PROCEDURES.

CARD TYPE	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80																																											
12	0	1	1	1	1	1	1	1	0																																																																																																																		
	ASUB(I)																																																																																																																										
13a	1	.	0	E+00		0	.	0	E+00		1	.	0	E+00		1	.	0	E+00		0	.	0	E+00		0	.	0																																																																																															
13a	1	.	0	E+00		0	.	0	E+00		0	.	0	E+00		0	.	0	E+00		0	.	0	E+00		0	.	0																																																																																															
	BSUB(I)																																																																																																																										
13a	1	.	0	E+00		0	.	0	E+00		6	.	1	4	1	9	0	3	E-01		6	.	0	0	0	2	8	6	E-01		6	.	3	9	5	4	1	E-01																																																																																					
13a	3	.	5	8	2	0	8	6	E-01		0	.	0	E+00		0	.	0	E+00		0	.	0	E+00		0	.	0																																																																																															
12/13a	2	.	0	3	9	0	6	5	E+01		-	1	.	5	4	0	9	3	3	E+01		4	.	6	1	3	6	8	6	E+00		-	3	.	6	6	4	3	2	2	E-01		0	.	0	E+00																																																																													
13a	0	.	0	E+00		0	.	0	E+00		6	.	6	0	3	2	4	1	E-03		1	.	6	0	7	6	8	8	E+00		3	.	0	4	1	2	6	4	E-01																																																																																				
13a	-	2	.	6	4	2	1	7	5	E-02		9	.	4	8	7	8	8	0	E-04		-	1	.	6	1	9	9	8	2	E-03		1	.	0	7	7	3	0	2	E-05		0	.	0	E+00																																																																													
13a	0	.	0	E+00		0	.	0	E+00		0	.	0	E+00		0	.	0	E+00		0	.	0	E+00		0	.	0																																																																																															
13a	0	.	0	E+00																																																																																																																							
	ATP(I)																																																																																																																										
13a	-	1	.	0	E+00		1	.	2	5	E+00		3	.	2	5	E+00		5	.	0	8	E+00		1	.	0	E+00		1	.	0																																																																																											
	IGJ(J)																																																																																																																										
14	1	1	1	1	1	1	1	1	1																																																																																																																		

Figure 3f INPUT DATA CARDS FOR SAMPLE NOZZLE FLOW CALCULATION

SAMPLE CALCULATION FOR THE NOZZLE FLOW PROGRAM

RUN NO.=1000 RESERVOIR TEMPERATURE= 6500.0 DEGREES KELVIN RESERVOIR PRESSURE= 1000.000 ATMOSPHERES UPSTREAM RUN

C= 4 S= 8 R= 11 NUMBER OF IONS= 1 INTERVAL SIZE CONTROL= 4 SMALL L= 1.000 BZERO= 0. DELT3= 0.00100
 TEMPERATURE SWITCH FROM THERMAL FIT TO HARMONIC OSCILLATOR DATA= 5000.000 DEGREES KELVIN DELTAX= 0.0100000 DELT2= 0.01000
 MAXIMUM VALUE OF X= 320.000CENTIMETERS MINIMUM VALUE OF TEMPERATURE= 3250.000 DEGREES KELVIN TPRINT= 0. VIBRATION EQUIL.
 TEMPERATURE TEST= 0.05000 GAMMA TEST= 0.10000

SPECIES	ATOM FRACTION	ELEMENT MOLECULAR WEIGHTS
N	1.561760E 00	1.400700E 01
O	4.195900E-01	1.600000E 01
AR	9.324000E-03	3.994400E 01
E-	0.	5.484700E-04

REACTION NO.	CONSTANT FACTOR AI	TEMP. POWER DEPENDENCE	ACTIVATION ENERGY	GHI TEST	THIRD BODY MATRIX
1	3.000000E 21	-1.500000E 00	2.249900E 05	0.1000000	01000000
2	1.500000E 22	-1.500000E 00	2.249900E 05	0.1000000	00001000
3	9.300000E 20	-1.500000E 00	2.249900E 05	0.1000000	00110110
4	3.600000E 21	-1.500000E 00	1.179600E 05	0.1000000	00100000
5	2.100000E 18	-5.000000E-01	1.179600E 05	0.1000000	00000100
6	1.200000E 21	-1.500000E 00	1.179600E 05	0.1000000	01011010
7	5.200000E 21	-1.500000E 00	1.499600E 05	0.1000000	01111110
8	1.000000E 12	5.000000E-01	6.200000E 03	0.1000000	
9	5.000000E 13	0.	7.552000E 04	0.1000000	
10	9.100000E 24	-2.500000E 00	1.291200E 05	0.1000000	
11	1.800000E 21	-1.500000E 00	0.	0.1000000	

SPECIES: THERMAL FIT INDICATOR ALPHA MATRIX

	N	O	AR	E-
E-	0.	0.	0.	1.
N2	1.	0.	0.	0.
O2	1.	2.	0.	0.
AR	1.	0.	1.	0.
N	1.	0.	0.	0.
O	1.	0.	1.	0.
NO	1.	1.	0.	0.
NO+	1.	1.	0.	-1.

REACT NO. NU PRIME MATRIX

	E-	N2	O2	AR	N	O	NO	NO+
1	0.	0.	0.	0.	2.	0.	0.	0.
2	0.	0.	0.	0.	2.	0.	0.	0.
3	0.	0.	0.	0.	2.	0.	0.	0.
4	0.	0.	0.	0.	0.	2.	0.	0.
5	0.	0.	0.	0.	0.	2.	0.	0.
6	0.	0.	0.	0.	0.	2.	0.	0.
7	0.	0.	0.	0.	1.	1.	0.	0.
8	0.	0.	0.	0.	0.	1.	1.	0.
9	0.	0.	0.	0.	1.	0.	1.	0.

Figure 4a PRINTOUT OF INPUT DATA FOR SAMPLE CALCULATION

10	0.	0.	0.	0.	0.	0.	2.	0.
11	0.	0.	0.	0.	1.	1.	0.	0.

REACT NO. NU MATRIX

	E-	N2	O2	AR	N	O	NO	NO+
1	0.	1.	0.	0.	0.	0.	0.	0.
2	0.	1.	0.	0.	0.	0.	0.	0.
3	0.	1.	0.	0.	0.	0.	0.	0.
4	0.	0.	1.	0.	0.	0.	0.	0.
5	0.	0.	1.	0.	0.	0.	0.	0.
6	0.	0.	1.	0.	0.	0.	0.	0.
7	0.	0.	0.	0.	0.	0.	1.	0.
8	0.	0.	1.	0.	1.	0.	0.	0.
9	0.	1.	0.	0.	0.	1.	0.	0.
10	0.	1.	1.	0.	0.	0.	0.	0.
11	1.	0.	0.	0.	0.	0.	0.	1.

UPSTREAM AREA POLYNOMIAL COEFFICIENTS

1.000000E 00	0.	1.000000E 00	1.000000E 00	0.	1.000000E 00	0.	0.
0.	0.						

DOWNSTREAM AREA POLYNOMIAL COEFFICIENTS

1.000000E 00	0.	6.141903E-01	6.000286E-01	6.399541E-01	3.502086E-01	0.	0.
0.	0.	2.039065E 01	-1.540933E 01	4.613686E 00	-3.664322E-01	0.	0.
0.	6.603241E-03	1.607688E 00	3.041264E-01	-2.642175E-02	9.487880E-04	-1.619982E-03	1.077302E-05
0.	0.	0.	0.	0.	0.	0.	0.

AREA FIT TRANSFER POINTS

-1.000000E 00 1.250000E 00 3.250000E 00 5.080000E 00 1.000000E 03

SPECIES	ATOMS PER MOLECULE	CHEMICAL CONSTANT	CHAR. VIBRATIONAL TEMP.	ENTHALPY OF FORMATION	ELECTRONIC LEVELS
E-	1.000000E 00	-1.492832E 01	-0.	-0.	1
N2	2.000000E 00	-4.216300E-01	3.353240E 03	-0.	4
O2	2.000000E 00	1.074500E-01	2.238970E 03	-0.	5
AR	1.000000E 00	1.865570E 00	-0.	-0.	3
N	1.000000E 00	2.986800E-01	-0.	1.125906E 05	5
O	1.000000E 00	4.932000E-01	-0.	5.898000E 04	6
NO	2.000000E 00	5.394100E-01	2.699180E 03	2.147700E 04	3
NO+	2.000000E 00	3.786100E-01	3.372950E 03	2.353300E 05	5

SPECIES (DEGENERACY, ELECTRONIC ENERGY LEVEL)

E-	2.	-0.						
N2	1.	-0.	3.	1.436850E 05	6.	1.704750E 05	1.	1.715400E 05
O2	3.	-0.	2.	2.263700E 04	1.	3.772500E 04	3.	1.031980E 05
AR	1.	-0.	5.	2.663070E 05	3.	2.680420E 05		
N	4.	-0.	6.	5.497400E 04	4.	5.512500E 04	6.	8.245500E 04
O	5.	-0.	3.	4.546200E 02	1.	6.489800E 02	5.	4.536800E 04
NO	4.	-0.	2.	1.257000E 05	4.	1.312830E 05		
NO+	1.	-0.	6.	1.152320E 05	3.	1.689870E 05	6.	2.087320E 05
							2.	2.095300E 05

SPECIES A B C D E K HEAT OF FORMATION

E-	2.500000E 00	-0.	-0.	-0.	-0.	-1.173500E 01	-0.
N2	3.451483E 00	3.088332E-04	-4.251428E-08	2.739295E-12	-5.468320E-17	3.071269E 00	-0.

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Figure 4b PRINTOUT OF INPUT DATA FOR SAMPLE CALCULATION

OZ	3.249473E	00	4.963449E-04	-6.701753E-08	4.443339E-12	-1.000281E-16	5.915022E	00	-0.
AR	2.563282E	00	-3.591770E-05	7.469208E-09	-6.747034E-13	2.234019E-17	4.000939E	00	-0.
N	3.008922E	00	-3.134625E-04	6.311813E-08	-4.165203E-12	9.334886E-17	1.303476E	00	1.125906E 05
O	2.594143E	00	-5.008914E-05	1.139502E-08	-8.681611E-13	2.148100E-17	4.600615E	00	5.890000E 04
NO	3.756216E	00	2.083961E-04	-2.639548E-08	1.690332E-12	-3.611523E-17	3.611167E	00	2.147700E 04
NO*	3.397385E	00	3.749384E-04	-6.062030E-08	4.637506E-12	-1.107704E-16	4.200563E	00	2.353300E 05

OUTPUT FORMAT FOR FROZEN FLOW SOLUTION

TEMPERATURE	PRESSURE	DENSITY	VELOCITY	MACH NUMBER	ENTROPY	AREA
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OUTPUT FORMAT FOR EQUILIBRIUM SOLUTION

TEMPERATURE	PRESSURE	DENSITY	VELOCITY	MACH NUMBER	ENTROPY	AREA
SPECIES CONCENTRATIONS						

OUTPUT FORMAT FOR NONEQUILIBRIUM SOLUTION

TEMPERATURE	PRESSURE	DENSITY	VELOCITY	MACH NUMBER	ENTROPY	AREA	X	INEQ
TEMPERATURE--SPECIES CONCENTRATIONS								
EQUILIBRIUM TEMPERATURE--EQUILIBRIUM VALUES								

Figure 4c PRINTOUT OF INPUT DATA FOR SAMPLE CALCULATION

RESERVOIR-1000
TEMPERATURE= 6500.00 DENSITY= 0.04905906 PRESSURE= 1000.000
ENTHALPY= 5.1334 ENTRUPY= 2.1602 MOLECULAR WEIGHT=26.1652
E- 2.292E-06
N2 2.433E-02
O2 1.415E-03
AR 3.219E-04
N 4.881E-04
O 6.888E-03
NO 4.768E-03
NO+ 2.292E-06

Figure 5 SAMPLE PRINTOUT FOR RESERVOIR CONDITIONS

FROZEN FLOW SOLUTION

1.00000E-00	1.00000E-00	1.00000E-00	0.	0.	2.16017E-00	0.
9.90000E-01	9.58201E-01	9.67880E-01	2.91493E-01	2.5617288E-01	2.16017E-00	2.37134E-00
9.80000E-01	9.17781E-01	9.36511E-01	4.12156E-01	3.6401555E-01	2.16017E-00	1.73329E-00
9.70000E-01	8.78705E-01	9.05882E-01	5.04692E-01	4.4798586E-01	2.16017E-00	1.46334E-00
9.60000E-01	8.40940E-01	8.75980E-01	5.82663E-01	5.1982439E-01	2.16017E-00	1.31079E-00
9.50000E-01	8.04454E-01	8.46793E-01	6.51321E-01	5.8406486E-01	2.16017E-00	1.21303E-00
9.40000E-01	7.69212E-01	8.18310E-01	7.13361E-01	6.4302566E-01	2.16017E-00	1.14609E-00
9.30000E-01	7.35184E-01	7.90521E-01	7.70385E-01	6.9807733E-01	2.16017E-00	1.09856E-00
9.20000E-01	7.02339E-01	7.63412E-01	8.23436E-01	7.5011946E-01	2.16017E-00	1.06428E-00
9.10000E-01	6.70645E-01	7.36973E-01	8.73240E-01	7.9976899E-01	2.16017E-00	1.03959E-00
9.00000E-01	6.40073E-01	7.11193E-01	9.20323E-01	8.4748038E-01	2.16017E-00	1.02216E-00
8.90000E-01	6.10595E-01	6.86062E-01	9.65086E-01	8.9359185E-01	2.16017E-00	1.01045E-00
8.80000E-01	5.82180E-01	6.61569E-01	1.00784E-00	9.3837811E-01	2.16017E-00	1.00341E-00
8.70000E-01	5.54802E-01	6.37703E-01	1.04882E-00	9.8204503E-01	2.16017E-00	1.00028E-00
8.60000E-01	5.28431E-01	6.14455E-01	1.08825E-00	1.0247714E-00	2.16017E-00	1.00052E-00
8.50000E-01	5.03042E-01	5.91815E-01	1.12627E-00	1.0666951E-00	2.16017E-00	1.00373E-00
8.40000E-01	4.78608E-01	5.69771E-01	1.16332E-00	1.1079490E-00	2.16017E-00	1.00961E-00
8.30000E-01	4.55102E-01	5.48315E-01	1.19864E-00	1.1486300E-00	2.16017E-00	1.01795E-00
8.20000E-01	4.32499E-01	5.27437E-01	1.23320E-00	1.1888301E-00	2.16017E-00	1.02859E-00
8.10000E-01	4.10773E-01	5.07128E-01	1.26680E-00	1.2286278E-00	2.16017E-00	1.04140E-00
8.00000E-01	3.89901E-01	4.87376E-01	1.29952E-00	1.2681034E-00	2.16017E-00	1.05633E-00
7.90000E-01	3.69858E-01	4.68174E-01	1.33141E-00	1.3073002E-00	2.16017E-00	1.07331E-00
7.80000E-01	3.50620E-01	4.49512E-01	1.36254E-00	1.3462991E-00	2.16017E-00	1.09233E-00
7.70000E-01	3.32164E-01	4.31381E-01	1.39236E-00	1.3851319E-00	2.16017E-00	1.11339E-00
7.60000E-01	3.14616E-01	4.14021E-01	1.42113E-00	1.4240312E-00	2.16017E-00	1.13696E-00
7.50000E-01	2.98071E-01	3.97287E-01	1.44703E-00	1.4630351E-00	2.16017E-00	1.16368E-00
7.40000E-01	2.82565E-01	3.80997E-01	1.47032E-00	1.5021657E-00	2.16017E-00	1.19304E-00
7.30000E-01	2.68026E-01	3.64414E-01	1.49210E-00	1.5414353E-00	2.16017E-00	1.22462E-00
7.20000E-01	2.54401E-01	3.49724E-01	1.51186E-00	1.5808033E-00	2.16017E-00	1.25751E-00
7.10000E-01	2.41655E-01	3.35726E-01	1.52806E-00	1.6202972E-00	2.16017E-00	1.29280E-00
7.00000E-01	2.29801E-01	3.22144E-01	1.54083E-00	1.6600502E-00	2.16017E-00	1.33061E-00
6.90000E-01	2.18899E-01	3.08972E-01	1.54918E-00	1.7002921E-00	2.16017E-00	1.37108E-00
6.80000E-01	2.08981E-01	2.96202E-01	1.55413E-00	1.7419572E-00	2.16017E-00	1.41436E-00
6.70000E-01	1.99964E-01	2.83827E-01	1.55570E-00	1.7850782E-00	2.16017E-00	1.46061E-00
6.60000E-01	1.91751E-01	2.71841E-01	1.55390E-00	1.8296823E-00	2.16017E-00	1.50991E-00
6.50000E-01	1.84354E-01	2.60237E-01	1.54875E-00	1.8758082E-00	2.16017E-00	1.56227E-00
6.40000E-01	1.77764E-01	2.49007E-01	1.54027E-00	1.9234810E-00	2.16017E-00	1.61891E-00
6.30000E-01	1.71981E-01	2.38145E-01	1.52845E-00	1.9727384E-00	2.16017E-00	1.67934E-00
6.20000E-01	1.66909E-01	2.27644E-01	1.51333E-00	1.9824103E-00	2.16017E-00	1.73365E-00
6.10000E-01	1.62547E-01	2.17498E-01	1.49491E-00	2.0235286E-00	2.16017E-00	1.86240E-00
6.00000E-01	1.58899E-01	2.07699E-01	1.47240E-00	2.0651331E-00	2.16017E-00	1.93590E-00
5.90000E-01	1.55862E-01	1.98240E-01	1.44632E-00	2.1072547E-00	2.16017E-00	2.01455E-00
5.80000E-01	1.53431E-01	1.89116E-01	1.41674E-00	2.1499306E-00	2.16017E-00	2.09876E-00
5.70000E-01	1.51620E-01	1.80319E-01	1.38362E-00	2.1931994E-00	2.16017E-00	2.18897E-00
5.60000E-01	1.50323E-01	1.71843E-01	1.34765E-00	2.2371015E-00	2.16017E-00	2.28571E-00
5.50000E-01	1.49520E-01	1.63682E-01	1.30863E-00	2.2816721E-00	2.16017E-00	2.38954E-00
5.40000E-01	1.49170E-01	1.55828E-01	1.26697E-00	2.3269632E-00	2.16017E-00	2.50109E-00
5.30000E-01	1.49257E-01	1.48275E-01	1.22288E-00	2.3730119E-00	2.16017E-00	2.62105E-00
5.20000E-01	1.49787E-01	1.41017E-01	2.01017E-00	2.4198656E-00	2.16017E-00	2.75021E-00
5.10000E-01	1.50833E-01	1.34047E-01	2.03024E-00	2.4675799E-00	2.16017E-00	2.88944E-00
5.00000E-01	1.52393E-01	1.07359E-01	2.05010E-00	2.5161951E-00	2.16017E-00	3.03971E-00

Figure 6 SAMPLE PRINTOUT FOR FROZEN FLOW SOLUTION

FROZEN THROAT-1000
TEMPERATURE= 0.065040 MASS FLOW= 0.6690 DENSITY= 0.627357 PRESSURE= 0.543711

Figure 7 SAMPLE PRINTOUT OF THROAT CONDITIONS FOR FROZEN FLOW

THROAT-1000
TEMPERATURE= 0.903984 MASS FLOW= 0.6559 DENSITY= 0.624117 PRESSURE= 0.557679
ENTHALPY= 4.5811 VELOCITY= 1.0507E 00

E- 1.099E-06
N2 2.454E-02
O2 1.820E-03
AR 3.219E-04
N 2.461E-04
O 6.250E-03
NO 4.598E-03
NO+ 1.099E-06

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Figure 8 SAMPLE PRINTOUT OF THROAT CONDITIONS FOR EQUILIBRIUM FLOW

EQUILIBRIUM SOLUTION

1.00000E 00	1.00000E 00	1.00000E 00	0.00000E-19	0.0000000E-19	2.16017E 00	0.00000E-39
2.292E-06	2.433E-02	1.415E-03	3.219E-04	4.481E-04	6.880E-03	4.760E-03
9.90000E-01	9.43920E-01	9.54523E-01	3.38803E-01	3.0595629E-01	2.16017E 00	2.02821E 00
2.138E-06	2.436E-02	1.453E-03	3.219E-04	4.577E-04	6.833E-03	4.754E-03
9.80000E-01	8.90413E-01	9.10640E-01	4.79117E-01	4.3513478E-01	2.16017E 00	1.50335E 00
1.992E-06	2.438E-02	1.486E-03	3.219E-04	4.285E-04	6.775E-03	4.738E-03
9.70000E-01	8.39377E-01	8.68299E-01	5.86793E-01	5.3601468E-01	2.16017E 00	1.28734E 00
1.853E-06	2.440E-02	1.524E-03	3.219E-04	4.006E-04	6.715E-03	4.723E-03
9.60000E-01	7.90711E-01	8.27451E-01	6.77597E-01	6.2260215E-01	2.16017E 00	1.16986E 00
1.721E-06	2.442E-02	1.564E-03	3.219E-04	3.719E-04	6.653E-03	4.706E-03
9.50000E-01	7.44320E-01	7.88048E-01	7.57640E-01	7.0031193E-01	2.16017E 00	1.09858E 00
1.595E-06	2.444E-02	1.605E-03	3.219E-04	3.484E-04	6.587E-03	4.689E-03
9.40000E-01	7.00113E-01	7.50044E-01	8.30062E-01	7.7191516E-01	2.16017E 00	1.05354E 00
1.476E-06	2.446E-02	1.648E-03	3.219E-04	3.241E-04	6.519E-03	4.671E-03
9.30000E-01	6.58002E-01	7.13397E-01	8.96728E-01	8.3905952E-01	2.16017E 00	1.02531E 00
1.363E-06	2.449E-02	1.693E-03	3.219E-04	3.009E-04	6.448E-03	4.652E-03
9.20000E-01	6.17904E-01	6.78064E-01	9.58859E-01	9.0282560E-01	2.16017E 00	1.00884E 00
1.257E-06	2.451E-02	1.740E-03	3.219E-04	2.790E-04	6.374E-03	4.632E-03
9.10000E-01	5.79739E-01	6.44007E-01	1.01730E 00	9.6396388E-01	2.16017E 00	1.00117E 00
1.156E-06	2.453E-02	1.789E-03	3.219E-04	2.581E-04	6.297E-03	4.611E-03
9.00000E-01	5.43430E-01	6.11187E-01	1.07267E 00	1.0230272E 00	2.16017E 00	1.00047E 00
1.062E-06	2.455E-02	1.840E-03	3.219E-04	2.384E-04	6.217E-03	4.589E-03
8.90000E-01	5.08905E-01	5.79569E-01	1.12544E 00	1.0804338E 00	2.16017E 00	1.00558E 00
9.727E-07	2.457E-02	1.894E-03	3.219E-04	2.197E-04	6.134E-03	4.565E-03
8.80000E-01	4.76094E-01	5.49118E-01	1.17598E 00	1.1365183E 00	2.16017E 00	1.01374E 00
8.893E-07	2.459E-02	1.949E-03	3.219E-04	2.021E-04	6.049E-03	4.541E-03
8.70000E-01	4.44930E-01	5.19803E-01	1.22457E 00	1.1915442E 00	2.16017E 00	1.03045E 00
8.112E-07	2.461E-02	2.006E-03	3.219E-04	1.856E-04	5.959E-03	4.515E-03
8.60000E-01	4.15349E-01	4.91592E-01	1.27145E 00	1.2457346E 00	2.16017E 00	1.04940E 00
7.383E-07	2.463E-02	2.066E-03	3.219E-04	1.700E-04	5.867E-03	4.487E-03
8.50000E-01	3.87291E-01	4.64458E-01	1.31681E 00	1.2992711E 00	2.16017E 00	1.07245E 00
6.703E-07	2.466E-02	2.129E-03	3.219E-04	1.554E-04	5.772E-03	4.458E-03
8.40000E-01	3.60697E-01	4.38372E-01	1.36082E 00	1.3523141E 00	2.16017E 00	1.09952E 00
6.071E-07	2.468E-02	2.193E-03	3.219E-04	1.417E-04	5.673E-03	4.428E-03

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Figure 9 SAMPLE PRINTOUT FOR EQUILIBRIUM FLOW SOLUTION

DENSITY FIT-ALPHA= 2.4733661E-01 CONSTANT= 4.2869943E-02

Figure 10 SAMPLE PRINTOUT OF DENSITY - FIT CONSTANTS FOR NONEQUILIBRIUM FLOW

NONEQUILIBRIUM SOLUTION

9.90000E-01	9.43920E-01	9.54523E-01	9.38803E-01	9.0596185E-01	2.16017E 00	2.02821E 00	-1.0140067E 00	0
0.990000	2.138E-06	2.436E-02	1.450E-03	9.219E-04	6.833E-03	4.754E-03	2.138E-06	
0.990000	2.138E-06	2.436E-02	1.450E-03	9.219E-04	6.833E-03	4.754E-03	2.138E-06	
9.80000E-01	8.90419E-01	9.10640E-01	4.79117E-01	4.3514837E-01	2.16017E 00	1.50334E 00	-7.0946776E-01	0
0.980000	1.992E-06	2.438E-02	1.486E-03	9.219E-04	6.775E-03	4.738E-03	1.992E-06	
0.980000	1.992E-06	2.438E-02	1.486E-03	9.219E-04	6.775E-03	4.738E-03	1.992E-06	
9.69999E-01	8.39377E-01	9.68299E-01	5.86793E-01	5.3603759E-01	2.16017E 00	1.28734E 00	-5.3603978E-01	0
0.969999	1.853E-06	2.440E-02	1.524E-03	9.219E-04	6.715E-03	4.723E-03	1.853E-06	
0.970000	1.853E-06	2.440E-02	1.524E-03	9.219E-04	6.715E-03	4.723E-03	1.853E-06	
9.59999E-01	7.90711E-01	9.27451E-01	6.77597E-01	6.2263877E-01	2.16017E 00	1.16986E 00	-4.1213865E-01	0
0.959999	1.721E-06	2.442E-02	1.564E-03	9.219E-04	6.653E-03	4.706E-03	1.721E-06	
0.960000	1.721E-06	2.442E-02	1.564E-03	9.219E-04	6.653E-03	4.706E-03	1.721E-06	
9.49998E-01	7.44320E-01	7.88048E-01	7.57640E-01	7.0036270E-01	2.16017E 00	1.09858E 00	-3.1397259E-01	0
0.949998	1.595E-06	2.444E-02	1.605E-03	9.219E-04	6.587E-03	4.689E-03	1.595E-06	
0.950000	1.595E-06	2.444E-02	1.605E-03	9.219E-04	6.587E-03	4.689E-03	1.595E-06	
9.39998E-01	7.00113E-01	7.50044E-01	8.30062E-01	7.7198248E-01	2.16017E 00	1.05354E 00	-2.3137960E-01	0
0.939998	1.476E-06	2.446E-02	1.648E-03	9.219E-04	6.519E-03	4.671E-03	1.476E-06	
0.940000	1.476E-06	2.446E-02	1.648E-03	9.219E-04	6.519E-03	4.671E-03	1.476E-06	
9.29997E-01	6.58002E-01	7.13397E-01	8.96729E-01	8.3914685E-01	2.16017E 00	1.02531E 00	-1.5908753E-01	0
0.929997	1.364E-06	2.449E-02	1.693E-03	9.219E-04	6.448E-03	4.652E-03	1.364E-06	
0.930000	1.363E-06	2.449E-02	1.693E-03	9.219E-04	6.448E-03	4.652E-03	1.363E-06	
9.19996E-01	6.17904E-01	6.78064E-01	9.58859E-01	9.0293329E-01	2.16017E 00	1.00884E 00	-9.4009612E-02	0
0.919996	1.257E-06	2.451E-02	1.740E-03	9.219E-04	6.374E-03	4.632E-03	1.257E-06	
0.920000	1.257E-06	2.451E-02	1.740E-03	9.219E-04	6.374E-03	4.632E-03	1.257E-06	
8.94938E-01	5.25757E-01	5.95054E-01	1.09965E 00	1.0524008E 00	2.16017E 00	1.00239E 00	6.2331046E-02	0
0.894938	1.017E-06	2.456E-02	1.867E-03	9.219E-04	6.176E-03	4.577E-03	1.017E-06	
0.894944	1.016E-06	2.456E-02	1.867E-03	9.219E-04	6.176E-03	4.577E-03	1.016E-06	
8.84936E-01	4.92107E-01	5.64030E-01	1.15125E 00	1.1091291E 00	2.16017E 00	1.01012E 00	1.2837669E-01	0
0.884936	9.308E-07	2.458E-02	1.921E-03	9.219E-04	6.092E-03	4.553E-03	9.308E-07	
0.884944	9.298E-07	2.458E-02	1.921E-03	9.219E-04	6.091E-03	4.553E-03	9.298E-07	
8.74934E-01	4.60137E-01	5.34158E-01	1.20077E 00	1.1646765E 00	2.16017E 00	1.02263E 00	1.9193800E-01	0
0.874934	8.503E-07	2.460E-02	1.978E-03	9.219E-04	6.004E-03	4.528E-03	8.503E-07	
0.874944	8.492E-07	2.460E-02	1.978E-03	9.219E-04	6.004E-03	4.528E-03	8.492E-07	
8.64932E-01	4.29781E-01	5.05405E-01	1.24847E 00	1.2192844E 00	2.16017E 00	1.03951E 00	2.5363904E-01	0
0.864932	7.751E-07	2.462E-02	2.036E-03	9.219E-04	5.914E-03	4.501E-03	7.751E-07	
0.864944	7.737E-07	2.462E-02	2.036E-03	9.219E-04	5.913E-03	4.501E-03	7.737E-07	
8.54928E-01	4.00978E-01	4.77742E-01	1.29456E 00	1.2731536E 00	2.16017E 00	1.06059E 00	3.1398265E-01	0
0.854928	7.048E-07	2.464E-02	2.097E-03	9.219E-04	5.820E-03	4.473E-03	7.048E-07	
0.854944	7.033E-07	2.464E-02	2.098E-03	9.219E-04	5.819E-03	4.473E-03	7.033E-07	

Figure 11a SAMPLE PRINTOUT FOR NONEQUILIBRIUM FLOW SOLUTION

NONEQUILIBRIUM SOLUTION

8.44925E-01	3.73667E-01	4.51141E-01	1.33922E 00	1.3264539E 00	2.16017E 00	1.08563E 00	3.7338972E-01	0
0.844925	6.395E-07	2.467E-02	2.161E-03	3.219E-04	1.484E-04	5.723E-03	4.443E-03	6.395E-07
0.844944	6.378E-07	2.467E-02	2.161E-03	3.219E-04	1.483E-04	5.722E-03	4.443E-03	6.378E-07
8.34920E-01	3.47791E-01	4.25575E-01	1.38261E 00	1.3793317E 00	2.16017E 00	1.11474E 00	4.3221639E-01	0
0.834920	5.787E-07	2.469E-02	2.226E-03	3.219E-04	1.351E-04	5.623E-03	4.412E-03	5.787E-07
0.834944	5.769E-07	2.469E-02	2.227E-03	3.219E-04	1.351E-04	5.622E-03	4.411E-03	5.769E-07
8.24914E-01	3.23297E-01	4.01018E-01	1.42484E 00	1.4319137E 00	2.16017E 00	1.16794E 00	4.9077750E-01	0
0.824914	5.225E-07	2.471E-02	2.295E-03	3.219E-04	1.228E-04	5.519E-03	4.379E-03	5.225E-07
0.824944	5.204E-07	2.471E-02	2.295E-03	3.219E-04	1.228E-04	5.519E-03	4.378E-03	5.204E-07
8.14907E-01	3.00129E-01	3.77447E-01	1.46633E 00	1.4843116E 00	2.16017E 00	1.18536E 00	5.4935507E-01	0
0.814907	4.705E-07	2.474E-02	2.365E-03	3.219E-04	1.113E-04	5.413E-03	4.344E-03	4.705E-07
0.814944	4.682E-07	2.474E-02	2.366E-03	3.219E-04	1.113E-04	5.412E-03	4.343E-03	4.682E-07
8.04899E-01	2.78239E-01	3.54839E-01	1.50626E 00	1.5366240E 00	2.16017E 00	1.22720E 00	6.0820536E-01	0
0.804899	4.225E-07	2.476E-02	2.439E-03	3.219E-04	1.006E-04	5.303E-03	4.307E-03	4.225E-07
0.804944	4.200E-07	2.476E-02	2.440E-03	3.219E-04	1.006E-04	5.302E-03	4.306E-03	4.200E-07
7.94888E-01	2.57576E-01	3.33171E-01	1.54564E 00	1.5889399E 00	2.16017E 00	1.27371E 00	6.6757068E-01	0
0.794888	3.784E-07	2.478E-02	2.515E-03	3.219E-04	9.074E-05	5.190E-03	4.267E-03	3.784E-07
0.794944	3.757E-07	2.478E-02	2.516E-03	3.219E-04	9.070E-05	5.189E-03	4.266E-03	3.757E-07
7.84876E-01	2.38095E-01	3.12424E-01	1.58421E 00	1.6413388E 00	2.16017E 00	1.32523E 00	7.2768123E-01	0
0.784876	3.380E-07	2.481E-02	2.594E-03	3.219E-04	8.160E-05	5.074E-03	4.226E-03	3.380E-07
0.784944	3.350E-07	2.481E-02	2.595E-03	3.219E-04	8.155E-05	5.072E-03	4.225E-03	3.350E-07
7.74860E-01	2.19748E-01	2.92576E-01	1.62205E 00	1.6938927E 00	2.16017E 00	1.38211E 00	7.8875956E-01	0
0.774860	3.010E-07	2.483E-02	2.675E-03	3.219E-04	7.316E-05	4.955E-03	4.183E-03	3.010E-07
0.774944	2.978E-07	2.484E-02	2.677E-03	3.219E-04	7.312E-05	4.953E-03	4.181E-03	2.978E-07
7.64827E-01	1.94573E-01	2.62418E-01	1.66572E 00	1.7500141E 00	2.16017E 00	1.50056E 00	9.0276632E-01	0
0.764827	2.588E-07	2.486E-02	2.673E-03	3.219E-04	6.800E-05	4.763E-03	4.173E-03	2.588E-07
0.764944	2.551E-07	2.486E-02	2.676E-03	3.219E-04	6.794E-05	4.966E-03	4.171E-03	2.551E-07
7.54802E-01	1.79083E-01	2.45180E-01	1.70198E 00	1.8028355E 00	2.16017E 00	1.57184E 00	9.6490768E-01	0
0.754802	2.292E-07	2.487E-02	2.760E-03	3.219E-04	6.057E-05	4.839E-03	4.128E-03	2.292E-07
0.754944	2.253E-07	2.487E-02	2.764E-03	3.219E-04	6.051E-05	4.836E-03	4.125E-03	2.253E-07
7.44771E-01	1.64544E-01	2.28733E-01	1.73766E 00	1.8560131E 00	2.16017E 00	1.65026E 00	1.0289479E 00	0
0.744771	2.024E-07	2.493E-02	2.851E-03	3.219E-04	5.377E-05	4.707E-03	4.080E-03	2.024E-07
0.744944	1.982E-07	2.493E-02	2.855E-03	3.219E-04	5.371E-05	4.702E-03	4.076E-03	1.982E-07
7.34733E-01	1.50920E-01	2.13059E-01	1.77281E 00	1.9039553E 00	2.16017E 00	1.73654E 00	1.0950785E 00	0
0.734733	1.782E-07	2.492E-02	2.943E-03	3.219E-04	4.759E-05	4.571E-03	4.030E-03	1.782E-07
0.734944	1.737E-07	2.493E-02	2.948E-03	3.219E-04	4.752E-05	4.566E-03	4.025E-03	1.737E-07
7.24687E-01	1.38173E-01	1.98144E-01	1.80746E 00	1.9636268E 00	2.16017E 00	1.83146E 00	1.1635074E 00	0
0.724687	1.564E-07	2.495E-02	3.039E-03	3.219E-04	4.196E-05	4.433E-03	3.977E-03	1.564E-07
0.724944	1.517E-07	2.496E-02	3.045E-03	3.219E-04	4.189E-05	4.427E-03	3.971E-03	1.517E-07

Figure 11b SAMPLE PRINTOUT FOR NONEQUILIBRIUM FLOW SOLUTION

NONEQUILIBRIUM SOLUTION

7.14629E-01	1.26268E-01	1.83972E-01	1.84162E 00	2.0181473E 00	2.16017E 00	1.73595E 00	1.2344562E 00	0
0.714629	1.367E-07	2.499E-02	3.137E-03	3.219E-04	3.687E-05	4.293E-03	3.922E-03	1.369E-07
0.716966	1.319E-07	2.499E-02	3.144E-03	3.219E-04	3.679E-05	4.285E-03	3.914E-03	1.319E-07
7.04555E-01	1.15168E-01	1.70526E-01	1.87533E 00	2.0731934E 00	2.16017E 00	2.05106E 00	1.3387140E 00	0
0.704565	1.195E-07	2.501E-02	3.237E-03	3.219E-04	3.227E-05	4.150E-03	3.864E-03	1.195E-07
0.706966	1.141E-07	2.502E-02	3.246E-03	3.219E-04	3.218E-05	4.141E-03	3.854E-03	1.141E-07
6.94489E-01	1.04838E-01	1.57791E-01	1.90860E 00	2.1287979E 00	2.16017E 00	2.17796E 00	1.3877389E 00	0
0.694887	1.039E-07	2.505E-02	3.340E-03	3.219E-04	2.814E-05	4.004E-03	3.804E-03	1.039E-07
0.696966	9.837E-08	2.505E-02	3.351E-03	3.219E-04	2.804E-05	3.994E-03	3.791E-03	9.837E-08
6.84394E-01	9.52446E-02	1.45749E-01	1.94145E 00	2.1849898E 00	2.16017E 00	2.31900E 00	1.4718823E 00	0
0.684394	9.017E-08	2.508E-02	3.445E-03	3.219E-04	2.443E-05	3.857E-03	3.741E-03	9.017E-08
0.684966	8.437E-08	2.509E-02	3.459E-03	3.219E-04	2.433E-05	3.845E-03	3.726E-03	8.437E-08
6.74277E-01	8.63528E-02	1.34385E-01	1.97389E 00	2.2417944E 00	2.16017E 00	2.47270E 00	1.5614833E 00	0
0.674277	7.808E-08	2.511E-02	3.552E-03	3.219E-04	2.112E-05	3.708E-03	3.676E-03	7.808E-08
0.674966	7.201E-08	2.512E-02	3.569E-03	3.219E-04	2.101E-05	3.693E-03	3.657E-03	7.201E-08
6.64132E-01	7.80530E-02	1.23681E-01	2.00594E 00	2.3001868E 00	2.16024E 00	2.64379E 00	1.6569121E 00	1
0.664132	6.749E-08	2.515E-02	3.660E-03	3.219E-04	1.818E-05	3.558E-03	3.609E-03	6.749E-08
6.63115E-01	7.72578E-02	1.22635E-01	2.00914E 00	2.3057093E 00	2.16025E 00	2.66209E 00	1.6669121E 00	1
0.663115	6.642E-08	2.515E-02	3.671E-03	3.219E-04	1.791E-05	3.543E-03	3.602E-03	6.642E-08
6.62099E-01	7.64717E-02	1.21600E-01	2.01235E 00	2.3098916E 00	2.16024E 00	2.68047E 00	1.6769121E 00	1
0.662099	6.537E-08	2.515E-02	3.683E-03	3.219E-04	1.763E-05	3.528E-03	3.595E-03	6.537E-08
6.61085E-01	7.56976E-02	1.20579E-01	2.01552E 00	2.3157162E 00	2.16025E 00	2.69892E 00	1.6869121E 00	1
0.661085	6.436E-08	2.516E-02	3.694E-03	3.219E-04	1.736E-05	3.513E-03	3.588E-03	6.436E-08
6.59971E-01	7.48573E-02	1.19469E-01	2.01839E 00	2.3216189E 00	2.16025E 00	2.71930E 00	1.6979121E 00	1
0.659971	6.333E-08	2.515E-02	3.706E-03	3.219E-04	1.707E-05	3.496E-03	3.580E-03	6.333E-08
6.58869E-01	7.40314E-02	1.18376E-01	2.02242E 00	2.3282421E 00	2.16025E 00	2.73976E 00	1.7089120E 00	1
0.658869	6.227E-08	2.517E-02	3.719E-03	3.219E-04	1.679E-05	3.480E-03	3.572E-03	6.227E-08
6.57769E-01	7.32169E-02	1.17296E-01	2.02585E 00	2.3340493E 00	2.16025E 00	2.76031E 00	1.7199120E 00	1
0.657769	6.130E-08	2.517E-02	3.730E-03	3.219E-04	1.650E-05	3.463E-03	3.564E-03	6.130E-08
6.56680E-01	7.24161E-02	1.16232E-01	2.02922E 00	2.3405331E 00	2.16025E 00	2.78095E 00	1.7309120E 00	1
0.656680	6.030E-08	2.518E-02	3.742E-03	3.219E-04	1.623E-05	3.447E-03	3.557E-03	6.030E-08
6.55485E-01	7.15481E-02	1.15076E-01	2.03233E 00	2.3470077E 00	2.16025E 00	2.80375E 00	1.7430120E 00	1
0.655485	5.927E-08	2.518E-02	3.755E-03	3.219E-04	1.594E-05	3.427E-03	3.549E-03	5.927E-08
6.54304E-01	7.06964E-02	1.13939E-01	2.03657E 00	2.3541979E 00	2.16025E 00	2.82665E 00	1.7551120E 00	1
0.654304	5.822E-08	2.518E-02	3.768E-03	3.219E-04	1.565E-05	3.412E-03	3.540E-03	5.822E-08

Figure 11c SAMPLE PRINTOUT FOR NONEQUILIBRIUM FLOW SOLUTION

