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Interim Revision
March 1976

Computer Program for Calculation of Complex Chemical Equilibrium Compositions, Rocket Performance, Incident and Reflected Shocks, and Chapman-Jouguet Detonations

GORDON and McBRIDE

(NASA-SP-273) COMPUTER PROGRAM FOR CALCULATION OF COMPLEX CHEMICAL EQUILIBRIUM COMPOSITIONS, ROCKET PERFORMANCE, INCIDENT AND REFLECTED SHOCKS, AND CHAPMAN-JOUGUET DETONATIONS (NASA) EC A07/MF A01 N78-17724
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NASA SP-273

Computer Program for Calculation of Complex Chemical Equilibrium Compositions, Rocket Performance, Incident and Reflected Shocks, and Chapman-Jouguet Detonations

Sanford Gordon and Bonnie J. McBride

NASA Lewis Research Center

Interim Revision
March 1976

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FOREWORD

NASA SP-273 has been reprinted with some omissions and a few additions to the original document, which is out of print. The reprint documents the current NASA Lewis chemical equilibrium computer program, CEC76. Since the program as well as the thermodynamic data is continuously being revised, the listings of these items are being omitted. However, the text is essentially adequate and has been reproduced without change. A few new input and output options are included in the tables for convenience.

The following items are not being reproduced:

(1) The program listing (appendix C)

(2) The thermodynamic data (appendix D except pp. 168 and 169)

(3) The examples (appendix E)

(4) Some flow diagrams (figs. 4 and 5)

Briefly, the additional input-output options are for

(1) Inputting the assigned energy value on a REACTANT card in units of kJ/kg-mole rather than cal/g-mole. See (6a) in table VI.

(2) Printing output tables in SI units. See SIUNIT in table VIII.

(3) Inputting a chamber temperature estimate for rocket problems. See TCEST in table IX.

(4) Freezing composition at either the throat or an exit point for rocket problems. See NFZ in table IX.

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PREFACE

This report presents the latest in a number of versions of chemical equilibrium and applications programs developed at the NASA Lewis Research Center in the past 25 years. These programs have changed over the years to include improved calculation techniques and to take advantage of constantly improving computer capabilities.

The current version, first prepared in 1967, is based on the minimization of free energy approach to chemical equilibrium calculations. One purpose of this report is to document the program for current and future users. Another purpose is to present in detail a number of topics of general interest in complex equilibrium calculations. These topics include mathematical analysis and techniques for obtaining chemical equilibrium; formulas for obtaining thermodynamic mixture properties and derivatives; criteria for inclusion of condensed phases; calculations at a triple point; inclusion of ionized species; and applications such as constant pressure or constant volume combustion, rocket performance (to assigned area ratios or pressure ratios), shock wave calculations, and Chapman-Jouguet detonations.

A number of examples are given in detail to illustrate the versatility of the program.

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COMPUTER PROGRAM FOR CALCULATION OF COMPLEX CHEMICAL EQUILIBRIUM COMPOSITIONS, ROCKET PERFORMANCE, INCIDENT AND REFLECTED SHOCKS, AND CHAPMAN-JOUGUET DETONATIONS

by Sanford Gordon and Bonnie J. McBride

Lewis Research Center

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SUMMARY

A detailed description of the equations and computer program for computations involving chemical equilibria in complex systems is given. A free-energy minimization technique is used. The program permits calculations such as (1) chemical equilibrium for assigned thermodynamic states (T,P), (H,P), (S,P), (T,V), (U,V), or (S,V), (2) theoretical rocket performance for both equilibrium and frozen compositions during expansion, (3) incident and reflected shock properties, and (4) Chapman-Jouguet detonation properties. The program considers condensed species as well as gaseous species.

INTRODUCTION

The knowledge of chemical equilibrium compositions of a chemical system permits one to calculate theoretical thermodynamic properties for the system. These properties can be applied to a wide variety of problems in chemistry and chemical engineering. Some applications are the design and analysis of equipment such as compressors, turbines, nozzles, engines, shock tubes, heat exchangers, and chemical processing equipment.

Considerable numerical calculations are necessary to obtain equilibrium compositions for complex chemical systems. This has resulted in a number of digital computer programs to do the calculations. (See refs. 1 and 2 for a discussion of mathematical procedures and references to programs.) A computer program written at NASA Lewis Research Center in 1961-1962 (refs. 3 and 4) has had a wide acceptance.

Because of the still current and active interest in a general equilibrium program, it was considered extremely desirable to rewrite, improve, and up-date the NASA program (CEC71, short for Chemical Equilibrium Calculations, 1971) for the following reasons:

(1) Many users of the previous program have made additions or deletions in order to do special problems. These modifications have often been difficult and/or time consuming to accomplish. CEC71 was written to make it simpler to use various parts as subroutines to other programs or to include modifications.

(2) CEC71 was written to be machine independent as much as possible. Thus, those parts of the previous program which were difficult to convert to other machines were eliminated. For example, we eliminated shift routines, subroutine BYPASS, and binary cards for thermodynamic data.

(3) CEC71 incorporates programming features which have become available since the previous program was written. These new features include the use of namelists to simplify input, block data for common storages, and the use of logical variables and IF's.

(4) Additional improvements have been made in the following ways: considerable saving of storage, improved technique for handling condensed phases, improved method for obtaining assigned area ratio data in rocket performance, inclusion of a routine to consider discontinuities at the nozzle throat, capability of considering ionized species, inclusion of an option to print mole fractions of trace species, inclusion of a special provision to handle certain singularities, inclusion of an option to calculate enthalpies of certain reactants, and writing chemical formulas in the output in a more conventional way.

(5) A new subroutine, SHOCK, has been added to calculate incident and reflected shock wave parameters.

(6) Programming has been included to permit calculation of equilibrium compositions with volume as one of the assigned thermodynamic functions.

The program is now capable of doing the following kinds of problems:

(1) Obtaining equilibrium compositions for assigned thermodynamic states. The thermodynamic states may be specified by the assigning two thermodynamic state functions (code names used in the program are given in parenthesis):

(a) Temperature and pressure (TP)
(b) Enthalpy and pressure (HP)
(c) Entropy and pressure (SP)
(d) Temperature and volume or density (TV)
(e) Internal energy and volume or density (UV)
(f) Entropy and volume or density (SV)

(2) Theoretical rocket performance

(3) Chapman-Jouguet detonations

(4) Shock tube parameter calculations

The program may be obtained by sending a magnetic tape (minimum length, 1200 ft) and a written request (specifying the type of computer) to the authors.

EQUATIONS DESCRIBING CHEMICAL EQUILIBRIUM

Chemical equilibrium is usually described by either of two equivalent formulations - equilibrium constants or minimization of free energy. References 1, 5, and 6 contain comparisons between the two formulations. In reference 5 it was shown that, if a generalized method of solution is used, the two formulations reduce to the same number of iteration equations. However, in reference 6 several disadvantages of the equilibrium constant method are discussed. Briefly, these disadvantages are more bookkeeping, numerical difficulties with use of components, more difficulty in testing for presence of some condensed species, and more difficulty in extending the generalized method for nonideal equations of state. For these reasons, the free-energy minimization formulation is used.

The condition for equilibrium may be stated in terms of any of several thermodynamic functions such as the minimization of the Gibbs free energy or Helmholtz free energy or the maximization of entropy. If one wishes to use temperature and pressure to characterize a thermodynamic state, the Gibbs free energy is most easily minimized inasmuch as temperature and pressure are its natural variables. Similarly, the Helmholtz free energy is most easily minimized if the thermodynamic state is characterized by temperature and volume (or density).

Reference 1 presents equations based on minimization of Gibbs free energy. Some of these equations will be repeated and expanded here for convenience. In addition, a set of equations based on minimization of the Helmholtz free energy will also be presented. However, because only ideal gases and pure condensed phases are being considered, the general notation of reference 1 is not used.

Units

In the sections prior to the COMPUTER PROGRAM section (p. 60), the International System of Units (SI Units) is used (ref. 7). These SI Units are as follows:

Physical quantity	Unit	Symbol
Length	meter	m
Mass	kilogram	kg
Time	second	sec
Temperature	kelvin	K
Force	newton	N
Pressure	newton per square meter	N/m^2
Work, energy	joule	J

The gas constant that is consistent with these units is $R = 8314.3$ J/(kg-mole)(K). In those sections dealing with the computer program, other units are used in addition to or instead of SI Units.

Equation of State

In this report we assume all gases to be ideal and that interactions among phases may be neglected. The equation of state for the mixture is

$$\left.\begin{aligned} PV &= nRT \\ \text{or} \qquad \frac{P}{\rho} &= nRT \end{aligned}\right\} \tag{1}$$

where P is pressure (N/m^2), V specific volume (m^3/kg), n moles (kg-mole/kg), T temperature (K), and ρ density (kg/m^3). Symbols used in this report are summarized in appendix A. Common variables used in the computer program are summarized in appendix B.

Equation (1) is assumed to be correct even when small amounts of condensed species (up to several percent by weight) are present. In this event, the condensed species are assumed to occupy a negligible volume and exert a negligible pressure compared to the gaseous species. In the variables V, n, and ρ, the volume and moles refer to gases only while the mass is for the entire mixture including condensed species. The word "mixture" will be used in this report to refer to mixtures of species as distinguished from mixtures of reactants which will be referred to as "total reactants."

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The molecular weight of the mixture M is then defined to be

$$M = \frac{1}{n} \tag{2}$$

where

$$n = \sum_{j=1}^{m} n_j \tag{3}$$

and n_j is the number of kilogram-moles of species j per kilogram of mixture. An equivalent expression for M is

$$M = \frac{\sum_{j=1}^{n} n_j M_j}{\sum_{j=1}^{m} n_j} \tag{4}$$

where M_j is the molecular weight of species j. As implied in equation (4), among the n possible species which may be considered, gases are indexed from 1 to m and condensed species from $m+1$ to n. This indexing system is just to simplify the subsequent presentation but is not used in the program where order of species is immaterial.

Minimization of Gibbs Free Energy

For a mixture of n species, the Gibbs free energy per kilogram of mixture (g) is given by

$$g = \sum_{j=1}^{n} \mu_j n_j \tag{5}$$

where the chemical potential per kilogram-mole of species j is defined to be

$$\mu_j = \left(\frac{\partial g}{\partial n_j}\right)_{T,P,n_{i\neq j}} \tag{6}$$

The condition for chemical equilibrium is the minimization of free energy. This minimization is usually subject to certain constraints such as the following mass balance constraints:

$$\sum_{j=1}^{n} a_{ij}n_j - b_i^o = 0 \qquad i = 1, \ldots, l \tag{7}$$

or

$$b_i - b_i^o = 0 \qquad i = 1, \ldots, l \tag{7a}$$

where the stoichiometric coefficients a_{ij} are the number of kilogram-atoms of element i per kilogram-mole of species j, b_i^o is the assigned number of kilogram-atoms of element i per kilogram of total reactants (see eq. (191)), and

$$b_i = \sum_{j=1}^{n} a_{ij}n_j \qquad i = 1, \ldots, l \tag{7b}$$

is the number of kilogram-atoms of element i per kilogram of mixture.

Defining a term G to be

$$G = g + \sum_{i=1}^{l} \lambda_i\left(b_i - b_i^o\right) \tag{8}$$

where λ_i are Lagrangian multipliers, the condition for equilibrium becomes

$$\delta G = \sum_{j=1}^{n}\left(\mu_j + \sum_{i=1}^{l} \lambda_i a_{ij}\right)\delta n_j + \sum_{i=1}^{l}\left(b_i - b_i^o\right)\delta\lambda_i = 0 \tag{9}$$

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Treating the variations δn_j and $\delta \lambda_i$ as independent gives

$$\mu_j + \sum_{i=1}^{l} \lambda_i a_{ij} = 0 \qquad j = 1, \ldots, n \tag{10}$$

and also the mass balance equation (7a).

Based on the assumptions in the section Equation of State (p. 4), the chemical potential may be written

$$\mu_j = \begin{cases} \mu_j^o + RT \ln\left(\frac{n_j}{n}\right) + RT \ln P_{atm} & (j = 1, \ldots, m) \\ \mu_j^o & (j = m + 1, \ldots, n) \end{cases} \tag{11}$$

where μ_j^o for gases ($j = 1$ to m) and for condensed phases ($j > m$) is the chemical potential in the standard state. For a gas, the standard state is the hypothetical ideal gas at unit fugacity. For a pure solid or liquid, the standard state is the substance in the condensed phase under a pressure of 1 atmosphere. The numerical values of μ_j^o that are generally found in the literature (ref. 8, e.g.) depend partly on a term involving units of atmospheres. Therefore, to be consistent, pressure P_{atm} in equation (11) must be in units of atmospheres.

Equations (7) and (10) permit the determination of equilibrium compositions for thermodynamic states specified by an assigned temperature T_o and pressure P_o. That is, in addition to equations (7) and (10), we have the pair of trivial equations

$$T = T_o \tag{12a}$$

$$P = P_o \tag{12b}$$

However, the thermodynamic state may be specified by assigning any two state functions. For example, the thermodynamic state corresponding to a constant pressure combustion is specified, instead of by equation (12), by

$$h = h_o \tag{13a}$$

$$P = P_o \tag{13b}$$

where h is the enthalpy of the mixture and h_o is a constant equal to the enthalpy of the reactants (see eq. (193)). The expression for h is

$$h = \sum_{j=1}^{n} n_j \left(H_T^o\right)_j \tag{14}$$

where $\left(H_T^o\right)_j$ is the standard state enthalpy for species j.

For assigned entropy and pressure (such as for an isentropic compression or expansion to a specified pressure), the thermodynamic state is specified by

$$s = s_o \tag{15a}$$

$$P = P_o \tag{15b}$$

where s is the entropy of the mixture and s_o is the assigned entropy, or entropy of the total reactant (see eq. (207)). The expression for s is

$$s = \sum_{j=1}^{n} n_j S_j \tag{16}$$

where

$$S_j = \begin{cases} \left(S_T^o\right)_j - R \ln\left(\frac{n_j}{n}\right) - R \ln P_{atm} & j = 1, \ldots, m \\ \left(S_T^o\right)_j & j = m + 1, \ldots, n \end{cases} \tag{17}$$

and $\left(S_T^o\right)_j$ is the standard state entropy for species j.

The equations required to obtain composition are not all linear in the composition variables and therefore an iteration procedure is generally required. In the iteration procedure described in the following section it will be convenient to treat n as an independent variable.

Gibbs iteration equations. - A descent Newton-Raphson method is used to solve for corrections to initial estimates of compositions n_j, Lagrangian multipliers λ_i, moles n, and (when required) temperature T. This method involves a Taylor series expansion of

the appropriate equations with all terms truncated containing derivatives higher than the first. The correction variables used are $\Delta \ln n_j (j = 1, \ldots, m)$, $\Delta n_j (j = m + 1, \ldots, n)$, $\Delta \ln n$, $\pi_i = -\lambda_i/RT$ and $\Delta \ln T$. As pointed out in reference 1, it is no restriction to start each iteration with the estimate for the Lagrangian multipliers equal to zero inasmuch as they appear linearly in equation (10). After making dimensionless those equations containing thermodynamic functions, the Newton-Raphson equations obtained from equations (10), (7), (3), (13a), and (15a) are

$$\Delta \ln n_j - \sum_{i=1}^{l} a_{ij}\pi_i - \Delta \ln n - \left[\frac{\left(H_T^o\right)_j}{RT}\right]\Delta \ln T = -\frac{\mu_j}{RT} \qquad j = 1, \ldots, m \tag{18}$$

$$-\sum_{i=1}^{l} a_{ij}\pi_i - \left[\frac{\left(H_T^o\right)_j}{RT}\right]\Delta \ln T = -\frac{\mu_j}{RT} \qquad j = m + 1, \ldots, n \tag{19}$$

$$\sum_{j=1}^{m} a_{kj} n_j \, \Delta \ln n_j + \sum_{j=m+1}^{n} a_{kj} \, \Delta n_j = b_k^o - b_k \qquad k = 1, \ldots, l \tag{20}$$

$$\sum_{j=1}^{m} n_j \, \Delta \ln n_j - n \, \Delta \ln n = n - \sum_{j=1}^{m} n_j \tag{21}$$

$$\sum_{j=1}^{m}\left[\frac{n_j\left(H_T^o\right)_j}{RT}\right]\Delta \ln n_j + \sum_{j=m+1}^{n}\left[\frac{\left(H_T^o\right)_j}{RT}\right]\Delta n_j + \left[\sum_{j=1}^{n}\frac{n_j\left(C_p^o\right)_j}{R}\right]\Delta \ln T = \frac{h_o - h}{RT} \tag{22}$$

$$\sum_{j=1}^{m}\left(\frac{n_j S_j}{R}\right)\Delta \ln n_j + \sum_{j=m+1}^{n}\left[\frac{\left(S_T^o\right)_j}{R}\right]\Delta n_j + \left[\sum_{j=1}^{n}\frac{n_j\left(C_p^o\right)_j}{R}\right]\Delta \ln T = \frac{(s_o - s)}{R} + n - \sum_{j=1}^{m} n_j \tag{23}$$

Reduced Gibbs iteration equations. - For problems with assigned thermodynamic states (T,P), (H,P), or (S,P), various combinations of equations (18) to (23) could be used to obtain corrections to estimates. However, for chemical systems containing many species, it would be necessary to solve a large number of simultaneous equations. This large number of equations can be reduced quite simply to a much smaller number by algebraic substitution. This is accomplished by substituting the expression for $\Delta \ln n_j$ obtained from equation (18) into equations (20) to (23). Including equation (19) written with signs reversed, the resulting reduced number of equations are

$$\sum_{i=1}^{l}\sum_{j=1}^{m} a_{kj}a_{ij}n_j\pi_i + \sum_{j=m+1}^{n} a_{kj}\,\Delta n_j + \sum_{j=1}^{m} a_{kj}n_j\,\Delta \ln n + \left[\sum_{j=1}^{m}\frac{a_{kj}n_j\left(H_T^o\right)_j}{RT}\right]\Delta \ln T = (b_k^o - b_k) + \sum_{j=1}^{m}\frac{a_{kj}n_j\mu_j}{RT} \quad (k = 1, \ldots, l) \tag{24}$$

$$\sum_{i=1}^{l} a_{ij}\pi_i + \left[\frac{\left(H_T^o\right)_j}{RT}\right]\Delta \ln T = \frac{\mu_j}{RT} \quad (j = m + 1, \ldots, n) \tag{25}$$

$$\sum_{i=1}^{l}\sum_{j=1}^{m} a_{ij}n_j\pi_i + \left(\sum_{j=1}^{m} n_j - n\right)\Delta \ln n + \left[\sum_{j=1}^{m}\frac{n_j\left(H_T^o\right)_j}{RT}\right]\Delta \ln T = n - \sum_{j=1}^{m} n_j + \sum_{j=1}^{m}\frac{n_j\mu_j}{RT} \tag{26}$$

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$$\sum_{i=1}^{l}\left[\sum_{j=1}^{m}\frac{a_{ij}n_j\left(H_T^o\right)_j}{RT}\right]\pi_i + \sum_{j=m+1}^{n}\left[\frac{\left(H_T^o\right)_j}{RT}\right]\Delta n_j + \left[\sum_{j=1}^{m}\frac{n_j\left(H_T^o\right)_j}{RT}\right]\Delta \ln n$$

$$+\left[\sum_{j=1}^{n}\frac{n_j\left(C_p^o\right)_j}{R} + \sum_{j=1}^{m}\frac{n_j\left(H_T^o\right)_j^2}{R^2T^2}\right]\Delta \ln T = \frac{h_o - h}{RT} + \sum_{j=1}^{m}\frac{n_j\left(H_T^o\right)_j\mu_j}{R^2T^2} \tag{27}$$

$$\sum_{i=1}^{l}\left[\sum_{j=1}^{m}\frac{a_{ij}n_jS_j}{R}\right]\pi_i + \sum_{j=m+1}^{n}\left(\frac{S_j}{R}\right)\Delta n_j + \left[\sum_{j=1}^{m}\frac{n_jS_j}{R}\right]\Delta \ln n$$

$$+\left[\sum_{j=1}^{n}\frac{n_j\left(C_p^o\right)_j}{R} + \sum_{j=1}^{m}\frac{n_j\left(H_T^o\right)_jS_j}{R^2T}\right]\Delta \ln T = \frac{s_o - s}{R} + n - \sum_{j=1}^{m}n_j + \sum_{j=1}^{m}\frac{n_jS_j\mu_j}{R^2T} \tag{28}$$

Equations (24) to (28) are given in table I in a form which will permit direct comparisons with other sets of simultaneous equations presented in later sections (tables II to IV). For the sake of compactness, the following symbols are used in table I:

$$
\left.
\begin{aligned}
\mathscr{H}_j &= \frac{\left(H_T^o\right)_j}{RT} & \mathscr{H} &= \frac{h}{RT} \\
\mathscr{G}_j &= \frac{\mu_j}{RT} & \mathscr{H}_o &= \frac{h_o}{RT} \\
\mathscr{S}_j &= \frac{S_j}{R} & \mathscr{S} &= \frac{s}{R} \\
\mathscr{C}_j &= \frac{\left(C_p^o\right)_j}{R} & \mathscr{S}_o &= \frac{s_o}{R}
\end{aligned}
\right\} \tag{29}
$$

The script symbols subscripted with j in equation (29) are dimensionless, whereas the other script symbols are in units of kilogram-mole per kilogram.

A summary of the correction equations required for several types of constant pressure problems are as follows ($i = 1$ to l, $j = m + 1$ to n):

Type of problem	Equations required	Correction variables
Assigned temperature and pressure (TP)	(24), (25), (26)	π_i, Δn_j, $\Delta \ln n$
Assigned enthalpy and pressure (HP)	(24), (25), (26), (27)	π_i, Δn_j, $\Delta \ln n$, $\Delta \ln T$
Assigned entropy and pressure (SP)	(24), (25), (26), (28)	π_i, Δn_j, $\Delta \ln n$, $\Delta \ln T$

After obtaining the previous correction variables, the corrections for gaseous species $\Delta \ln n_j (j = 1, \ldots, m)$ are then obtained from equation (18). In a later section, Convergence (p. 24), a discussion is given on the control of the size of corrections before they are applied to obtain improved estimates.

Minimization of Helmholtz Free Energy

The equations to be presented in this section are similar to those in the previous section. Whatever differences appear are due to the different forms of the chemical potential $\mu_j (j = 1, \ldots, m)$. In the previous section, pressure was one of the assigned

thermodynamic states and consequently the Gibbs free energy was minimized. In this section volume (or density) is one of the assigned thermodynamic states and consequently the Helmholtz free energy will be minimized.

The two free energies have the following thermodynamic relationship:

$$f = g - PV \tag{30}$$

where f is the Helmholtz free energy per kilogram of mixture, and g is given by equation (5) - that is,

$$f = \sum_{j=1}^{n} \mu_j n_j - PV \tag{31}$$

The chemical potential μ_j can be expressed as a thermodynamic derivative in several ways (ref. 9). One way is given by equation (6). Another expression is

$$\mu_j = \left(\frac{\partial f}{\partial n_j}\right)_{T,V,n_{i\neq j}} \tag{32}$$

If

$$F = f + \sum_{i=1}^{l} \lambda_i \left(b_i - b_i^o\right) \tag{33}$$

the condition for equilibrium based on the minimization of the Helmholtz free energy subject to mass balance constraints is

$$\delta F = \sum_{j=1}^{n} \left(\mu_j + \sum_{i=1}^{l} \lambda_i a_{ij}\right)\delta n_j + \sum_{i=1}^{l} \left(b_i - b_i^o\right)\delta\lambda_i = 0 \tag{34}$$

Treating the δn_j and $\delta\lambda_i$ as independent again gives, as in the previous section, equations (7) and (10). Now, however, instead of equation (11),

$$\mu_j = \begin{cases} \mu_j^o + RT \ln \dfrac{n_j R' T}{V} & (j=1, \ldots, m) \\ \\ \mu_j^o & (j=m+1, \ldots, n) \end{cases} \tag{35}$$

where $R' = R/101325$ to take care of units as discussed for equations (11) and (17).

Equations (7) and (10), with μ_j given by equation (35), permit the determination of equilibrium compositions for thermodynamic states specified by an assigned temperature T_o and volume V_o; that is, in addition to equation (7) and (10), we have the pair of trivial equations

$$T = T_o$$

$$V = V_o \quad . \tag{36}$$

Analogous to equation (13) for a constant pressure combustion process, we can set down the following conditions for constant volume combustion:

$$u' = u'_o \tag{37a}$$

$$V = V_o \tag{37b}$$

where u' is the internal energy of the mixture and u'_o is a constant equal to the internal energy of the reactants. The expression for u' is

$$u' = \sum_{j=1}^{n} n_j \left(U_T^o\right)_j \tag{38}$$

where $\left(U_T^o\right)_j$ is the standard state internal energy for species j.

Analogous to equation (15), for assigned entropy and volume (such as for an isentropic compression or expansion to a specified volume), the thermodynamic state is specified by

$$s = s_o \tag{39a}$$

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$$V = V_o \tag{39b}$$

Iteration equations are derived in the next section which permit solution of the composition variables for constant volume problems.

Helmholtz iteration equations. - Correction equations are obtained in a manner similar to that described in "Gibbs iteration equations" (p. 8). In this case, however, the expression for μ_j is equation (35) rather than equation (11). Because n does not appear explicitly as a variable in equation (35), $\Delta \ln n$ no longer appears as a correction variable. The Newton-Raphson equations obtained from equations (10), (7), (37a), and (39a) are

$$\Delta \ln n_j - \sum_{i=1}^{l} a_{ij}\pi_i - \left[\frac{\left(U_T^o\right)_j}{RT}\right]\Delta \ln T = -\frac{\mu_j}{RT} \qquad (j=1, \ldots, m) \tag{40}$$

$$-\sum_{i=1}^{l} a_{ij}\pi_i - \left[\frac{\left(U_T^o\right)_j}{RT}\right]\Delta \ln T = -\frac{\mu_j}{RT} \qquad (j=m+1, \ldots, n) \tag{41}$$

$$\sum_{j=1}^{m} a_{kj}n_j \Delta \ln n_j + \sum_{j=m+1}^{n} a_{kj}\,\Delta n_j = b_k^o - b_k \qquad (k=1, \ldots, l) \tag{42}$$

$$\sum_{j=1}^{m}\left[\frac{n_j\left(U_T^o\right)_j}{RT}\right]\Delta \ln n_j + \sum_{j=m+1}^{n}\left[\frac{\left(U_T^o\right)_j}{RT}\right]\Delta n_j + \left[\sum_{j=1}^{n}\frac{n_j\left(C_v^o\right)_j}{R}\right]\Delta \ln T = \frac{u_o' - u'}{RT} \tag{43}$$

$$\sum_{j=1}^{m} n_j\left[\left(\frac{S_j}{R}\right) - 1\right]\Delta \ln n_j + \sum_{j=m+1}^{n}\left(\frac{S_j}{R}\right)\Delta n_j + \left[\sum_{j=1}^{n}\frac{n_j\left(C_v^o\right)_j}{R}\right]\Delta \ln T = \frac{s_o - s}{R} \tag{44}$$

Reduced Helmholtz iteration equations. - Equations (40) to (44) may be reduced to a much smaller set of working correction equations by eliminating $\Delta \ln n_j$, obtained from equation (40), from equations (42) to (44). Including equation (41) written with signs reversed the resulting reduced number of equations are

$$\sum_{i=1}^{l} \sum_{j=1}^{m} a_{kj} a_{ij} n_j \pi_i + \sum_{j=m+1}^{n} a_{kj} \Delta n_j + \left[\sum_{j=1}^{m} \frac{a_{kj} n_j \left(U_T^o\right)_j}{RT} \right] \Delta \ln T = b_k^o - b_k + \sum_{j=1}^{m} \frac{a_{kj} n_j \mu_j}{RT} \quad (k=1, \ldots, l) \tag{45}$$

$$\sum_{i=1}^{l} a_{ij} \pi_i + \left[\frac{\left(U_T^o\right)_j}{RT} \right] \Delta \ln T = \frac{\mu_j}{RT} \quad (j=m+1, \ldots, n) \tag{46}$$

$$\sum_{i=1}^{l} \left[\sum_{j=1}^{m} \frac{a_{ij} n_j \left(U_T^o\right)_j}{RT} \right] \pi_i + \sum_{j=m+1}^{n} \left[\frac{\left(U_T^o\right)_j}{RT} \right] \Delta n_j + \left[\sum_{j=1}^{n} \frac{n_j \left(C_v^o\right)_j}{R} + \sum_{j=1}^{m} \frac{n_j \left(U_T^o\right)_j^2}{R^2 T^2} \right] \Delta \ln T = \frac{u_o' - u}{RT} + \sum_{j=1}^{m} \frac{n_j \left(U_T^o\right)_j \mu_j}{R^2 T^2} \tag{47}$$

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$$\sum_{i=1}^{l}\left[\sum_{j=1}^{m} a_{ij}n_j\left(\frac{S_j - R}{R}\right)\right]\pi_i + \sum_{j=m+1}^{n}\left(\frac{S_j}{R}\right)\Delta n_j + \left[\sum_{j=1}^{n}\frac{n_j\left(C_v^o\right)_j}{R} + \sum_{j=1}^{m}\frac{n_j\left(U_T^o\right)_j\left(S_j - R\right)}{R^2T}\right]$$

$$\times \Delta \ln T = \frac{s_o - s}{R} + \sum_{j=1}^{m}\frac{n_j(S_j - R)\mu_j}{R^2T} \tag{48}$$

Equations (45) to (48) are given in table II in a form which will permit direct comparison with the iteration equations in table I and the derivative equations in tables III and IV. For the sake of compactness the following symbols (in addition to some already defined in eq. (29) for table I) are used in table II: $\mathscr{U}_j = \left(U_T^o\right)_j \Big/ RT$, $\mathscr{U} = u'/RT$, $\mathscr{U}_o = u_o'/RT$, and $\left(\mathscr{C}_v\right)_j = \left(C_v^o\right)_j \Big/ R$.

A summary of the correction equations required for several types of constant volume problems are as follows ($i = 1$ to l, $j = m + 1$ to n):

Type of problem	Equations required	Correction variables
Assigned temperature and volume (TV)	(45), (46)	π_i, Δn_j
Assigned internal energy and volume (UV)	(45), (46), (47)	π_i, Δn_j, $\Delta \ln T$
Assigned entropy and volume (SV)	(45), (46), (48)	π_i, Δn_j, $\Delta \ln T$

After obtaining the previous correction variables, the corrections for gaseous species $\Delta \ln n_j (j = 1, \ldots, m)$ are then obtained from equation (40). (See Convergence section (p. 24) for discussion on control of size of corrections before applying them to obtain improved estimates.)

Thermodynamic Derivatives from Matrix Solutions

All thermodynamic first derivatives can be expressed in terms of any three inde-

pendent first derivatives. The Bridgman tables, as tabulated for example in reference 10, express first derivatives in terms of $(\partial V/\partial T)_P$, $(\partial V/\partial P)_T$, and $(\partial h/\partial T)_P \equiv c_p$. We will use the logarithmic form of the volume derivatives inasmuch as in that form they give an indication of the extent of chemical reaction occurring among the reaction species. From equation (14),

$$c_p \equiv \left(\frac{\partial h}{\partial T}\right)_P = \sum_{j=1}^{n} n_j \left(C_p^o\right)_j + \sum_{j=1}^{m} n_j \frac{\left(H_T^o\right)_j}{T}\left(\frac{\partial \ln n_j}{\partial \ln T}\right)_P + \sum_{j=m+1}^{n} \frac{\left(H_T^o\right)_j}{T}\left(\frac{\partial n_j}{\partial \ln T}\right)_P \tag{49}$$

From equation (1),

$$\left(\frac{\partial \ln V}{\partial \ln T}\right)_P = 1 + \left(\frac{\partial \ln n}{\partial \ln T}\right)_P \tag{50}$$

$$\left(\frac{\partial \ln V}{\partial \ln P}\right)_T = -1 + \left(\frac{\partial \ln n}{\partial \ln P}\right)_T \tag{51}$$

Derivatives with respect to temperature. - The derivatives of n_j and n with respect to temperature are needed to evaluate equations (49) and (50). These may be obtained from differentiation of equations (10), (7), and (3), which gives the following:

$$\left(\frac{\partial \ln n_j}{\partial \ln T}\right)_P - \sum_{i=1}^{l} a_{ij}\left(\frac{\partial \pi_i}{\partial \ln T}\right)_P - \left(\frac{\partial \ln n}{\partial \ln T}\right)_P = \frac{\left(H_T^o\right)_j}{RT} \qquad (j=1, \ldots, m) \tag{52}$$

$$-\sum_{i=1}^{l} a_{ij}\left(\frac{\partial \pi_i}{\partial \ln T}\right)_P = \frac{\left(H_T^o\right)_j}{RT} \qquad (j=m+1, \ldots, n) \tag{53}$$

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$$\sum_{j=1}^{m} a_{kj} n_j \left(\frac{\partial \ln n_j}{\partial \ln T}\right)_P + \sum_{j=m+1}^{n} a_{kj} \left(\frac{\partial n_j}{\partial \ln T}\right)_P = 0 \qquad (k=1, \ldots, \ell) \tag{54}$$

$$\sum_{j=1}^{m} n_j \left(\frac{\partial \ln n_j}{\partial \ln T}\right)_P - n\left(\frac{\partial \ln n}{\partial \ln T}\right)_P = 0 \tag{55}$$

As in the case of the iteration correction equations previously discussed, the derivative equations can be reduced to a much smaller number of simultaneous equations by eliminating $(\partial \ln n_j/\partial \ln T)_P$, obtained from equation (52), from equations (54) and (55). Including equation (53) written with signs reversed, the resulting reduced number of temperature derivative equations are

$$\sum_{i=1}^{\ell} \sum_{j=1}^{m} a_{kj} a_{ij} n_j \left(\frac{\partial \pi_i}{\partial \ln T}\right)_P + \sum_{j=m+1}^{n} a_{kj} \left(\frac{\partial n_j}{\partial \ln T}\right)_P + \sum_{j=1}^{m} a_{kj} n_j \left(\frac{\partial \ln n}{\partial \ln T}\right)_P$$

$$= - \sum_{j=1}^{m} \frac{a_{kj} n_j \left(H_T^o\right)_j}{RT} \qquad (k=1, \ldots, \ell) \tag{56}$$

$$\sum_{i=1}^{\ell} a_{ij} \left(\frac{\partial \pi_i}{\partial \ln T}\right)_P = - \frac{\left(H_T^o\right)_j}{RT} \qquad (j=m+1, \ldots, n) \tag{57}$$

$$\sum_{i=1}^{\ell} \sum_{j=1}^{m} a_{ij} n_j \left(\frac{\partial \pi_i}{\partial \ln T}\right)_P = - \sum_{j=1}^{m} \frac{n_j \left(H_T^o\right)_j}{RT} \tag{58}$$

Equations (56) to (58) are given in table III in a form which simplifies the comparison of derivative equations with the iteration equations in tables I and II. The values of the derivatives obtained from equations (56) to (58) could be used in equation (52) to obtain derivatives for the gaseous species $(\partial \ln n_j/\partial \ln T)_P (j = 1, \ldots, m)$, and all of the temperature derivatives could then be used to evaluate c_p from equation (49). However, there is an alternate and much simpler procedure for obtaining c_p. By substituting $(\partial \ln n_j/\partial \ln T)_P$ obtained from equation (52) into equation (49) and dividing by R, one obtains

$$\frac{c_p}{R} = \sum_{i=1}^{l}\left[\sum_{j=1}^{m} \frac{a_{ij}n_j\left(H_T^o\right)_j}{RT}\right]\left(\frac{\partial \pi_i}{\partial \ln T}\right)_P + \sum_{j=m+1}^{n}\left[\frac{\left(H_T^o\right)_j}{RT}\right]\left(\frac{\partial n_j}{\partial \ln T}\right)_P$$

$$+\left[\sum_{j=1}^{m} \frac{n_j\left(H_T^o\right)_j}{RT}\right]\left(\frac{\partial \ln n}{\partial \ln T}\right)_P + \sum_{j=1}^{n} \frac{n_j\left(C_p^o\right)_j}{R} + \sum_{j=1}^{m} \frac{n_j\left(H_T^o\right)_j^2}{R^2T^2} \tag{59}$$

In equation (59) only the temperature derivatives obtained directly from solution of equations (56) to (58) are required. Furthermore, all the coefficients in equation (59) are exactly the coefficients appearing in the reduced enthalpy equation (27).

Derivatives with respect to pressure. - The derivative $(\partial \ln n/\partial \ln P)_T$ can be obtained in a manner similar to that described for obtaining derivatives with respect to the temperature. Differentiation of equations (10), (7), and (3) gives

$$\left(\frac{\ln n_j}{\partial \ln P}\right)_T - \sum_{i=1}^{l} a_{ij}\left(\frac{\partial \pi_i}{\partial \ln P}\right)_T - \left(\frac{\partial \ln n}{\partial \ln P}\right)_T = -1 \qquad (j=1, \ldots, m) \tag{60}$$

$$-\sum_{i=1}^{l} a_{ij}\left(\frac{\partial \pi_i}{\partial \ln P}\right)_T = 0 \qquad (j=m+1, \ldots, n) \tag{61}$$

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$$\sum_{j=1}^{m} a_{kj} n_j \left(\frac{\partial \ln n_j}{\partial \ln P}\right)_T + \sum_{j=m+1}^{n} a_{kj} \left(\frac{\partial n_j}{\partial \ln P}\right)_T = 0 \qquad (k=1, \ldots, l) \tag{62}$$

$$\sum_{j=1}^{m} n_j \left(\frac{\partial \ln n_j}{\partial \ln P}\right)_T - n\left(\frac{\partial \ln n}{\partial \ln P}\right)_T = 0 \tag{63}$$

Equations (60) to (63) can be reduced to a smaller set by eliminating $(\partial \ln n_j/\partial \ln P)_T$, obtained from equation (60), from equations (62) and (63). When equation (61) written with the sign reversed is included, the results are

$$\sum_{i=1}^{l} \sum_{j=1}^{m} a_{kj} a_{ij} n_j \left(\frac{\partial \pi_i}{\partial \ln P}\right)_T + \sum_{j=m+1}^{n} a_{kj} \left(\frac{\partial n_j}{\partial \ln P}\right)_T + \sum_{j=1}^{m} a_{kj} n_j \left(\frac{\partial \ln n}{\partial \ln P}\right)_T$$

$$= \sum_{j=1}^{m} a_{kj} n_j \qquad (k=1, \ldots, l) \tag{64}$$

$$\sum_{i=1}^{l} a_{ij} \left(\frac{\partial \pi_i}{\partial \ln P}\right)_T = 0 \qquad (j=m+1, \ldots, n) \tag{65}$$

$$\sum_{i=1}^{l} \sum_{j=1}^{m} a_{ij} n_j \left(\frac{\partial \pi_i}{\partial \ln P}\right)_T = \sum_{j=1}^{m} n_j \tag{66}$$

Equations (64) to (66) are given in table IV for comparison with tables I, II, and III. The only derivative obtained from solution of equations (64) to (66) which is used is $(\partial \ln n/\partial \ln P)_T$ (see eq. (51)).

Other Thermodynamic Derivatives

As stated previously, all thermodynamic first derivatives can be expressed in terms of the three thermodynamic first derivatives discussed in the previous sections - namely, c_p, $(\partial \ln V/\partial \ln T)_P$, and $(\partial \ln V/\partial \ln P)_T$ (see Bridgman tables in ref. 10). Velocity of sound a is a frequently used parameter defined by

$$a^2 = \left(\frac{\partial P}{\partial \rho}\right)_S = \frac{P}{\rho}\left(\frac{\partial \ln P}{\partial \ln \rho}\right)_S = -\frac{P}{\rho}\left(\frac{\partial \ln P}{\partial \ln V}\right)_S \tag{67}$$

From Bridgman tables,

$$\left(\frac{\partial \ln P}{\partial \ln V}\right)_S = \frac{c_p}{c_p\left(\frac{\partial \ln V}{\partial \ln P}\right)_T + \frac{PV}{T}\left(\frac{\partial \ln V}{\partial \ln T}\right)_P^2} \tag{68}$$

This may be written as

$$\left(\frac{\partial \ln P}{\partial \ln V}\right)_S = \frac{c_p}{c_v\left(\frac{\partial \ln V}{\partial \ln P}\right)_T} \tag{69}$$

where

$$c_v \equiv \left(\frac{\partial u'}{\partial T}\right)_V = c_p + \frac{\frac{PV}{T}\left(\frac{\partial \ln V}{\partial \ln T}\right)_P^2}{\left(\frac{\partial \ln V}{\partial \ln P}\right)_T} \tag{70}$$

Using the symbols

$$\gamma_S \equiv \left(\frac{\partial \ln P}{\partial \ln \rho}\right)_S \tag{71}$$

and

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$$\gamma \equiv \frac{c_p}{c_v} \tag{72}$$

equation (69) may be written as

$$\gamma_S = \frac{-\gamma}{\left(\frac{\partial \ln V}{\partial \ln P}\right)_T} \tag{73}$$

Using the equation of state given in equation (1), we obtain from equation (67) the familiar expression for velocity of sound

$$a = \sqrt{nRT\gamma_S} \tag{74}$$

It should be noted that γ_S defined by equation (71) is required in equation (74) and not the specific heat ratio γ defined in equation (72).

In the Phase Transitions and Special Derivatives section (p. 28) an alternate expression is derived for γ_S for the special situation of triple phases where the expressions in equations (68), (69), and (73) are no longer valid.

In reference 11 numerous first derivative relations are given that are of interest in rocket performance calculations. One of these relations which will be used in a later section is

$$\left(\frac{\partial \ln P}{\partial \ln T}\right)_S = \frac{c_p}{nR\left(\frac{\partial \ln V}{\partial \ln T}\right)_P} \tag{75}$$

PROCEDURE FOR OBTAINING EQUILIBRIUM COMPOSITIONS

In principle, obtaining equilibrium compositions by means of the Newton-Raphson iteration procedure discussed in a previous section should offer no difficulties. However, there are a number of practical items which require detailed attention in order to avoid numerical difficulties. These items include initial estimates, tests for condensed phases, phase transitions and triple points, convergence, accidental singularities, special handling of ions, and consideration of trace species.

Initial Estimates

An extremely simple procedure is used in this report to assign initial estimates for composition. For the first iteration of the first point, we assign $n = 0.1$. This is equivalent to an estimate of 10 for molecular weight. Then the number of kilogram-moles of each gaseous species per kilogram of mixture is set equal to $0.1/m$, where m is the number of gaseous species being considered. The number of moles of each condensed species is set equal to zero. For HP, SP, UV, and SV problems, an arbitrary initial estimate of $T = 3800$ K is used by the program unless a different estimate is included with other input.

Admittedly, this simple procedure will often give poor initial estimates. However, for a general chemistry program, we find this technique preferable to the alternate of devising numerous special routines for obtaining good estimates for numerous possible chemical systems. Furthermore, the estimating technique is used only for the first point in any schedule of points (see Main Program section, p. 79). For all points after the first, the results of a preceding point serve as initial estimates.

Because no attempt is made to obtain good initial estimates, the question arises whether convergence can be "guaranteed". This is discussed in the next section.

Convergence

The problem of convergence was discussed in references 1 and 3. It was pointed out in reference 3 that the iteration equations sometimes give large corrections, which, if used directly, could lead to divergence. Two situations can cause large corrections. The first situation occurs in the early stages of the calculation and is due to poor estimates. The second may occur at later stages of the calculation when the iteration process sometimes attempts to make extremely large increases in moles of species that are present in trace amounts. An example of this second situation is given in reference 1. In both of these cases a control factor λ is used to restrict the size of the corrections to $\ln n_j (j = 1, \ldots, m)$ and $n_j (j = m + 1, \ldots, n)$ as well as to $\ln n$ and $\ln T$ obtained from solution of equations in tables I and II.

The numerical value of λ is determined on the basis of two empirical rules which experience has shown to be satisfactory. For T, n, and n_j for those gaseous species for which $n_j/n > 10^{-8}$ (or $\ln(n_j/n) > -18.420681$) and for which $\Delta \ln n_j > 0$, a number λ_1 is defined as

$$\lambda_1 = \frac{2}{\max\left(|\Delta \ln T|,\ |\Delta \ln n|,\ |\Delta \ln n_j|\right)} \qquad (j = 1, 2, \ldots, m) \tag{76}$$

This limits the change in T and n and the increase in n_j, for those species whose gas phase mole fraction exceeds 10^{-8}, to a factor $e^2 = 7.3891$.

For those gaseous species for which $\ln(n_j/n) \leq -18.420681$ and $\Delta \ln n_j > 0$, a number λ_2 is defined as

$$\lambda_2 = \min \left| \frac{-\ln\left(\frac{n_j}{n}\right) - 9.2103404}{\Delta \ln n_j - \Delta \ln n} \right| \quad (j = 1, \ldots, m) \tag{77}$$

This prevents a gaseous species with a mole fraction less than 10^{-8} from increasing to more than 10^{-4}. The control factor λ to be used in equation (79) is defined in terms of λ_1 and λ_2 as

$$\lambda = \min(1, \lambda_1, \lambda_2) \tag{78}$$

A value for λ is determined for each iteration. Whenever current estimates of composition and/or temperature are far from their equilibrium values, λ will be less than 1. Whenever they are close to their equilibrium values, λ will equal 1. New estimates for composition and temperature are then obtained from the following correction equations:

$$\ln n_j^{(i+1)} = \ln n_j^{(i)} + \lambda^{(i)}(\Delta \ln n_j)^{(i)} \quad (j = 1, \ldots, m)$$

$$n_j^{(i+1)} = n_j^{(i)} + \lambda^{(i)}(\Delta n_j)^{(i)} \quad (j = m + 1, \ldots, n)$$

$$\ln n^{(i+1)} = \ln n^{(i)} + \lambda^{(i)}(\Delta \ln n)^{(i)}$$

$$\ln T^{(i+1)} = \ln T^{(i)} + \lambda^{(i)}(\Delta \ln T)^{(i)} \tag{79}$$

where the superscript i represents the ith estimate.

The iteration procedure is continued until corrections to composition satisfy the following criteria:

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$$\left.\begin{aligned}
&\frac{n_j\left|\Delta \ln n_j\right|}{\sum_{j=1}^{m} n_j} \le 0.5\times10^{-5} \qquad (j = 1, \ldots, m) \\
&\frac{\left|\Delta n_j\right|}{\sum_{j=1}^{m} n_j} \le 0.5\times10^{-5} \qquad (j = m+1, \ldots, n) \\
&\left|\Delta \ln n\right| \le 0.5\times10^{-5}
\end{aligned}\right\} \tag{80}$$

For a constant entropy problem (SP, SV, or RKT) the following convergence test on entropy is also required

$$\left|\frac{s_o - s}{R}\right| \le 0.5\times10^{-4} \tag{81}$$

The convergence tests in equations (80) and (81) ensure accuracy to five places in composition when expressed as mole fractions.

In literally hundreds of different kinds of problems which have been solved by the CEC71 program, convergence has always been obtained in less than the 35 iterations permitted by the program. For the first point, which starts with arbitrary initial estimates as discussed previously, a typical number of iterations is 8 to 12. For succeeding points, which use compositions of a previously calculated point for initial estimates, a typical number of iterations is 3 to 5. Once in a rare while a problem may be singular and solutions to the correction matrix are then unobtainable. Techniques for handling this situation are discussed in the section Singularities (p. 30).

Tests for Condensed Phases

For the first point in an INPT2 schedule of points, unless INSERT cards are used (see section on NAMELISTS Input (p. 64)), the program considers only gaseous species during iteration to convergence. For each point after the first, the program uses the results of a previous point for its initial estimate. After every convergence, the program automatically checks for the inclusion or elimination of condensed species.

The test is based on the minimization of free energy. At equilibrium, equation (9)

is satisfied (i.e., $\delta G = 0$). The requirement for a condensed species j, which was not previously included as a possible species, to now be included is that its inclusion will decrease free energy (i.e., from eq. (9)):

$$\frac{\partial G}{\partial n_j} = \left(\frac{\mu_j^o}{RT}\right)_c - \sum_{i=1}^{l} \pi_i a_{ij} < 0 \tag{82}$$

The subscript c in equation (82) refers to a condensed species. Equation (82) is identical to the vapor pressure test used in reference 3 when data for the gas phase as well as the condensed phase are available. The vapor pressure test is

$$\left(\frac{\mu_j^o}{RT}\right)_c - \left[\frac{\mu_j^o}{RT} + \ln\left(\frac{n_j P_{atm}}{n}\right)\right]_g < 0 \tag{83}$$

In equation (83) the subscript g refers to the gas phase of the same species as the solid phase referred to by the subscript c. It may be seen that equations (82) and (83) are equivalent from the following. The term $\sum_{i=1}^{l} \pi_i a_{ij}$ in equation (82) is identical for the gas and condensed phases of the same species. From equation (10), this term for the gas phase equals $(\mu_j/RT)_g$ which, using the definition of μ_j in equation (11), leads directly to equation (83). The advantage of equation (82) over (83) is that equation (83) can be used only when the gas phase of the species corresponding to the condensed phase to be tested is present, whereas equation (82) can always be used. The use of equation (82) eliminates the need for the extensive programming required in reference 3 to accommodate $Al_2O_3(s,l)$ for which gas phase data are not available.

At most, only one new condensed species is included after each convergence. In the event that several condensed species pass the test required by equation (82), only that species giving the largest negative change to free energy is included as a possible species and convergence to a new equilibrium composition is obtained. This process is repeated until all condensed species required by equation (82) are included.

If, after convergence, the concentration of a condensed species is negative, the species is removed from the list of currently considered species and convergence to a new equilibrium composition is obtained.

Phase Transitions and Special Derivatives

The calculation method is based on the assumption that condensed phases are pure. Therefore, the possibility exists of encountering phase transition between solid and liquid (melting points) or between two stable solid phases. Such transitions constitute triple points since three phases of the same species coexist, one gaseous and two condensed. Such triple points are characterized by a definite vapor pressure and temperature, independent of the relative proportions of each phase. This is shown by the fact that the iteration equations of table I become singular for an assigned temperature and pressure and the inclusion of two condensed phases of the same species. At a triple point, for a specified system pressure, the relative amounts of the phases can be determined only if either the enthalpy or the entropy is assigned.

The program can obtain equilibrium compositions containing either one or two condensed phases of a species with or without the corresponding gas phase. When temperature is assigned, no problems arise as to which one of two or more condensed phases is to be considered. However, when temperature is a variable, such as in HP, SP, UV, SV, or RKT problems, then several possibilities exist which need to be considered. For example, if a liquid phase is being considered by the program and the temperature at convergence is below the melting point, two possibilities exist. First, the solid phase might be substituted for the liquid phase and a new convergence obtained, or, secondly, both liquid and solid might be considered simultaneously and a new convergence obtained. Similar possibilities exist when convergence is obtained with a solid phase above the melting point. These possibilities and methods of treating them are discussed in detail in reference 3 and the discussion will not be repeated here. In brief, the following criteria are used by the program to determine whether or not to switch one condensed phase of a species to another or whether to consider both simultaneously:

Liquid present at temperature $T < T_m$:

If $T_m - T > 150$ K, switch solid for liquid.

If $T_m - T \leq 150$ K, include solid and liquid.

Solid present at temperature $T > T_m$:

If $T - T_m > 150$ K, switch liquid for solid.

If $T - T_m \leq 150$ K, include liquid with solid.

Similar tests apply for two solid phases of a species. The programming details of switching species are given in figure 4(c).

The unusual situation of constant temperature during an isentropic compression or expansion process can occur when two phases of the same species coexist. The transition temperature remains constant while one phase is being converted to the other. Under this circumstance, derivatives with respect to temperature are not defined. Thus, several of

the derivatives previously discussed, c_p, c_v, and $(\partial \ln V/\partial \ln T)_P$, cannot be obtained in this case. As a consequence, equation (73) cannot be used to obtain γ_S.

In reference 12, the following expression was derived for the situation of constant temperature and entropy:

$$\gamma_{S,T} \equiv \left(\frac{\partial \ln P}{\partial \ln \rho}\right)_{S,T} = -\frac{1}{\left(\frac{\partial \ln V}{\partial \ln P}\right)_T} \tag{84}$$

The velocity of sound for this situation is no longer given by equation (74) but rather by

$$a_{S,T} = \sqrt{nRT\gamma_{S,T}} \tag{85}$$

These derivatives will be used in connection with discontinuities in a rocket throat (see Discontinuities section, p. 38).

Ions

The program is capable of calculating equilibrium properties of plasmas (mixtures containing ionized species) if the plasma is considered ideal. Ideal is here meant to imply that no coulombic interactions are considered. In plasma textbooks, such as reference 13, it is pointed out that effects of coulombic interactions do need to be considered in plasmas (by means of the Debye-Hückel approximation, e.g.). However, very special programming is needed to take care of these effects (such as accounting for ionization potential lowering and partition function cutoff). Therefore, the results of the plasma calculations made with this program will be valid only for those conditions where the ionic density is small so that the coulombic effects are unimportant.

In order for ions to be considered, a charge balance equation is required:

$$\sum_{j=1}^{m} a_{\ell j} n_j = 0 \tag{86}$$

where $a_{\ell j}$ indicates the excess or deficiency of electrons in the ion relative to the neutral species. For example, in a mole of an ionized species, $a_{\ell j} = -3$ for Ar^{+++} and $+1$ for O_2^-.

The section NAMELISTS Input (p. 64) discusses the instruction required by the program to consider ions.

In order to prevent difficulties in matrix solutions, the program automatically removes the charge balance equation when the mole fraction of each ion being considered is less than 10^{-8}.

Singularities

The iteration method used in this report has successfully handled numerous chemical systems under a wide variety of thermodynamic conditions. Nevertheless, special procedures are required to take care of a few rare situations which would otherwise cause the iteration method to fail.

One such situation is a singularity which occurs when two rows of the coefficient matrix are identical. This happens when the ratio of the assigned elements in these two rows is equal to the ratio of the stoichiometric coefficients of these two elements in every gaseous species for which $(n_j/n) > 10^{-8}$ and which contains both elements. That is,

$$\frac{a_{ij}}{a_{kj}} = \frac{b_i^o}{b_k^o} \qquad (j = 1, \ldots, m), \left(\frac{n_j}{n} > 10^{-8}\right) \tag{87}$$

For example, for stoichiometric hydrogen and oxygen at 300 K and P = 1000 newtons per square meter, the only species with $n_j/n > 10^{-8}$ is $H_2O(g)$ and equation (87) applies. Another example is stoichiometric lithium and fluorine at 500 K and P = 101 325 newtons per square meter.

A procedure which usually takes care of this difficulty is to assign values in the input that will make the b_i^o/b_k^o ratio in equation (87) differ from the left side in the 6th or 7th figure. The program does this automatically if an equivalence ratio r = 1.0 is read in by reassigning r = 1.000005. Both of the previous examples are taken care of by this procedure.

However, even if the b_i^o/b_k^o ratio in equation (87) is made to differ from the left side in the 6th or 7th figure, there may be a temporary singularity. This can occur when the iteration procedure temporarily removes some species for which $(n_j/n) < 10^{-8}$ leading temporarily to two identical coefficient rows in the correction matrix. This difficulty is usually remedied by an automatic restart feature in the program. Whenever a singular matrix occurs, the program automatically reinserts the species with $n_j/n < 10^{-8}$ and reassigns them values of $n_j = 10^{-6}$. If, after restart, the iteration procedure still leads

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to a singular matrix, a message is printed and a test is made for another possible cause of singularity.

This singularity occurs if the program is considering several condensed species whose determinant of stoichiometric coefficients is zero. In this case, if two or more of the condensed species are composed of the same chemical elements, the program will remove all of these species except the one with the most negative contribution to the free energy of the mixture based on the test of equation (82). If, after restart, a singular matrix again occurs, a message is printed, any results up to this point are printed, and the program skips to the next problem.

THERMODYNAMIC DATA

Thermodynamic data are included with the program for 62 reactants and 421 reaction species (solid, liquid, and gas phases of a species are counted as separate species). With few exceptions, data are taken from JANAF tables (refs. 8 and 14). Data for the reaction species are reduced to functional form by means of the PAC program (ref. 15).

Assigned Enthalpies

For each species, heats of formation (and, when applicable, heats of transition) were combined with sensible heats to give assigned enthalpies H_T^o. By definition,

$$H_T^o \equiv H_{298.15}^o + \left(H_T^o - H_{298.15}^o\right) \tag{88}$$

We have arbitrarily assumed $H_{298.15}^o = \left(\Delta H_f^o\right)_{298.15}$. Equation (88) then becomes

$$H_T^o = \left(\Delta H_f^o\right)_{298.15} + \left(H_T^o - H_{298.15}^o\right) \tag{89}$$

In general, $H_T^o \neq \left(\Delta H_f^o\right)_T$ for $T \neq 298.15$ K. For reference elements, $\left(\Delta H_f^o\right)_{298.15} = H_{298.15}^o = 0$. For the species included with the program these reference elements are Al(s), Ar(g), B(s) (beta), Be(s), $Br_2(l)$, C(s) (graphite), Cl_2(g), Cs(s), F_2(g), Fe(s), H_2(g), He(g), K(s), Li(s), Mg(s), N_2(g), Na(s), Ne(g), O_2(g), P(s) (red, V), S(s) (rhombic), Si(s), and Xe(g).

Assigned enthalpies for reactants are given in table VII (in cal/mole as required for program input) together with some other reactant data. For cryogenic liquids, assigned

enthalpies are given at their boiling points. These are usually obtained by subtracting the following quantities from the heat of formation of the gas phase at 298.15 K: sensible heat between 298.15 K and the boiling point, difference in enthalpy between ideal gas and real gas at the boiling point, and heat of vaporization at the boiling point.

Least Squares Coefficients

For each reaction species, the thermodynamic functions specific heat, enthalpy, and entropy as functions of temperature are given in the form of least squares coefficients as follows:

$$\frac{C_p^o}{R} = a_1 + a_2T + a_3T^2 + a_4T^3 + a_5T^4 \tag{90}$$

$$\frac{H_T^o}{RT} = a_1 + \frac{a_2}{2}T + \frac{a_3}{3}T^2 + \frac{a_4}{4}T^3 + \frac{a_5}{5}T^4 + \frac{a_6}{T} \tag{91}$$

$$\frac{S_T^o}{R} = a_1 \ln T + a_2T + \frac{a_3}{2}T^2 + \frac{a_4}{3}T^3 + \frac{a_5}{4}T^4 + a_7 \tag{92}$$

For gases, the PAC program (ref. 15) first calculates thermodynamic functions from molecular constant data given in reference 8, and then reduces these functions to coefficient form. For condensed species, the thermodynamic functions are taken directly from reference 8 for reduction to coefficient form. However, for condensed species, we first calculate and include data at the transition points inasmuch as these data are not given in the reference 8 tables. For each species, two sets of coefficients are included for two adjacent temperature intervals, 300 to 1000 K and 1000 to 5000 K. The data have been constrained to be equal at 1000 K. Details on the use of cards or tapes containing the coefficient data are given in section THERMO Data (p. 61). The format and listing of coefficient data are given in appendix D.

CHEMICAL EQUILIBRIUM FOR ASSIGNED THERMODYNAMIC STATES

A thermodynamic state is defined by specifying two state parameters. The following combination of assigned parameters are permitted by the program:

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(1) Temperature and pressure, (T,P)

(2) Enthalpy and pressure, (H,P)

(3) Entropy and pressure, (S,P)

(4) Temperature and volume (or density), (T,V)

(5) Internal energy and volume (or density), (U,V)

(6) Entropy and volume (or density), (S,V)

Some of the problems handled by the program (the TP, HP, SP, TV, UV, SV, and SHOCK problems) use just one combination of assigned states. For example, the TP problem consists of a schedule of one or more assigned temperatures and pressures. The TP problem might be used to construct Mollier diagrams. The HP problem gives constant pressure combustion properties by using an assigned enthalpy equal to that of the reactants and a schedule of one or more pressures. Similarly, the UV problem gives constant volume combustion properties by using an assigned internal energy equal to that of the reactants and a schedule of one or more volumes. The SHOCK problem uses only the (T,P) combination. In appendix E (p. 197), case 950 illustrates a TP problem, case 1565 illustrates a UV problem, and case 123 illustrates an HP problem. On the other hand, some of the application problems discussed in succeeding sections make use of more than one combination of assigned thermodynamic states. For example, the rocket problem uses (H,P) or (T,P) and also (S,P) and the detonation problem uses (H,P) and (T,P).

ROCKET PERFORMANCE

The program provides routines for the calculation of theoretical rocket performance for both equilibrium and frozen composition during expansion. Combustion and throat parameters are always calculated while exit conditions are assigned optionally either as pressure ratios, area ratios, or both. The section DESCRIPTION OF PROGRAM INPUT describes in detail the various options which are permitted for this problem. Examples of rocket performance problems in the OUTPUT section are cases 51, 122, 679, and 5612.

Assumptions

The calculation of various performance parameters are based on the following assumptions: one-dimensional form of the continuity, energy, and momentum equations; zero velocity in the combustion chamber; complete combustion; adiabatic combustion;

isentropic expansion; homogeneous mixing; ideal gas law; and zero temperature and velocity lags between condensed and gaseous species. For equilibrium performance, composition is assumed to attain equilibrium instantaneously during expansion. For frozen performance, composition is assumed to remain fixed at the combustion composition during expansion.

Parameters

Conservation equations. - Rocket performance, as well as other fluid dynamic problems in the program, is based on the following conservation equations:
Continuity:

$$\rho_2 A_2 u_2 = \rho_1 A_1 u_1 \tag{93}$$

Momentum:

$$P_2 + \rho_2 u_2^2 = P_1 + \rho_1 u_1^2 \tag{94}$$

Energy:

$$h_2 + \frac{u_2^2}{2} = h_1 + \frac{u_1^2}{2} \tag{95}$$

Equation (93) describes the condition of constant mass flow rate which will be given the symbol $\dot{m}$ - that is,

$$\dot{m} = \rho A u \tag{96}$$

Velocity of flow. - Using subscripts c and e instead of 1 and 2 in equation (95) and assuming the velocity in the combustion chamber to be negligible give equation (95) as

$$u_e = \sqrt{2(h_c - h_e)} \tag{97}$$

When h is in units of joules per kilogram, u is in units of meters per second.

Force. - From the momentum principle of fluid mechanics, the external force on a body in a steadily flowing fluid is due to the change of momentum of the fluid and to in-

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crease in pressure forces acting on the body. For rocket applications, this is expressed as

$$F = \frac{\dot{m}u_e}{g_c} + (P_e - P_a)A_e \tag{98}$$

The conversion factor g_c has been introduced to allow for various units. For some commonly used systems of units, such as the cgs system or International System (ref. 7), $g_c = 1$. However, in the English Technical System, commonly used by engineers,

$$g_c = 32.1740 \frac{(\text{lb mass})}{(\text{lb force})} \left(\frac{\text{ft}}{\text{sec}^2}\right)$$

Specific impulse. - Specific impulse is defined as force per unit mass flow rate. From equation (98)

$$I = \frac{F}{\dot{m}} = \frac{u_e}{g_c} + \frac{(P_e - P_a)A_e}{\dot{m}} \tag{99}$$

In rocket literature, specific impulse is usually expressed in English engineering units of pounds force per (pound mass per second). However, for those systems of units previously mentioned for which $g_c = 1$, I is both dimensionally and numerically equal to velocity.

In this report, when the exit pressure is equal to the ambient pressure, specific impulse will be given the symbol I_{sp} - that is,

$$I_{sp} = \frac{u_e}{g_c} \tag{100}$$

When the ambient pressure is assumed to be zero (vacuum conditions), specific impulse will be given the symbol I_{vac} - that is,

$$I_{vac} = I_{sp} + \frac{P_e A_e}{\dot{m}} \tag{101}$$

Mach number. - Mach number is defined as the ratio of velocity of flow to velocity of sound:

$$\mathcal{M} = \frac{u}{a} \tag{102}$$

Velocity of flow is given by equation (97). Velocity of sound is given by equation (74) (or eq. (85)).

Characteristic velocity. - This parameter is given the symbol c^* and is defined as

$$c^* = \frac{P_c A_t g_c}{\dot{m}} \tag{103}$$

Area per unit mass flow rate. - From equation (96)

$$\frac{A}{\dot{m}} = \frac{1}{\rho u} \tag{104}$$

The terms ρ and u are obtained from equations (1) and (97), respectively.

Coefficient of thrust. - This parameter is defined in terms of previously defined parameters

$$C_F = \frac{u}{c^*} \tag{105}$$

Area ratio. - The ratio of area at any exit nozzle station to area at the throat is obtained from the values of equation (104) at these two points

$$\frac{A_e}{A_t} = \frac{(A/\dot{m})_e}{(A/\dot{m})_t} \tag{106}$$

Procedure for Obtaining Equilibrium Rocket Performance

Rocket performance is obtained by first determining combustion properties in the rocket chamber and then determining exhaust properties at various stations in the nozzle exit including the throat.

Combustion conditions. - Combustion temperature and equilibrium compositions are obtained by the program for an assigned chamber pressure and the reactant enthalpy (in the program HP = .TRUE.). From the combustion compositions and temperature the combustion entropy s_c and other combustion properties are determined.

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Exit conditions. - Exit conditions may be desired for assigned pressure ratios or area ratios. Throat conditions, however, are always determined by the program after combustion conditions are completed and before any assigned pressure ratios or other assigned area ratios are considered. Isentropic expansion is assumed.

For an assigned pressure ratio, equilibrium compositions and exit temperature are determined for the pressure P corresponding to the assigned pressure ratio and for the combustion entropy s_c (in the program, SP = .TRUE.). For throat and other assigned area ratios, iteration procedures are used to determine the correct pressure ratios. These procedures are described in the following sections.

After equilibrium compositions and temperature are obtained for an assigned pressure ratio or area ratio, all the rocket parameters given in the previous section may be determined.

Throat conditions. - Throat conditions may be determined by locating the pressure ratio for which area ratio is a minimum or, equivalently, for which velocity of flow is equal to the velocity of sound. The second procedure is used in this report. This pressure ratio is determined by iteration.

The initial estimate for the pressure ratio at the throat is obtained from

$$\frac{P_c}{P_t} = \left(\frac{\gamma_S + 1}{2}\right)^{\gamma_S/(\gamma_S - 1)} \tag{107}$$

The program uses the value of γ_S from the combustion point.

Equilibrium properties for the P_t from equation (107) and for s_c are obtained as for any exit point. From these properties, u^2 and a^2 are calculated and the following test for convergence is made:

$$\left|\frac{u^2 - a^2}{u^2}\right| < 0.4\times10^{-4} \tag{108}$$

This criterion is equivalent to ensuring that, at the throat, the Mach number is within the value of $1\pm0.2\times10^{-4}$.

If the convergence test is not met, an improved estimate of the throat pressure ratio is obtained from the following iteration formula:

$$\left(\frac{P_c}{P_t}\right)_{k+1} = \frac{\left(\frac{P_c}{P_t}\right)_k}{1 + \left[\frac{u^2 - a^2}{(\lambda_S + 1)nRT}\right]_k} \tag{109}$$

A maximum of four iterations on throat pressure ratio is permitted. Usually, no more than two are required.

Discontinuities. - A special procedure for obtaining throat conditions when velocity of sound is discontinuous is given in reference 12. The three steps in this procedure are summarized here for completeness. Steps 1 and 2 are used for all throat calculations while step 3 is used only for the special case of discontinuities at the throat. Case 5612 in appendix E illustrates this particular kind of problem.

Step 1. Obtain an initial estimate of throat pressure ratio by means of equation (107). For the first chamber pressure in case 5612 this gives $P_c/P_t = 1.7469$. The temperature for this estimate is 2820 K (the melting point of BeO) with liquid and solid BeO both present.

Step 2. Obtain a second estimate of throat pressure ratio by means of equation (109). For case 5612, this gives $P_c/P_t = 1.6161$. The temperature for this estimate is 2846 K which is above the melting point with no BeO(s) present. The sequence of steps 1 and 2 (namely, liquid and solid at one estimate of throat pressure ratio and liquid only at the next estimate) indicates that discontinuities exist at the throat. In this event proceed with step 3. Otherwise, continue with the usual procedure of using equation (109) until convergence.

Step 3. Estimate the pressure ratio at the melting point where the solid phase just begins to appear by means of

$$\ln P_t = \ln P + \left(\frac{\partial \ln P}{\partial \ln T}\right)_S (\ln T_m - \ln T) \tag{110}$$

where the derivative is given by equation (75). The values for the right side of equation (110) are for the point in step 2.

In case 5612, equation (110) gave $P_c/P_t = 1.7282$ for which the mole fraction of BeO(s) equaled 0,00005. The correct value for which the mole fraction of BeO(s) is zero is $P_c/P_t = 1.7277$ so that the error in P_c/P_t using equation (110) is 0.0005 (0.03 percent). In the example in reference 12, the error is even less.

Assigned subsonic or supersonic area ratios. - In previous programs (ref. 4), conditions for assigned area ratios were obtained by interpolation of data generated for a

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somewhat arbitrary schedule of assigned pressure ratios. In the present program, an iteration scheme is used to obtain the pressure ratios corresponding to the assigned area ratios.

We generally use empirical formulas that we obtained from fitting data to give initial estimates for the pressure ratios. However, for supersonic area ratios greater than 2, if the previous point were also for a supersonic area ratio greater than 2, an analytic expression is used to obtain the initial estimate. The same analytic expression is also used in all cases to obtain improved estimates for the pressure ratios.

Empirical formulas for initial estimates of P_c/P_e. - Initial estimates of pressure ratios corresponding to subsonic area ratios are obtained from the following empirical formulas:

$$\ln \frac{P_c}{P_e} = \frac{\ln \frac{P_c}{P_t}}{\frac{A_e}{A_t} + 10.587\left(\ln \frac{A_e}{A_t}\right)^3 + 9.454 \ln \frac{A_e}{A_t}} \qquad \frac{A_e}{A_t} \geq 1.09 \tag{111}$$

and

$$\ln \frac{P_c}{P_e} = \frac{0.9 \ln \frac{P_c}{P_t}}{\frac{A_e}{A_t} + 10.587\left(\ln \frac{A_e}{A_t}\right)^3 + 9.454 \ln \frac{A_e}{A_t}} \qquad 1.0001 < \frac{A_e}{A_t} < 1.09 \tag{112}$$

When an assigned supersonic area ratio requires an initial estimate of pressure ratio to be obtained from an empirical formula, the following formulas are used:

$$\ln \frac{P_c}{P_e} = \ln \frac{P_c}{P_t} + \sqrt{3.294\left(\ln \frac{A_e}{A_t}\right)^2 + 1.535 \ln \frac{A_e}{A_t}} \qquad 1.0001 < \frac{A_e}{A_t} < 2 \tag{113}$$

and

$$\ln \frac{P_c}{P_e} = \gamma_S + 1.4 \ln \frac{A_e}{A_t} \qquad \frac{A_e}{A_t} \geq 2 \tag{114}$$

In equation (114), the value of γ_S is that determined for throat conditions. The equilibrium properties which are obtained for the initial and each subsequently improved estimate of P_c/P_e are used in the following two equations to obtain the improved estimates of P_c/P_e.

Analytic expression for improved estimates of P_c/P_e. - From table I of reference 11, the following derivative may be obtained:

$$\left(\frac{\partial \ln \frac{P_c}{P_e}}{\partial \ln \frac{A_e}{A_t}}\right)_S = \frac{1}{\left[\frac{1}{\gamma_S} - \frac{nRT}{2(h_c - h)}\right]} = \frac{\gamma_S u^2}{u^2 - a^2} \tag{115}$$

This derivative is used in the following correction formula to obtain an improved estimate for P_c/P_e:

$$\left(\ln \frac{P_c}{P_e}\right)_{k+1} = \left(\ln \frac{P_c}{P_e}\right)_k + \left[\left(\frac{\partial \ln \frac{P_c}{P_e}}{\partial \ln \frac{A_e}{A_t}}\right)_S\right]_k \left[\ln \frac{A_e}{A_t} - \left(\ln \frac{A_e}{A_t}\right)_k\right] \tag{116}$$

where the subscript k refers to the kth estimate.

The iteration procedure is continued until

$$\left|\left(\ln \frac{P_c}{P_e}\right)_{k+1} - \left(\ln \frac{P_c}{P_e}\right)_k\right| < 0.00004 \tag{117}$$

with a maximum of 10 iterations permitted. Generally, convergence is reached within two to four iterations.

Procedure for Obtaining Frozen Rocket Performance

The procedure for obtaining rocket performance assuming composition is frozen

(infinitely slow reaction rates) during expansion is simpler than for that assuming equilibrium composition. This is due to the fact that equilibrium compositions need to be determined only for combustion conditions. After obtaining combustion conditions in the identical way described for equilibrium rocket performance, the remainder of the procedure is as follows.

Exit conditions. - Improved estimates of the exit temperature corresponding to some assigned P_c/P_e are obtained by means of the following iteration formulas:

$$\left(\ln T_e\right)_{k+1} = \left(\ln T_e\right)_k + \left(\Delta \ln T_e\right)_k \tag{118}$$

where

$$\left(\Delta \ln T_e\right)_k = \frac{s_c - \left(s_e\right)_k}{\left(c_p\right)_{e,k}} \tag{119}$$

and where k refers to the kth estimate. The initial estimate of an exit temperature is the value of temperature for the preceding point. The iteration procedure is continued until

$$\left|\Delta \ln T_e\right| < 0.5\times10^{-4} \tag{120}$$

The maximum number of iterations permitted by the program is eight although the convergence criterion of equation (120) is generally reached in two to four iterations.

Phases are also considered to be frozen. Therefore, the program will calculate frozen rocket performance for assigned schedules of pressure and/or area ratios only until an exit temperature is reached that is 50 K below the transition temperature of any condensed species present at the combustion point. If a calculated exit temperature is more than 50 K below the transition temperature, this point and all subsequent points in the schedule are ignored by the program and do not appear in the output. In addition, the following message is printed: CALCULATIONS WERE STOPPED BECAUSE NEXT POINT IS MORE THAN 50 DEG BELOW TEMP RANGE OF A CONDENSED SPECIES.

After an exit temperature has been determined, all the rocket performance parameters, given in a previous section, can be determined.

Throat conditions. - Calculations for frozen throat conditions are similar to those discussed for equilibrium conditions. That is, equation (107) is used to get initial estimates for P_c/P_t, equation (109) is used to get improved estimates for P_c/P_t, and equation (108) is used as the convergence criterion. With composition and phases frozen,

there is no possibility of discontinuities at the throat as in the case of equilibrium compositions.

Thermodynamic derivatives for frozen composition. - The thermodynamic derivatives discussed in previous sections were based on the assumption that, in any thermodynamic process from one condition to another, composition reaches its equilibrium values instantaneously. If, on the other hand, reaction times are assumed to be infinitely slow, composition remains fixed (frozen). In this event, expressions for derivatives become simpler (see refs. 1 and 6 for further discussion). Some derivatives, based on frozen composition, are as follows:

From equations (49), (50), and (51), respectively,

$$c_p = \sum_{j=1}^{n} n_j \left(C_p^o\right)_j \tag{121}$$

$$\left(\frac{\partial \ln V}{\partial \ln T}\right)_P = 1 \tag{122}$$

$$\left(\frac{\partial \ln V}{\partial \ln P}\right)_T = -1 \tag{123}$$

From equation (70),

$$c_v = c_p - nR \tag{124}$$

From equations (73) and (123), it is clear that for frozen composition $\gamma_S = \gamma$.

INCIDENT AND REFLECTED SHOCKS

The solution to the conservation equations which describe conditions for incident and reflected shocks is most conveniently obtained in terms of assigned temperature before and after shock. Therefore, theoretical values for shock parameters such as velocities and gas compositions are generally found tabulated as functions of assigned temperatures (or temperature ratios). However, in shock tube experiments, shock velocities are generally known, rather than temperature ratios, thus requiring interpolation for purposes of comparison. It is therefore useful to have a calculating scheme which calculates shock properties in terms of assigned velocities, and that is the scheme used in this report. Case 52 is an example of a typical shock problem.

No consistent nomenclature has been found in the literature for shock parameters. For example, in reference 16, u is the velocity of the gases relative to the velocity of the shock front w, and v is the actual velocity of the gases in the shock tube. In reference 17, however, the converse is given. We will use essentially the nomenclature of reference 16.

Figure II.6 in reference 16 shows the usual incident and reflected conditions in both laboratory- and shock-fixed coordinates. Velocities may be expressed as

$$\vec{u} = \vec{v} - \vec{w} = \vec{v} + \vec{w} \quad \text{or} \quad \vec{u} = \vec{w} - \vec{v} \tag{125}$$

For incident shock waves, equation (125) gives

$$\vec{u}_1 = \vec{w}_S - \vec{v}_1 = \vec{w}_S \tag{126}$$

and

$$\vec{u}_2 = \vec{w}_S - \vec{v}_2 \tag{127}$$

In equation (126) it is assumed that the test gas is at rest ($\vec{v}_1 = 0$). For reflected waves, equation (125) gives

$$\vec{u}_2^* = \vec{v}_2 + \vec{w}_R \tag{128}$$

and

$$\vec{u}_5 = \vec{v}_5 + \vec{w}_R = \vec{w}_R \tag{129}$$

In equation (129) it is assumed that the shocked gases at the end of the shock tube are brought to rest ($\vec{v}_5 = 0$). The asterisk is used with $\vec{u}_2^*$ in equation (128) to differentiate it from $\vec{u}_2$ in equation (127). The gas properties are the same for condition 2 but the relative velocities are different. All quantities that appear in equations (126) to (129) are positive and henceforth the arrows will be dropped.

Incident Shocks

The conservation equations describing incident conditions are exactly those given by equations (93) to (95) with area assumed to be constant ($A_1 = A_2$). For iterative purposes, it is convenient to reduce these equations to a form similar to that given in reference 18 as follows:

$$\frac{P_2}{P_1} = 1 - \left(\frac{\rho_1 u_1^2}{P_1}\right)\left(\frac{\rho_1}{\rho_2} - 1\right) \tag{130}$$

$$h_2 = h_1 + \left(\frac{u_1^2}{2}\right)\left[1 - \left(\frac{\rho_1}{\rho_2}\right)^2\right] \tag{131}$$

It will also be convenient to use the symbols P^* and h^* for the right sides of equations (130) and (131), respectively. These equations then become

$$P^* - \frac{P_2}{P_1} = 0 \tag{132}$$

$$h^* - h_2 = 0 \tag{133}$$

In equation (133), h_2 is defined by means of equation (14).

Iteration equations. - Applying the Newton-Raphson method to equations (132) and (133) divided by R and using for the independent variables the logarithm of temperature ratio and pressure ratio across the shock give

$$\frac{\partial\left(P^* - \frac{P_2}{P_1}\right)}{\partial \ln\left(\frac{P_2}{P_1}\right)} \Delta \ln \frac{P_2}{P_1} + \frac{\partial\left(P^* - \frac{P_2}{P_1}\right)}{\partial \ln\left(\frac{T_2}{T_1}\right)} \Delta \ln \frac{T_2}{T_1} = \frac{P_2}{P_1} - P^* \tag{134}$$

$$\frac{\partial\left[\frac{(h^* - h_2)}{R}\right]}{\partial \ln\left(\frac{P_2}{P_1}\right)} \Delta \ln \frac{P_2}{P_1} + \frac{\partial\left[\frac{(h^* - h_2)}{R}\right]}{\partial \ln\left(\frac{T_2}{T_1}\right)} \Delta \ln \frac{T_2}{T_1} = \frac{h_2 - h^*}{R} \tag{135}$$

where

$$\left.\begin{aligned}\left(\Delta \ln \frac{P_2}{P_1}\right)_k &= \ln\left(\frac{P_2}{P_1}\right)_{k+1} - \ln\left(\frac{P_2}{P_1}\right)_k \\ \left(\Delta \ln \frac{T_2}{T_1}\right)_k &= \ln\left(\frac{T_2}{T_1}\right)_{k+1} - \ln\left(\frac{T_2}{T_1}\right)_k\end{aligned}\right\} \tag{136}$$

and the subscript k stands for the kth iteration.

The partial derivatives and right sides in equations (134) and (135) are given as follows:

$$\frac{\partial\left(P^* - \frac{P_2}{P_1}\right)}{\partial \ln\left(\frac{P_2}{P_1}\right)} = -\left(\frac{\rho_1}{\rho_2}\right)\left(\frac{M_1 u_1^2}{RT_1}\right)\left(\frac{\partial \ln V}{\partial \ln P}\right)_{T,2} - \frac{P_2}{P_1} \tag{137}$$

$$\frac{\partial\left(P^* - \frac{P_2}{P_1}\right)}{\partial \ln\left(\frac{T_2}{T_1}\right)} = -\left(\frac{\rho_1}{\rho_2}\right)\left(\frac{M_1 u_1^2}{RT_1}\right)\left(\frac{\partial \ln V}{\partial \ln T}\right)_{P,2} \tag{138}$$

$$\frac{P_2}{P_1} - P^* = \frac{P_2}{P_1} - 1 + \left(\frac{M_1 u_1^2}{RT_1}\right)\left(\frac{\rho_1}{\rho_2} - 1\right) \tag{139}$$

$$\frac{\partial\left[\frac{(h^* - h_2)}{R}\right]}{\partial \ln\left(\frac{P_2}{P_1}\right)} = -\frac{u_1^2}{R}\left(\frac{\rho_1}{\rho_2}\right)^2\left(\frac{\partial \ln V}{\partial \ln P}\right)_{T,2} + \frac{T_2}{M_2}\left[\left(\frac{\partial \ln V}{\partial \ln T}\right)_{P,2} - 1\right] \tag{140}$$

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$$\frac{\partial\left[\frac{(h^* - h_2)}{R}\right]}{\partial \ln\left(\frac{T_2}{T_1}\right)} = -\left(\frac{u_1^2}{R}\right)\left(\frac{\rho_1}{\rho_2}\right)^2\left(\frac{\partial \ln V}{\partial \ln T}\right)_{P,2} - \frac{T_2(c_p)_2}{R} \tag{141}$$

$$\frac{h_2 - h^*}{R} = \frac{h_2 - h_1}{R} - \left(\frac{u_1^2}{2R}\right)\left[1 - \left(\frac{\rho_1}{\rho_2}\right)^2\right] \tag{142}$$

where, from equations (1) and (2),

$$\frac{\rho_1}{\rho_2} = \left(\frac{P_1}{P_2}\right)\left(\frac{M_1}{M_2}\right)\left(\frac{T_2}{T_1}\right) \tag{143}$$

Corrections and convergence. - An arbitrary control factor λ is applied to the corrections obtained from solution of equations (134) and (135) before using the corrections in equation (136) to obtain improved estimates. This control factor permits a maximum correction of 1.5 of the previous estimates of P_2/P_1 and T_2/T_1. This is the same as permitting a maximum absolute correction of 0.4054652 on $\ln P_2/P_1$ and $\ln T_2/T_1$. The control factor λ is obtained by means of the following equations:

$$\lambda_3 = \frac{0.4054652}{\left|\Delta \ln\left(\frac{P_2}{P_1}\right)\right|} \tag{144}$$

$$\lambda_4 = \frac{0.4054652}{\left|\Delta \ln\left(\frac{T_2}{T_1}\right)\right|} \tag{145}$$

$$\lambda = \min(\lambda_3, \lambda_4, 1) \tag{146}$$

Improved estimates are then obtained by using equation (146) with equation (136) to give

$$\left.\begin{aligned} \ln\left(\frac{P_2}{P_1}\right)_{k+1} &= \ln\left(\frac{P_2}{P_1}\right)_k + \lambda\left[\Delta \ln\left(\frac{P_2}{P_1}\right)\right]_k \\ \ln\left(\frac{T_2}{T_1}\right)_{k+1} &= \ln\left(\frac{T_2}{T_1}\right)_k + \lambda\left[\Delta \ln\left(\frac{T_2}{T_1}\right)\right]_k \end{aligned}\right\} \tag{147}$$

The iteration process is continued until corrections obtained from equations (134) and (135) meet the following criteria:

$$\left.\begin{aligned} \left|\Delta \ln\left(\frac{P_2}{P_1}\right)\right| &< 0.00005 \\ \left|\Delta \ln\left(\frac{T_2}{T_1}\right)\right| &< 0.00005 \end{aligned}\right\} \tag{148}$$

A maximum number of eight iterations is permitted by the program. Convergence is generally reached in three to five iterations.

Initial estimates of T_2/T_1 and P_2/P_1. - Formulas for temperature ratio and pressure ratio across the incident shock, assuming constant γ, may be found in texts such as reference 16. These formulas, slightly rearranged, are

$$\frac{P_2}{P_1} = \frac{\left(2\gamma_1 \mathcal{M}_1^2 - \gamma_1 + 1\right)}{(\gamma_1 + 1)} \tag{149}$$

$$\frac{T_2}{T_1} = \left(\frac{P_2}{P_1}\right)\frac{\left(\frac{2}{\mathcal{M}_1^2} + \gamma_1 - 1\right)}{(\gamma_1 + 1)} \tag{150}$$

If γ is constant over the temperature range of T_1 to T_2, then equations (149) and (150) give exact theoretical values for P_2/P_1 and T_2/T_1. However, if γ varies, then

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equations (149) and (150) give first estimates which vary from poor to excellent. If composition is assumed frozen across the incident shock, then equations (149) and (150) generally give excellent first estimates. Improved estimates are then obtained as described in the previous sections. However, if equilibrium composition is assumed across the shock then equation (150) generally gives estimates of temperature ratio that are too high. An empirical correction factor is therefore used to obtain better first estimates. If equilibrium composition is to be assumed and equation (150) gives a value of T_2/T_1 which makes $T_2 > 2000$ K, then the initial estimate of T_2/T_1 is taken to be

$$\frac{T_2}{T_1} = 0.7\,\frac{T_2}{T_1}\,(\text{from eq. (150)}) + \frac{600}{T_1} \tag{151}$$

If T_2 from equation (150) is greater than 2000 K, equation (151) lowers this estimate by three-tenths of the difference of T_2 from 2000 K.

Reflected Shocks

The reflected shock conservation equations could be written in a manner similar to equations (93) to (95); however, it is more convenient to use the relations in equations (128) and (129) which give

$$\rho_5 w_R = \rho_2(v_2 + w_R) \tag{152}$$

$$P_5 + \rho_5 w_R^2 = P_2 + \rho_2\left(v_2 + w_R\right)^2 \tag{153}$$

$$h_5 + \frac{1}{2} w_R^2 = h_2 + \frac{1}{2}\left(v_2 + w_R\right)^2 \tag{154}$$

For iterative purposes, it is convenient to reduce equations (152) to (154) to a form similar to equations (130) and (131) as follows:

$$\frac{P_5}{P_2} = 1 + \left(\frac{\rho_2 v_2^2}{P_2}\right)\left[\frac{\left(\frac{\rho_5}{\rho_2}\right)}{\left(\frac{\rho_5}{\rho_2} - 1\right)}\right] \tag{155}$$

$$h_5 = h_2 + \left(\frac{v_2^2}{2}\right)\left[1 + \frac{2}{\left(\frac{\rho_5}{\rho_2} - 1\right)}\right] \tag{156}$$

For convenience, the right sides of equations (155) and (156) will be given the symbols P' and h'. The reflected shock parameters may now be solved by the simultaneous solution of

$$P' - \frac{P_5}{P_2} = 0 \tag{157}$$

$$h' - h_5 = 0 \tag{158}$$

Iteration equations. - Applying the Newton-Raphson method to equation (157) and to equation (158) divided by R and using for independent variables the logarithm of temperature ratio and pressure ratio across the shock give

$$\frac{\partial\left(P' - \frac{P_5}{P_2}\right)}{\partial \ln\left(\frac{P_5}{P_2}\right)} \Delta \ln \frac{P_5}{P_2} + \frac{\partial\left(P' - \frac{P_5}{P_2}\right)}{\partial \ln\left(\frac{T_5}{T_2}\right)} \Delta \ln \frac{T_5}{T_2} = \frac{P_5}{P_2} - P' \tag{159}$$

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$$\frac{\partial\left[\frac{(h' - h_5)}{R}\right]}{\partial \ln\left(\frac{P_5}{P_2}\right)} \Delta \ln \frac{P_5}{P_2} + \frac{\partial\left[\frac{(h' - h_5)}{R}\right]}{\partial \ln\left(\frac{T_5}{T_2}\right)} \Delta \ln \frac{T_5}{T_2} = \frac{h_5 - h'}{R} \tag{160}$$

where

$$\left(\Delta \ln \frac{P_5}{P_2}\right)_k = \ln\left(\frac{P_5}{P_2}\right)_{k+1} - \ln\left(\frac{P_5}{P_2}\right)_k \tag{161}$$

$$\left(\Delta \ln \frac{T_5}{T_2}\right)_k = \ln\left(\frac{T_5}{T_2}\right)_{k+1} - \ln\left(\frac{T_5}{T_2}\right)_k \tag{162}$$

The partial derivatives and right sides for equations (159) and (160) are given as follows:

$$\frac{\partial\left(P' - \frac{P_5}{P_2}\right)}{\partial \ln\left(\frac{P_5}{P_2}\right)} = \left(\frac{M_2 v_2^2}{RT_2}\right) \frac{\left(\frac{\rho_5}{\rho_2}\right)}{\left(\frac{\rho_5}{\rho_2} - 1\right)^2} \left(\frac{\partial \ln V}{\partial \ln P}\right)_{T,5} - \frac{P_5}{P_2} \tag{163}$$

$$\frac{\partial\left(P' - \frac{P_5}{P_2}\right)}{\partial \ln\left(\frac{T_5}{T_2}\right)} = \left(\frac{M_2 v_2^2}{RT_2}\right) \frac{\left(\frac{\rho_5}{\rho_2}\right)}{\left(\frac{\rho_5}{\rho_2} - 1\right)^2} \left(\frac{\partial \ln V}{\partial \ln T}\right)_{P,5} \tag{164}$$

$$\frac{P_5}{P_2} - P' = \frac{P_5}{P_2} - 1 - \left(\frac{M_2 v_2^2}{RT_2}\right)\left(\frac{\frac{\rho_5}{\rho_2}}{\frac{\rho_5}{\rho_2} - 1}\right) \tag{165}$$

$$\frac{\partial\left[\frac{(h' - h_5)}{R}\right]}{\partial \ln\left(\frac{P_5}{P_2}\right)} = \frac{v_2^2}{R} \frac{\left(\frac{\rho_5}{\rho_2}\right)}{\left(\frac{\rho_5}{\rho_2} - 1\right)^2} \left(\frac{\partial \ln V}{\partial \ln P}\right)_{T,5} + \frac{T_5}{M_5}\left[\left(\frac{\partial \ln V}{\partial \ln T}\right)_{P,5} - 1\right] \tag{166}$$

$$\frac{\partial\left[\frac{(h' - h_5)}{R}\right]}{\partial \ln\left(\frac{T_5}{T_2}\right)} = \frac{v_2^2}{R} \frac{\left(\frac{\rho_5}{\rho_2}\right)}{\left(\frac{\rho_5}{\rho_2} - 1\right)^2} \left(\frac{\partial \ln V}{\partial \ln T}\right)_{P,5} - \frac{T_5\left(c_p\right)_5}{R} \tag{167}$$

$$\frac{h_5 - h'}{R} = \frac{h_5 - h_2}{R} - \frac{v_2^2}{2R}\left(\frac{\frac{\rho_5}{\rho_2} + 1}{\frac{\rho_5}{\rho_2} - 1}\right) \tag{168}$$

Corrections and convergence. - The same control factors, correction equations, and tests for convergence discussed in the previous section for $\ln P_2/P_1$ and $\ln T_2/T_1$ (eqs. (144) to (148)) are applicable for $\ln P_5/P_2$ and $\ln T_5/T_2$.

Initial estimates of T_5/T_2 and P_5/P_2. - A value of $T_5/T_2 = 2$ is generally a satisfactory initial estimate. An estimate for P_5/P_2 in terms of T_5/T_2 may be obtained from inverting equation (2.36) in reference 16. For $T_5/T_2 = 2$ this gives

$$\left(\frac{P_5}{P_2}\right)^2 - \left(\frac{\gamma_S + 1}{\gamma_S - 1}\right)\left(\frac{P_5}{P_2}\right) - 2 = 0 \tag{169}$$

Only one solution of equation (169) is positive.

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CHAPMAN-JOUGUET DETONATIONS

The method used for obtaining Chapman-Jouguet detonation parameters is described in reference 18. There are three steps in the calculation procedure. The first step consists in obtaining an initial estimate of the detonation pressure and temperature. The second step is an improved estimate of these parameters by means of a recursion formula. The third step is obtaining the correct values by means of a Newton-Raphson iteration procedure. The derivation of the required equations is given in reference 18 and they are summarized here for convenience in slightly modified form.

The same conservation equations (93) to (95) for continuity, momentum, and energy

that apply for shock also apply here with the additional constraint that $u_2 = a_2$. For iterative purposes, as was true for the shock equations, it is convenient to reduce the three conservation equations to the following two:

$$\frac{P_1}{P_2} = 1 - (\gamma_{S,2})\left(\frac{\rho_2}{\rho_1} - 1\right) \tag{170}$$

$$h_2 = h_1 + \left(\frac{R\gamma_{S,2}T_2}{2M_2}\right)\left[\left(\frac{\rho_2}{\rho_1}\right)^2 - 1\right] \tag{171}$$

The pressure ratio in equation (170) is the reciprocal of the pressure ratio in equation (130) because, as pointed out in reference 18, the Newton-Raphson iteration encounters fewer problems in the form of equation (170).

For convenience in writing the iteration equations the symbols P'' and h'' will be used to represent the right sides of equations (170) and (171), respectively. These equations then become

$$P'' - \frac{P_1}{P_2} = 0 \tag{172}$$

$$h'' - h_2 = 0 \tag{173}$$

Iteration Equations

Applying the Newton-Raphson method to equation (172) and (173) divided by R and using for independent variables the logarithm of temperature ratio and pressure ratio across the detonation gives

$$\frac{\partial\left(P'' - \frac{P_1}{P_2}\right)}{\partial \ln\left(\frac{P_2}{P_1}\right)} \Delta \ln \frac{P_2}{P_1} + \frac{\partial\left(P'' - \frac{P_1}{P_2}\right)}{\partial \ln\left(\frac{T_2}{T_1}\right)} \Delta \ln \frac{T_2}{T_1} = \frac{P_1}{P_2} - P'' \tag{174}$$

$$\frac{\partial\left[\frac{(h'' - h_2)}{R}\right]}{\partial \ln\left(\frac{P_2}{P_1}\right)} \Delta \ln \frac{P_2}{P_1} + \frac{\partial\left[\frac{(h'' - h_2)}{R}\right]}{\partial \ln\left(\frac{T_2}{T_1}\right)} \Delta \ln \frac{T_2}{T_1} = \frac{h_2 - h''}{R} \tag{175}$$

where $\Delta \ln P_2/P_1$ and $\Delta \ln T_2/T_1$ are defined by equation (136).

The partial derivatives appearing in equations (174) and (175) can be evaluated if γ_S is taken to be independent of temperature and pressure. This is a reasonable assumption for moderate ranges of temperatures and pressures. To within the accuracy of this assumption, the partial derivatives and right sides of equations (174) and (175) are

$$\frac{\partial\left(P'' - \frac{P_1}{P_2}\right)}{\partial \ln\left(\frac{P_2}{P_1}\right)} = \frac{P_1}{P_2} + \gamma_{S,2}\left(\frac{\rho_2}{\rho_1}\right)\left(\frac{\partial \ln V}{\partial \ln P}\right)_{T,2} \tag{176}$$

$$\frac{\partial\left(P'' - \frac{P_1}{P_2}\right)}{\partial \ln\left(\frac{T_2}{T_1}\right)} = \gamma_{S,2}\left(\frac{\rho_2}{\rho_1}\right)\left(\frac{\partial \ln V}{\partial \ln T}\right)_{P,2} \tag{177}$$

$$\left(\frac{P_1}{P_2}\right) - P'' = \left(\frac{P_1}{P_2}\right) - 1 + \gamma_{S,2}\left(\frac{\rho_2}{\rho_1} - 1\right) \tag{178}$$

$$\frac{\partial\left[\frac{(h'' - h_2)}{R}\right]}{\partial \ln\left(\frac{P_2}{P_1}\right)} = \frac{\gamma_{S,2}T_2}{2M_2}\left\{\left(\frac{\rho_2}{\rho_1}\right)^2 - 1 - \left(\frac{\partial \ln V}{\partial \ln P}\right)_{T,2}\left[1 + \left(\frac{\rho_2}{\rho_1}\right)^2\right]\right\}$$

$$+ \frac{T_2}{M_2}\left[\left(\frac{\partial \ln V}{\partial \ln T}\right)_{P,2} - 1\right] \tag{179}$$

$$\frac{\partial\left[\frac{(h'' - h_2)}{R}\right]}{\partial \ln\left(\frac{T_2}{T_1}\right)} = -\frac{\gamma_{S,2}T_2}{2M_2}\left[\left(\frac{\rho_2}{\rho_1}\right)^2 + 1\right]\left(\frac{\partial \ln V}{\partial \ln T}\right)_{P,2} - \frac{T_2\left(c_p\right)_2}{R} \tag{180}$$

$$\frac{(h_2 - h'')}{R} = \frac{(h_2 - h_1)}{R} - \frac{\gamma_{S,2}T_2}{2M_2}\left[\left(\frac{\rho_2}{\rho_1}\right)^2 - 1\right] \tag{181}$$

Corrections and Convergence

The discussion of convergence controls and corrections for shock calculations applies equally well for Chapman-Jouguet detonations. Equations (144) to (146) give the control factor λ; equation (147) gives the new estimates to P_2/P_1 and T_2/T_1; and equation (148) is the test for convergence.

Initial Estimates of T_2/T_1 and P_2/P_1

A good initial estimate for pressure ratio is not as important as a good estimate for temperature ratio. For a number of chemical systems that were investigated, an initial estimate of $\left(P_2/P_1\right)_o = 15$ has been found to be satisfactory. An initial estimate for temperature ratio is found by calculating the flame temperature T_2 (HP problem) corresponding to the following enthalpy:

$$h_2 = h_1 + \frac{3}{4}\frac{RT_1}{M_1}\left(\frac{P_2}{P_1}\right)_o \tag{182}$$

Improved initial estimates to the assumed value of $\left(P_2/P_1\right)_o$ and the estimated value of $\left(T_2/T_1\right)_o$ corresponding to h_2 in equation (182) can be obtained by use of the following recursion formulas:

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$$\left(\frac{P_2}{P_1}\right)_{k+1} = \frac{1 + \gamma_{S,2}}{2\gamma_{S,2}\alpha_k}\left\{1 + \left[1 - \frac{4\gamma_{S,2}\alpha_k}{\left(1 + \gamma_{S,2}\right)^2}\right]^{1/2}\right\} \tag{183}$$

$$\left(\frac{T_2}{T_1}\right)_{k+1} = \left(\frac{T_2}{T_1}\right)_o - \frac{3}{4}\frac{R}{M_1\left(c_p\right)_2}\left(\frac{P_2}{P_1}\right)_o + \frac{R\gamma_{S,2}}{2M_1\left(c_p\right)_2}\left(\frac{r_{k+1}^2 - 1}{r_{k+1}}\right)\left(\frac{P_2}{P_1}\right)_{k+1} \tag{184}$$

where

$$\alpha_k = \left(\frac{T_1}{T_2}\right)_k\left(\frac{M_2}{M_1}\right) \tag{185}$$

$$r_{k+1} = \alpha_k\left(\frac{P_2}{P_1}\right)_{k+1} \tag{186}$$

The quantities M_2, $\gamma_{S.2}$ and $\left(c_p\right)_2$ in equations (183) to (185) are the equilibrium values for $\left(P_2/P_1\right)_o$ and $\left(T_2/T_1\right)_o$. Repeating the use of equations (183) to (186) three times in the program generally provides excellent initial estimates for the Newton-Raphson iteration.

INPUT CALCULATIONS

A number of options are provided in the program for specifying input and these options are discussed in detail in the sections describing the computer program. Part of the input concerns reactants. The total reactant may be composed of a number of reactants and each of these reactants may be specified as an oxidant or a fuel. If the total reactant contains more than one oxidant, these oxidants may be combined into a total oxidant by specifying the relative proportion of each oxidant. Similarly, if the total reactant contains more than one fuel, they may be combined into a total fuel by specifying the relative proportion of each fuel. The overall properties of the total reactant (such as elemental compositions b_i^o, enthalpy $\mathscr{H}_o$, internal energy $\mathscr{U}_o$, molecular weight M_o, density ρ_o, positive and negative oxidation states V^+ and V^-, specific heat $\mathscr{C}_o$, and entropy $\mathscr{S}_o$) can then be calculated by specifying the relative amounts of total oxidant and

total fuel. This method is particularly convenient if calculations are to be obtained for a number of oxidant-fuel ratios.

In order to obtain assigned properties for the total reactant, each reactant j must be specified as either a fuel or an oxidant even though a reactant may ordinarily be thought of as inert (as, for example, N_2). Letting the superscript k equal 1 for oxidant and 2 for fuel, the kilogram-atoms of the ith element per kilogram of total oxidant or total fuel is

$$b_i^{(k)} = \sum_{j=1}^{NREAC} a_{ij}^{(k)} n_j^{(k)} \qquad \begin{array}{l} i = 1, \ldots, l \\ k = 1, 2 \end{array} \tag{187}$$

where NREAC is the total number of reactants and where $n_j^{(k)}$ is the number of kilogram-moles of the jth reactant per kilogram of total oxidant (k = 1) or total fuel (k = 2). If the amounts of oxidants and fuels are specified in terms of weights, then $n_j^{(k)}$ is obtained by

$$n_j^{(k)} = \frac{W_j^{(k)}}{M_j^{(k)} \sum_{j=1}^{NREAC} W_j^{(k)}} \qquad \begin{array}{l} j = 1, \ldots, NREAC \\ k = 1, 2 \end{array} \tag{188}$$

where $W_j^{(k)}$ is the weight of the jth reactant and $M_j^{(k)}$ is the molecular weight of the jth reactant. If, however, amounts of oxidants and fuels are specified in terms of kilogram-moles $N_j^{(k)}$, then

$$n_j^{(k)} = \frac{N_j^{(k)}}{\sum_{j=1}^{NREAC} N_j^{(k)} M_j^{(k)}} \qquad \begin{array}{l} j = 1, \ldots, NREAC \\ k = 1, 2 \end{array} \tag{189}$$

The $M_j^{(k)}$ may be calculated from the atomic weights of the chemical elements M_i as follows:

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$$M_j^{(k)} = \sum_{i=1}^{l} a_{ij}^{(k)} M_i \qquad \begin{array}{l} j = 1, \ldots, \text{NREAC} \\ k = 1, 2 \end{array} \tag{190}$$

The $b_i^{(k)}$ may be combined by means of the following equation to give the kilogram-atoms per kilogram of total reactant:

$$b_i^o = \frac{b_i^{(2)} + (o/f) b_i^{(1)}}{1 + (o/f)} \qquad i = 1, \ldots, l \tag{191}$$

where o/f is the oxidant to fuel weight ratio.

Formulas analogous to equations (187) and (191) may be used to obtain other properties of the total oxidant, total fuel, and total reactant (such as enthalpies, internal energies, molecular weights, and densities).

Enthalpy of total oxidant (k = 1) or total fuel (k = 2) $\mathscr{H}^{(k)}$, $(\text{kg-mole/kg})^{(k)}$:

$$\mathscr{H}^{(k)} = \sum_{j=1}^{\text{NREAC}} \frac{\left(H_T^o\right)_j^{(k)} n_j^{(k)}}{RT} \qquad k = 1, 2 \tag{192}$$

where $\left(H_T^o\right)^{(k)}$ is the enthalpy of the jth reactant, $(\text{J/kg-mole})_j^{(k)}$.

Enthalpy of total reactant $\mathscr{H}_o$, kg-mole/kg:

$$\mathscr{H}_o = \frac{h_o}{RT} = \frac{\mathscr{H}^{(2)} + (o/f)\mathscr{H}^{(1)}}{1 + (o/f)} \tag{193}$$

Internal energy of total oxidant (k = 1) or total fuel (k = 2) $\mathscr{U}^{(k)}$, $(\text{kg-mole/kg})^{(k)}$:

$$\mathscr{U}^{(k)} = \sum_{j=1}^{\text{NREAC}} \frac{\left(U_T^o\right)_j^{(k)} n_j^{(k)}}{RT} \qquad k = 1, 2 \tag{194}$$

where $\left(U_T^o\right)_j^{(k)}$ is the internal energy of the jth reactant, $(J/kg\text{-}mole)_j^{(k)}$.
Internal energy of total reactant $\mathscr{U}_o$, kg-mole/kg:

$$\mathscr{U}_o = \frac{u_o'}{RT} = \frac{\mathscr{U}^{(2)} + (o/f)\mathscr{U}^{(1)}}{1 + (o/f)} \tag{195}$$

Molecular weight of total oxidant (k = 1) or total fuel (k = 2):

$$M^{(k)} = \frac{1}{\sum_{j=1}^{NREAC} n_j^{(k)}} \qquad k = 1, 2 \tag{196}$$

Molecular weight of total reactant, kg/kg-mole:

$$M_o = \frac{\left[(o/f) + 1\right] M^{(1)} M^{(2)}}{M^{(1)} + (o/f) M^{(2)}} \tag{197}$$

(If $M^{(1)} = 0$, $M_o = M^{(2)}$ and if $M^{(2)} = 0$, $M_o = M^{(1)}$.)
Density of total oxidant or fuel:

$$\rho^{(k)} = \frac{1}{\sum_{j=1}^{NREAC} \frac{n_j^{(k)} M_j^{(k)}}{\rho_j^{(k)}}} \qquad k = 1, 2 \tag{198}$$

Density of total reactant:

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$$\rho_o = \frac{\left[(o/f) + 1\right] \rho^{(1)} \rho^{(2)}}{\rho^{(1)} + (o/f) \rho^{(2)}} \tag{199}$$

In the Main Program section (p. 79) several alternate expressions are given for specifying the relative amounts of total oxidant to total fuel and for relating them to o/f.

In the event that an equivalence ratio is specified, it will be necessary to make use of oxidation states. Let V_i^+ and V_i^- be positive and negative oxidation states of the ith element in its commonly occurring compounds. At least one of these will be zero. Thus, for example, the negative oxidation state for chlorine is -1 and its positive oxidation state is zero. The oxidation states per kilogram of total oxidant or total fuel are

$$V^{+(k)} = \sum_{i=1}^{l} V_i^+ b_i^{(k)} \qquad k = 1, 2 \tag{200}$$

$$V^{-(k)} = \sum_{i=1}^{l} V_i^- b_i^{(k)} \qquad k = 1, 2 \tag{201}$$

The positive and negative oxidation states for the total reactant are then

$$V^+ = \frac{V^{+(2)} + (o/f)V^{+(1)}}{1 + (o/f)} \tag{202}$$

$$V^- = \frac{V^{-(2)} + (o/f)V^{-(1)}}{1 + (o/f)} \tag{203}$$

Equivalence ratio is now defined as

$$r \equiv -\frac{V^+}{V^-} \tag{204}$$

One of the options in the SHOCK problem requires reactant compositions relative to the total reactant. These may be obtained as follows:

$$m_j = \begin{cases} \dfrac{(o/f)n_j^{(k)}}{1 + (o/f)} & \text{for } k = 1 \\[2ex] \dfrac{n_j^{(k)}}{1 + (o/f)} & \text{for } k = 2 \end{cases} \qquad j = 1, \ldots, \text{NREAC} \tag{205}$$

where m_j is kilogram-mole of jth reactant per kilogram of total reactant.

Specific heat and entropy for the total reactant in kilogram-mole per kilogram may be calculated using the m_j, $\left(C_p^o\right)_j$, and S_j of the j reactants:

$$\mathscr{C}_o = \sum_{j=1}^{NREAC} m_j \left(\frac{C_p^o}{R}\right)_j \tag{206}$$

$$\mathscr{S}_o = \frac{s_o}{R} = \sum_{j=1}^{NREAC} m_j \left(\frac{S_j}{R}\right) \tag{207}$$

COMPUTER PROGRAM

The CEC71 computer program was written in FORTRAN IV. It was designed to work on any operating system compatible with FORTRAN IV. At Lewis Research Center it was checked out on an IBM 7094 II/7044 direct couple system, IBSYS version 13 using ALTIO.

Due to shorter word length, the IBM 360 system required some double precision variables not required by the IBM 7094. These are indicated on the source listing in appendix C. Machines such as the CDC 6600 which have 60-bit words do not require any double precision variables.

The source program is available to other organization as stated in the INTRODUCTION. Thermodynamic data such as the data listed in appendix D as well as input for some sample problems (appendix E) will be included. The thermodynamic data are updated periodically.

As a consequence, the answers for the sample problems given in appendix E may change somewhat from time to time.

DESCRIPTION OF PROGRAM INPUT

Program input data will be discussed under four categories. Three of the catagories are required and one is optional. The three required categories and the code names by which they will be referred are as follows:

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(1) Equivalence ratio (ERATIO is true)

(2) Oxidant to fuel weight ratio (OF is true)

(3) Fuel percent by weight (FPCT is true)

(4) Fuel to air or fuel to oxidant weight ratio (FA is true)

For each option, the values are given in the MIX array of INPT2 (described in NAMELISTS Input section). This feature is illustrated by cases 52, 122, 950, and 5612 in appendix E. Cases 52 and 950 show ERATIO = T and the reactants identified as fuel or oxidant in column 72. Since these cases involve just one fuel and one oxidant, the amounts of each (as given in columns 46 to 52) are shown as 100. This means that the oxidizer is 100 percent of the total oxidizers and the fuel is 100 percent of the total fuels. Cases 122 and 5612 are examples which have more than one fuel. Case 122 shows that each fuel is 50 percent (by weight) of the total fuels and the one oxidizer is 100 percent of the total oxidizer.

The purpose of the previous namelist variables is to permit using one set of reactant cards with any number of values (up to 15), of the variables such as oxidant to fuel ratio (OF = T). Case 950, for example, specifies three values of equivalence ratio (ERATIO = T).

Reactant enthalpy. - Assigned enthalpy values for initial conditions are required for HP, RKT, DETN, and SHOCK problems. An assigned internal energy is required for the UV problem. These assigned values for the total reactant are calculated automatically by the program from the enthalpies or internal energies of the individual reactants.

The values for the individual reactants are either keypunched on the REACTANTS cards or calculated from the THERMO data. The choice varies according to the type of problem as follows:

(1) RKT, UV, HP problems: Enthalpies or internal energies are taken from the REACTANTS cards unless zeros are punched in card columns 37 and 38. For each REACTANTS card with the "00" code, an enthalpy will be calculated for the species from the THERMO data for the temperature given in card columns 64 to 71. See MgO(s) in case 51, appendix E.

(2) SHOCK problems: Enthalpies for all of the reactants are calculated from the THERMO data for the temperatures in the T schedule of namelist INPT2 (see table VIII). If enthalpy values are punched in card columns 64 to 71 (table VI) they will be ignored. It is not necessary to punch zeros in card columns 37 and 38.

(3) DETN problems: If no T schedule is given in namelist INPT2, the option for calculating reactant enthalpies is the same as for RKT, UV, and HP problems. However, if a T schedule is given in INPT2, the enthalpies will be calculated from the THERMO data for the temperatures in the T schedule, the same as for the SHOCK problem.

When the program is calculating the individual reactant enthalpy or internal energy

values from the THERMO data, the following two conditions are required:

(1) The reactant must also be one of the species in the set of THERMO data. For example, $NH_3(g)$ is in the set of THERMO data but $NH_3(l)$ is not. Therefore, if $NH_3(g)$ is used as a reactant its enthalpy could be calculated automatically, but that of $NH_3(l)$ could not be.

(2) The temperature T must be in the range $T_{low}/1.2 \leq T \leq T_{high} \times 1.2$ where T_{low} to T_{high} is the temperature range of the THERMO data.

NAMELISTS Input

As indicated in table V, the NAMELISTS code card precedes the NAMELISTS input. All problems require an INPT2 input. Rocket and shock problems each require an additional set, namely RKTINP and SHKINP. These additional sets simply follow INPT2 directly.

The variables in each namelist are listed in tables V, VIII, IX, and X. Table V indicates which variables are required and which are optional for the various types of problems. Tables VIII, IX, and X give a brief definition of each variable. Some additional information about some of these variables follows:

Pressure units. - The program assumes the pressure in the P schedule to be in units of atmospheres unless either PSIA = T, NSQM = T, or MMHG = T.

Relative amounts of fuel(s) and oxidizer(s). - These quantities may be specified by assigning 1 to 15 values for either o/f, %F, f/a, or r. If no value is assigned for any of these, the program assumes the relative amounts of fuel(s) and oxidizer(s) to be those specified on the REACTANTS cards. (See discussion in REACTANTS Cards section.)

Printing mole fractions of trace species. - The program automatically prints compositions of species with mole fractions $>5\times10^{-6}$ in F-format for all problems except SHOCK. The TRACE option permits printing smaller mole fractions. If the variable TRACE is set to some positive value, mole fractions greater than or equal to this value will be printed. When this option is used, a special E-format for mole fraction output is used automatically. A TRACE value of 1.E - 38 is the lowest value allowed by the program. (See case 1565 in appendix E.)

For SHOCK problems, mole fractions of trace species are often desired. Thus for SHOCK problems, the program will set TRACE to 5.E - 9 and the E-format for output is always used. This value may be changed by using the TRACE option in INPT2 namelist input. See case 1207 in appendix E.

Intermediate output. - Intermediate output will be listed for whatever point IDEBUG is set equal to and all following points. As an example, setting IDEBUG = 3 will result in intermediate output for all points except the first two.

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(a) Library of thermodynamic data for reaction products (THERMO data)

(b) Data pertaining to reactants (REACTANTS cards)

(c) Namelist data which include the type of problem, required schedules, and options (NAMELISTS input)

The optional category of data are chemical formulas of species which are singled out for special purposes (OMIT and INSERT cards).

The words THERMO, REACTANTS, NAMELISTS, OMIT, and INSERT are control codes used by the program to identify the input read from data cards. The THERMO, REACTANTS, and NAMELISTS codes are punched on separate cards, each preceding their appropriate data cards. The OMIT and INSERT codes are on the same card as the data.

The required order of the data cards is as follows:

(1) THERMO code card

(2) THERMO data (these cards and the preceding THERMO code card may be omitted if the thermodynamic data are to be read from tape)

(3) REACTANTS code card

(4) REACTANTS cards

(5) OMIT and INSERT cards (if any)

(6) NAMELISTS code card

(7) NAMELISTS data

In a particular run, there may be any number of sets of REACTANTS cards (items 3 and 4), each followed by any number of sets of OMIT and INSERT cards (item 5) and NAMELISTS input (items 6 and 7).

The program contains 3 namelists for input: INPT2, RKTINP, and SHKINP. Namelist INPT2 is required for all problems. Rocket and shock problems require a second namelist, namely RKTINP and SHKINP, respectively.

Table V is a schematic of the input and namelist variables required for various problems.

Figure 1 is a flow chart of the main program which controls the reading, processing, and storing of input data.

Examples of input cards for several typical problems are given in appendix E. Each category of input data is discussed in detail in the following sections.

THERMO Data

The library of thermodynamic data for reaction products are in the functional form discussed in the THERMODYNAMIC DATA section. The order and format of the THERMO data are detailed in appendix D. A listing of the card input included with the

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program is also given in appendix D. This listing includes revisions in thermodynamic data through June 1970.

THERMO data may be read either from cards or from tape. If the data are read in from cards, the program will write these data on tape 4. During a computer run, the appropriate reaction product data consistent with each new set of REACTANTS cards will be automatically selected from tape 4 and stored in core.

THERMO data may be read in from cards for each run. However, a permanent tape or disk containing the data may be made during any run by using the required type of control cards preceding the operating deck.

When adding, removing, or changing data for various species on the tape, the whole set of THERMO data cards must be included in the input for making a new tape.

Data for one or more species may be omitted from consideration during any particular run (without removing the data from the tape) by using OMIT cards (see OMIT and INSERT cards section, p. 66).

REACTANTS Cards

This set of cards is required for all problems. The first card in the set contains the word REACTANTS punched in card columns 1 to 9. The last card in the set is blank. In between the first and last cards may be any number of cards up to a maximum of 15, one for each reactant species being considered. The cards for each reactant must give the chemical formula and the relative amount of the reactant. For some problems, enthalpy values are required. The format and contents of the cards are summarized in table VI. A list of some REACTANTS cards is given in table VII. The card format is the same as required for the program described in references 3 and 4.

Relative amounts of reactants. - The relative amounts of reactants may be specified in several ways. They may be specified in terms of moles, mole fraction, or mole percent (by keypunching M in card column 53) or in terms of weight, weight fraction, or weight percent (blank in column 53). For example, in appendix E, cases 679 and 1207 specify reactants in terms of moles and problem 51 in terms of weight.

For these cases, the relative amounts of the reactants are completely specified by the values on the REACTANTS cards. However, there are optional variables which may be set in namelist INPT2 that indicate relative amounts of total fuel to total oxidants. For this situation, each reactant must be specified as a fuel or an oxidizer by keypunching an F or O, respectively, in column 72 of the REACTANTS card. The amounts given on the REACTANTS cards are relative to total fuel or total oxidant rather than total reactant.

There are four options in INPT2 for indicating relative amounts of total fuel to total oxidant. They include

TP, HP, SP, TV, UV, or SV problems. - In these problems, from 1 to 26 values of T, P, and V (or RHO) may be assigned. However, only one value of entropy S0 may be assigned in INPT2 for the SP or SV problem. Only one value of enthalpy is permitted for the HP problem and only one value of internal energy is permitted for the UV problem. However, these values of enthalpy and internal energy are not assigned in INPT2 but are calculated by the program (eqs. (192) to (195)). In a TP problem, if 26 values of T and 26 values of P are assigned in INPT2, properties will be calculated for the 676 possible P and T combinations. Similarly, up to 676 combinations can be calculated for a TV problem.

DETN problem. - Calculations will be made for all combinations of initial pressure P and initial temperature T. Initial temperatures may be specified in INPT2 namelist or on the REACTANTS card.

RKT problem. - At least one chamber pressure value P is required in INPT2, although as many as 26 chamber pressures may be assigned. A complete set of calculations will be done for each chamber pressure.

The RKT problem requires a second namelist for input (RKTINP) discussed in the next section.

RKTINP namelist (RKT problem only). - This namelist is required for RKT problems. It follows the INPT2 namelist. A list of variables and definitions is given in table IX. All variables are optional, although usually a pressure ratio schedule (PCP), an area ratio schedule (SUBAR) or (SUPAR), or some combination of these schedules will be assigned.

Pressure ratio and area ratio schedules must not include values for the chamber and throat inasmuch as these values are assigned or calculated automatically by the program. If both a pressure ratio schedule and an area ratio schedule are given in RKTINP, the pressure ratios will be calculated first. If both schedules are omitted, only chamber and throat conditions will be calculated.

The program will calculate both equilibrium and frozen performance unless RKTINP contains FROZ = F or EQL = F. If FROZ = F, only equilibrium performance will be calculated. If EQL = F, only frozen performance will be calculated.

SHOCK problem. - The program requires a P and T schedule in INPT2 and either a U1 or MACH1 schedule in a second namelist SHKINP, which is described next. These values all refer to the unshocked gas and must correspond one to one with each other. The pressure and temperature schedules are limited to 13 values for SHOCK problems only. This corresponds to the 13-value limit for U1 or MACH1 schedules.

REACTANTS cards must be only for gaseous reactants that are also included as reaction species in the THERMO data. This permits the program to calculate enthalpy and specific heat values of the reactants from the THERMO data.

The SHKINP namelist follows the INPT2 namelist.

SHKINP namelist (SHOCK problem only). - A list of variables and definitions is given in table X. SHKINP must include from 1 to 13 values of either U1 or MACH1 of the unshocked gas. The program will calculate incident shock parameters assuming both equilibrium and frozen composition unless SHKINP contains either INCDEQ = F, or INCDFZ = F. If INCDEQ = F, only frozen composition will be used. If INCDFZ = F, only equilibrium composition will be used. In addition there are options for calculating reflected shock parameters. For each incident condition called for, reflected shock parameters will be calculated assuming either a frozen composition (REFLFZ = T), an equilibrium composition (REFLEQ = T), or both (REFLFZ = T, REFLEQ = T).

OMIT and INSERT Cards

As indicated in table V, OMIT and/or INSERT cards may follow the REACTANTS cards. Their inclusion is optional. They contain the names of particular species in the library of thermodynamic data for the specific purposes to be discussed. Each card contains the word OMIT (in card columns 1 to 4) or INSERT (in card columns 1 to 6) and the names of from one to four species starting in columns 16, 31, 46, and 61. The names must be exactly the same as they appear in the THERMO data (appendix D).

OMIT cards. - These cards list species to be omitted from the THERMO data. If OMIT cards are not used, the program will consider as possible species all those species in the THERMO data which are consistent with the chemical system being considered. Occasionally it may be desired to specifically omit one or more species from considerations as possible species. This may be accomplished by means of OMIT cards.

INSERT cards. - These cards contain the names of condensed species only. They have been included as options for two reasons.

The first and more important reason for including the INSERT card option is that, in rare instances, it is impossible to obtain convergence for assigned enthalpy problems (HP or RKT) without the use of an INSERT card. This occurs when, by considering gases only, the temperature becomes extremely low (say several degrees Kelvin). In these rare cases, the use of an INSERT card containing the name of the required condensed species will eliminate this kind of convergence difficulty. When this difficulty occurs, the following message is printed by the program: "LOW TEMPERATURE IMPLIES CONDENSED SPECIES SHOULD HAVE BEEN INCLUDED ON AN INSERT CARD".

The second and less important reason is that if one knows that one or several particular condensed species will be present among the final equilibrium compositions for the first assigned point, then a small amount of computer time can be saved by using an INSERT card. Those condensed species whose chemical formulas are included on an INSERT card will be considered by the program during the initial iterations for the first

assigned point. If the INSERT card were not used, only gaseous species would be considered during the initial iterations. However, after convergence, the program would automatically insert the appropriate condensed species and reconverge. For all other assigned points the inclusion of condensed species is handled automatically by the program. Therefore, it usually is immaterial whether or not INSERT cards are used for the purpose of saving computer time.

DESCRIPTION OF PROGRAM OUTPUT

The program prints four kinds of output: tables of results, input data used to calculate these tables, information concerning iteration convergence, and optional intermediate output.

Tables of Results

The final output of the program is in the form of tables that are designed to be self-explanatory. While each problem has its own kind of table, all tables have many features in common. These features are

(1) Heading
(2) Case number
(3) Reactant data
(4) Proportion of oxidant to fuel
(5) Thermodynamic mixture properties and derivatives (P, T, ρ, h, s, M, $(\partial \ln V/\partial \ln P)_T$, $(\partial \ln V/\partial \ln T)_P$, c_p, γ_S, and a)
(6) Equilibrium compositon (mole fractions)

In addition to these, certain problems list additional information:

(1) Rocket performance: P_c/P_e, $\mathcal{M}$, A_e/A_t, c^*, C_F, I_{vac}, and I_{sp}
(2) Detonation: P/P_1, T/T_1, M/M_1, ρ/ρ_1, $\mathcal{M}$, and detonation velocity
(3) Shock: $\mathcal{M}_1$, u_1, u_2, P_2/P_1, T_2/T_1, M_2/M_1, ρ_ρ/ρ_1, v_2, u_5, P_5/P_2, T_5/T_2, M_5/M_2, ρ_5/ρ_2, and $u_5 + v_2$
(4) Assigned internal energy and volume: u'

Input Data

Input data have been previously described. The general procedure used in this program is to list the input as they are read in and before they are processed by the program. The purpose is to show, in as clear a way as possible, what is actually on the input cards. All problems list the following input data:

(1) The word REACTANTS

(2) Reactant data

(3) INSERT and/or OMIT card data

(4) The word NAMELISTS

(5) All data in namelist INPT2 given in table VIII (P and RHO use same storage)

Following the INPT2 data is the statement "SPECIES BEING CONSIDERED IN THIS SYSTEM". Each species in the list is preceded by some identification such as J12/65. The J refers to JANAF data (ref. 8). The letter L refers to unpublished data calculated at the Lewis Research Center. The number refers to the month and the year the data were published or calculated (12/65 is December 1965).

For a rocket problem, the namelist RKTINP data given in table IX are listed. For a shock problem, the namelist SHKINP data given in table X are listed.

Following the list of chemical species (or RKTINP or SHKINP data, if any) is the current value of o/f. This is followed by a listing of the enthalpies or internal energies of the total fuel and oxidant (eqs. (192) and (194)) and of the total reactant (eqs. (193) and (195)). Following this is a list of the kilogram-atom per kilogram of each element in the total fuel and oxidant (eq. (187)) and in the total reactant (eq. (191)).

Information Concerning the Iteration Procedure

All problems except SHOCK print information regarding iteration for each point. For the SHOCK problem this information was omitted inasmuch as the printing of the final table in its present form would not be possible without extensive additional storage. Case 122 will be used to illustrate the iteration information. Following the data on kilogram-atoms per kilogram of the reactants is a line containing the letters PT and the chemical symbols of the elements for the problem (for case 122, C, N, H, and F). The numbers under PT refer to the points corresponding to the columns in the final table. The numbers under the chemical symbols are values of π_i. The last column (without a heading) is the number of iterations required to converge to equilibrium composition. In general there is only one line for each point unless there has been an addition or deletion of a condensed species. For example, in case 122 there is one line printed for point 1. For point 3, however, there are two lines. The first line is the result of converging with no condensed phases (using the estimates of the previous point) while the second line is the result of convergence with the inclusion of C(s).

For rocket and detonation problems, more than one line may be printed for conditions other than a change in condensed species. For a rocket problem these conditions are for throat and for an assigned area ratio, where a line is printed out for each estimate of pressure ratio. For example, for the first point 5 of case 122, which is for an

assigned area ratio, the six lines indicate that six separate convergences were required to make a phase change and to find the correct pressure ratio for the assigned area ratio. For throat, additional information is given for pressure ratio and temperature estimates. For a detonation problem, a line is printed for each set of temperature and pressure estimates.

Intermediate Output

The option of printing intermediate output is provided primarily as a means of obtaining additional information for debugging purposes. There is usually no point in using this option when the program is working well. We have used this option in the past for the following reasons:

(1) To find programming errors

(2) To study the iteration process and rate of convergence

(3) To verify that thermodynamic data have been properly prepared

(4) To study the test for inclusion of condensed species

As discussed in the NAMELISTS Input section intermediate output for point N and all following points is obtained by setting IDEBUG = N.

Table XI is a sample of the intermediate output for the first iteration of case 123. It was obtained by setting IDEBUG = 1. Following the first line, which gives the iteration number, is the matrix corresponding to table I. The line underneath the chemical symbols contains the solution to this matrix. The next line contains some additional information in regard to the matrix - that is, T, n, ln n (ENNL), P, ln(P/n), and λ. The next group of lines contains information on the individual species used in setting up the preceding matrix and the values of $\Delta \ln n_j$ obtained from the matrix solution and equation (18). The information on the individual species includes the chemical symbol, n_j, $\ln n_j$, dimensionless enthalpy, dimensionless entropy ($S0J/R \equiv S_j^o/R$), negative dimensionless standard state Gibbs free enrgy ($-G0J/RT \equiv -\mu_j^o/RT$), and negative dimensionless Gibbs free energy ($-GJ/RT \equiv -\mu_j/RT$).

The two derivative matrices (tables III and IV) and their solutions are also given for the first point of case 123. These derivative matrices are set up after convergence, which, for this point, required 10 iterations. This is followed by two lines of output which summarize the results for point NPT. The printed variables are labeled POINT, P, T, H/R, S/R, MW, CP/R, DLVPT, DLVTP, GAMMA(S), and V. The corresponding FORTRAN symbols which are defined in appendix B are NPT, PPP, TTT, HSUM, SSUM, WM, CPR, DLVPT, DLVTP, GAMMAS and VLM, respectively.

Table XII is part of the intermediate output showing the test for condensed phases after convergence. The data in table XII are for case 51 (appendix E), but with a short-

tened pressure ratio schedule that goes directly from $P_c/P_e = 10$ to $P_c/P_e = 10\,000$. In appendix E it may be noted that for $P_c/P_e = 10$, which serves as the initial estimate for the next point, the only condensed species present is $Al_2O_3(s)$. Table XII shows the results of testing the condensed species after convergence of $P_c/P_e = 10\,000$ with just $Al_2O_3(s)$ being the only condensed species present. The notation G0-SUM(ALJ*PII) refers to the quantity given in equation (82). This quantity, as previously mentioned, must be negative for a condensed species not included in the previous convergence to be now considered for inclusion. Further, only that species with the most negative value will be included. In table XII it may be seen that only one species, $Al_2O_3(s)$, has a positive value for IUSE which means it was the only condensed species in the previous convergence. The temperature for this previous convergence (not shown in table XII) is 669.9 K. For this temperature the free energy test is not made for the following species because their temperature range does not include this temperature: $Al(l)$, $AlCl_3(s)$, $Al_2O_3(l)$, $H_2O(s)$, $H_2O(l)$, $Mg(l)$, $MgCl_2(l)$, $MgO(l)$, and $S(s)$. The following species have positive values of G0-SUM(ALJ*PII) and therefore would not be considered for inclusion: $Al(s)$, $AlCl_3(l)$, $AlN(s)$, $Mg(s)$, and $S(l)$. The following species have negative values of G0-SUM(ALJ*PII): $C(s)$, $MgCl_2(s)$, and $MgO(s)$. The largest negative value for all preceding species tested is shown by MAX NEG DELTA G. After all condensed species have been tested, only that species with the largest negative value, in this case $MgO(s)$, is included as a possible reaction species and the iteration procedure is restarted. After convergence the next test for condensed species (not shown in table XII), gave no negative values for G0-SUM(ALJ*PII) which completes the test for condensed species for this point.

Error Messages

This section gives a list of error messages, where they occur in the program, and some discussion concerning them.

CONDENSED REACTANTS NOT PERMITTED IN DETN OR SHOCK PROBLEMS

Main program, statement 1302. As discussed in sections DETN problem and SHOCK problem (p. 65) the program accommodates only gaseous reactants for detonation or shock problems. After message is printed program goes on to next problem.

CONSERVATION EQNS WERE NOT SATISFIED IN 8 ITERATIONS

Subroutine DETON, statement 34. Convergence of conservation equations for the DETN problem is usually obtained in three or four iterations. The program limits the number of iterations to eight although we have never run a problem that required this many iterations. Therefore, we have not yet seen this message printed.

DERIVATIVE MATRIX SINGULAR

Subroutine EQLBRM, statement 172. This situation occurs very rarely inasmuch as, if singularities in the matrix solutions occur, they generally occur first in the iteration matrices and the program does not get as far as the derivative matrices. However, it is possible for the iteration matrix to just barely avoid being singular and for the derivative matrix to be singular. When this occurs the above message is printed, DLVPT is set equal to -1, DLVTP is set equal to 1, and the program continues.

DID NOT CONVERGE FOR AREA RATIO = (Value of area ratio)

Subroutine ROCKET, statement 841. The program permits a maximum of 10 iterations to converge to the pressure ratio corresponding to the assigned area ratio. The usual number of iterations required is 1 to 5. The only time the number of iterations has exceeded 10, in our experience, has been for an assigned area ratio very close to 1 such as $1. < A_e/A_t < 1.0001$. This is due to the fact that the converged throat conditions do not correspond exactly to an area ratio of 1 (see eq. (108)).

DID NOT CONVERGE FOR U1 = (Value of u_1) ANSWERS PROBABLY NOT RELIABLE, SOLUTION MAY NOT EXIST

Subroutine SHCK, statement 125. This message usually occurs when the assigned values of u_1, T_1, and P_1 do not have a solution. For example, for the system containing mole fractions of Ar = 0.9522, H_2 = 0.0430, and O_2 = 0.0048 and for T_1 = 302 K, P_1 = 100.2 mm Hg, the minimum value of u_1 for shock to occur is 1094 meters per second. If u_1 is assigned any value less than 1094 meters per second in SHKINP, the previous error message will be printed.

ERROR IN ABOVE CARD. CONTENTS IGNORED

Main program, statement 1024. This message indicates a keypunching error in a control card, a missing control card, or an extraneous card. The entire contents of this card are ignored by the program.

ERROR IN ORDER OF CARDS FOR (Name of species)

Main program, statement 22. The cards containing THERMO data for the species named are out of order.

ERROR IN REACTANT CARDS

Main program, statement 52. This is due to an error in a chemical symbol such as the symbol not being left-adjusted or not included in BLOCK DATA. Program skips to next problem.

FROZEN DID NOT CONVERGE IN 8 ITERATIONS

Subroutine FROZEN, statement 70. Frozen expansion points generally require from

one to four iterations. We have not yet encountered a problem that required eight iterations. The error message was included primarily as a precaution to avoid infinite cycling of the iteration loop in the event of a machine error.

INSUFFICIENT STORAGE FOR FOLLOWING (Number of) SPECIES

Subroutine SEARCH, statement 871. This statement shows that for the chemical system under consideration, the program found more possible species in THERMO data than can be accommodated by storages reserved for the thermodynamic data in labeled common /SPECES/. This excess number of species is given in the error message. When this situation occurs, the names of the possible species are printed and control is returned to the main program where the next problem is read in.

This situation can be resolved in two ways. First, the program can be recompiled with dimensions increased to accommodate the excess species (see section Changing Number of Possible Reaction Species). Secondly, OMIT cards can be used to eliminate the required number of excess species.

The program is currently dimensioned for 150 species which has been found adequate for all problems calculated by the authors to date.

LOW TEMPERATURE IMPLIES SPECIES SHOULD HAVE BEEN INCLUDED ON AN INSERT CARD, RESTART

Subroutine EQLBRM, statement 874. This message can occur only for an HP or UV problem. It occurs only when the omission of an important condensed product of reaction causes the program to seek a combustion temperature that is unrealistically low ($T < 100$ K). When this occurs the program skips to the next problem.

PHASES OF A CONDENSED SPECIES ARE OUT OF ORDER

Subroutine EQLBRM, statement 156. This statement is written when the thermodynamic data for three or more condensed phases of a species are not in a permitted order as discussed in appendix D. After the statement is written, a table of output for all completed points is written and program goes to next problem.

REACTANT (Number) IS NOT IN THERMO DATA

Subroutine HCALC, statement 85. As discussed in the Subroutine HCALC section (p. 83) enthalpies can be calculated by the program only for those reactants that are also included as reaction species in the thermodynamic data. The error message is printed when this condition is not met. The program skips to the next problem.

REACTANT TEMPERATURE OUT OF RANGE OF THERMO DATA

Subroutine HCALC, statement 76. Subroutine HCALC permits calculation of thermodynamic data for reactants for temperatures that extend up to 20 percent beyond the temperature range over which the data have been fitted. However, if the assigned tem-

perature is more than 20 percent beyond this range, the error message is printed and the program skips to the next problem.

SINGULAR MATRIX

Subroutine EQLBRM, statement 74. Singularities rarely occur in the course of obtaining a matrix solution in GAUSS. When they do occur the program restarts with new estimates as discussed in the Singularities section (p. 30). However, if the singularity occurs again even with new estimates, the above error message is printed and control is returned to the main program which starts the next problem. One possible way to get through this difficulty, discussed in the Singularities section, is to assign a slightly modified equivalence ratio or o/f.

TEMPERATURE IS OUT OF RANGE OF THE THERMO DATA

Subroutine SHCK, statement 1152. This message is printed whenever a converged temperature for a SHOCK problem is outside the following temperature range of the THERMO data: TLOW/1.5 > T > 1.25 THIGH. The program continues but the answers may be very inaccurate.

THE TEMPERATURE = (degrees K) IS OUT OF RANGE FOR POINT (Number)

Subroutine EQLBRM, statement 306. Except for the SHOCK problem, this message is printed whenever the converged temperature for the indicated point is outside the temperature range read in on the card following the THERMO control card. This temperature range, which at present is 300 to 5000 K, is the one over which the gas phase thermodynamic data have been fitted. Generally the thermodynamic data can be extrapolated a short distance without much loss in accuracy. However, to prevent large errors due to extrapolation if TLOW/1.5 > T > 1.25 THIGH, then after the message has been printed, the program writes the output for all completed points and then skips to the next problem.

35 ITERATIONS DID NOT SATISFY CONVERGENCE REQUIREMENTS FOR THE POINT (Number)

Subroutine EQLBRM, statement 973. As indicated in the Convergence section (p. 24), compositions are typically obtained in 3 to 12 iterations. The number 35 was arbitrarily selected to indicate that if convergence has not been reached by that number the problem probably will not converge at all. This situation occurs rarely. All completed points up to this point are printed and program goes to the next problem. If the cause of nonconvergence is not obvious from the output, it is recommended that the problem be rerun with intermediate output.

Sample Problems

Nine sample problems are given that illustrate some of the features of the program. Four are rocket performance problems, RKT = T, (cases 51, 122, 679, and 5612); two are combustion problems (case 123 is for combustion at constant pressure, HP = T, and case 1565 is for combustion at constant volume, UV = T); case 52 is a detonation problem, DETN = T; case 1207 is a shock problem, SHOCK = T; and case 950 is an assigned temperature and pressure problem, TP = T.

It would not be practical to illustrate every possible variation of options permitted by the program. However, the sample problems were selected to illustrate many of the possible variations and in particular those variations which we feel might most often be used. Included in the features illustrated are the following:

(1) Specifying proportions of various reactants
  (a) o/f: cases 122, 123, 1565
  (b) Equivalence ratios: cases 52, 950
  (c) Percent fuel by weight: case 5612
  (d) Complete information on reactant cards: cases 51, 679, 1207
  (e) Relative weights of reactants: cases 51, 52, 122, 123, 950, 1565, 5612
  (f) Relative moles of reactants: cases 679, 1207

(2) Specifying enthalpies
  (a) On reactant cards: cases 51 (partly), 122, 123, 679, 950, 1565 (partly), 5612
  (b) Calculated by program: cases 51 (partly), 52, 1207, 1565 (partly)

(3) Pressure units
  (a) psia: cases 51, 122, 679, 5612
  (b) atm: cases 52, 123, 950
  (c) mm Hg: case 1207

(4) INSERT: cases 51, 5612

(5) OMIT: case 950

(6) Composition in floating point format: case 1565

(7) Program considers ions: case 679

(8) Special derivatives due to two condensed phases of a species: cases 51, 5612

(9) Special throat interpolation: case 5612

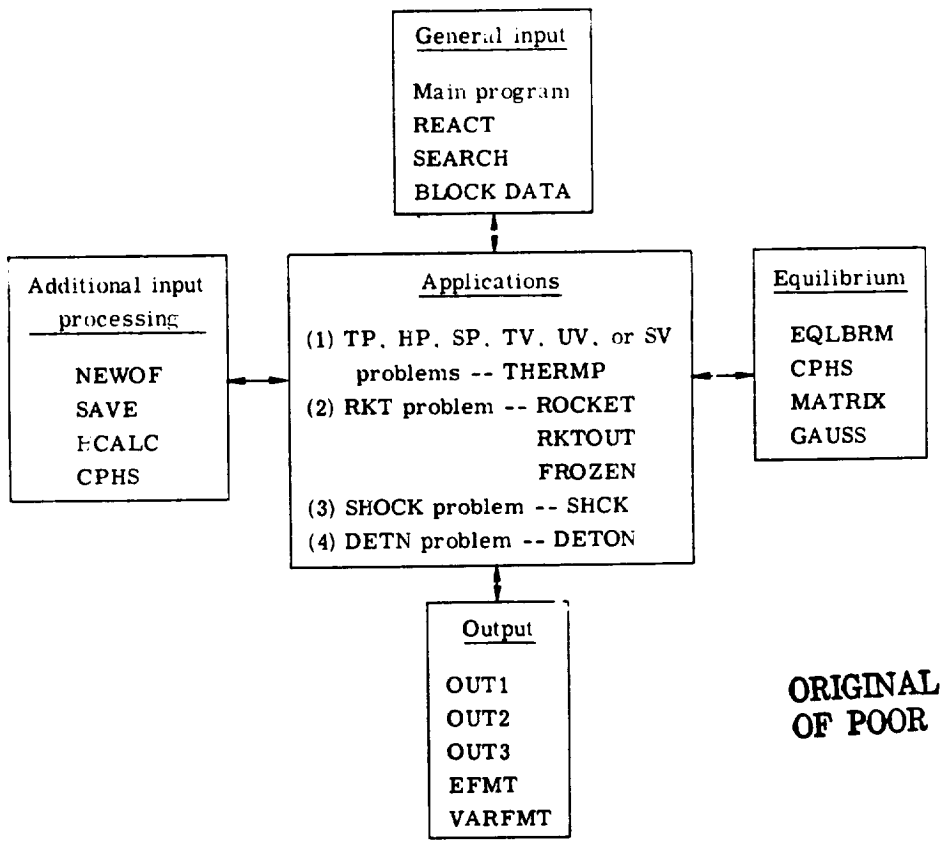
Some additional features of the program illustrated by the various cases are the following:

Case 51: This case shows several condensed species being automatically inserted and removed by the program. Frozen expansion is stopped at point 3 inasmuch as exit temperature is below melting point of 2315 K.

Case 122: This case shows that it is possible to assign a schedule of points which include a mixture of pressure ratios, subsonic area ratios, and supersonic area ratios.

MODULAR FORM OF THE PROGRAM

In order to facilitate adding or deleting applications of the chemical equilibrium part of the program, the program was set up in eight modules. These modules are concerned with general input, additional input processing, four applications, equilibrium calculations, and output. The general flow of these modules and associated routines are given in the following schematic:



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A subroutine tree diagram is given in figure 2. From these diagrams it is clear that, for example, the rocket application could be eliminated by omitting subroutines ROCKET, RKTOUT, and FROZEN and by omitting the statement which calls ROCKET in the main program.

Some details of the individual routines are given in the ROUTINES section (p. 78).

The following section gives: (1) the general purpose of each module, and (2) common variables set by the module which are either required or set by the equilibrium module.

General Input Module

This module is controlled by the main program. A flow diagram of the main program is given in figure 1. The module sets up input required by all application modules. Some of these input data include the following:

(1) THERMO data. The main program reads the thermodynamic data cards for all species and writes the data on tape 4. Subroutine SEARCH pulls the data for the appropriate species for a particular chemical system from tape 4 and stores the data in core.

(2) REACTANTS cards. These cards are read and processed by subroutine REACT.

(3) INPT2 namelist data. The main program initializes the variables, reads and writes the data, and converts some of the data to the form required by the remainder of the program.

(4) BLOCK DATA. These data are set and remain for the entire computer run.

(5) Composition estimates. These estimates and associated variables are set for the first iteration for the first point only.

The variables having to do with composition which are used directly by the equilibrium module include ENN, ENNL, IQ1, IUSE, JSOL, JLIQ, EN(j,1), and ENLN(j). (All common variables are defined in appendix B.) The remaining variables set in the general input module which are used by the equilibrium module include A, COEF, IONS, LLMT, RR, NS, NLM, NC, SHOCK, IDEBUG, TEMP, TRACE, and TMID. These latter variables usually remain unchanged for an entire problem set.

Application Modules

Each application module is called from the main program according to the type of problem designated in namelist INPT2. The module controls the flow of the program until the problem is completed. Control is then returned to the main program where the next code card is read. A general flow diagram is given in figure 3. The module is responsible for the following items:

(1) Reading any additional input for the particular problem (namelist RKTINP for the RKT problem and SHKINP for the SHOCK problem).

(2) Doing any calculation peculiar to the problem.

(3) Calling routines in the additional input processing module (p. 75) as required.

(4) Setting a point number NPT and setting certain variables required for the assigned thermodynamic states for that point if they have not already been set in the main program. These variables are set as follows for various assigned states:

Variable	Temperature and pressure	Enthalpy and pressure	Entropy and pressure	Temperature and volume	Internal energy and volume	Entropy and volume
TP	True	False	False	True	False	False
HP	False	True	False	False	True	False
SP	False	False	True	False	False	True
VOL	False	False	False	True	True	True
TT	T_o	Estimated T	Estimated T	T_o	Estimated T	Estimated T
PP	P_o	P_o	P_o	---	---	---
VLM(NPT)	---	---	---	V_o	V_o	V_o
S0	---	---	s_o	---	---	s_o
HSUB0	---	h_o/R	---	---	u_o'/R	---

Estimated T is set equal to 3800 K for the first point only. For succeeding points the temperature estimate is set equal to the value of some previous converged point.

(5) Calling the equilibrium module (subroutine EQLBRM).

(6) Printing special output for the problem and calling the output module to print general output.

Equilibrium Module

The equilibrium module calculates compositions and thermodynamic properties for a particular point NPT. The module is controlled by subroutine EQLBRM which is diagrammed in figures 4(a), (b), and (c).

Subroutine EQLBRM calls three subroutines: (1) CPHS to calculate thermodynamic functions of the individual species, (2) MATRIX to set up the matrix according to tables I, II, III, and IV as required, and (3) GAUSS to solve the set of equations.

Common variables either calculated or set by the EQLBRM module include CPR, CPSUM, DLVPT, DLVTP, EN, ENLN, ENN, GAMMAS, H0, HSUM, JLIQ, JSOL, PPP, S, SSUM, TOTN, TTT, VLM, and WM.

Additional Input Processing Module

The additional input processing module consists of a set of routines which are called for various purposes:

(1) NEWOF is called by an application module to adjust values of b_i^o, ρ_o, r, and u_o'/R or h_o/R for each o/f.

(2) SAVE is called to save or move composition data from one point to another. The purpose is to use the calculated results from some previous point as initial estimates for the current point.

(3) HCALC is called from three places:

NEWOF - to calculate enthalpies for reactants where one or more REACTANTS cards had zeros in columns 37 and 38

SHCK - to calculate compositions and thermodynamic properties when composition is frozen to the reactants composition

DETON - to calculate enthalpy, HSUB0, for reactants at the temperatures assigned in the T array in namelist INPT2

(4) CPHS is called by HCALC to calculate thermodynamic functions for an individual reactant using the THERMO data.

Variables set by this module which are required by the equilibrium module include B0, HSUB0, and EQRAT.

Output Module

The output module consists of the three subroutines VARFMT, EFMT, and OUT1 with two entries OUT2 and OUT3. OUT1 lists data given on the REACTANTS cards as well as o/f, %F, r, and ρ_o. OUT2 lists the properties P_{atm}, T, ρ(g/cc), h(cal/g), s(cal/(g)(K)), $(\partial \ln V/\partial \ln P)_T$, $(\partial \ln V/\partial \ln T)_P$, c_p(cal/(g)(K)), γ_S, and a. OUT3 lists equilibrium mole fractions of the reaction species.

Subroutines VARFMT and EFMT are called from OUT2 and OUT3. VARFMT adjusts the number of decimal places in a variable format according to the size of the numbers. EFMT sets up a special E-type format for printing density ρ and mole fractions.

ROUTINES

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The program consists of a main program, 17 subroutines, 3 entries, and block data. A description of the function of each of these is given in the following sections.

Most program variables used in these sections are in labeled common and are defined in appendix B.

Main Program

A flow chart of the main program is given in figure 1. Generally, the routine performs the following functions:

(1) Reads code cards THERMO, REACTANTS, OMIT, INSERT, and NAMELISTS and directs flow of program accordingly.

(2) Stores THERMO data on tape 4.

(3) Calls subroutine REACT to read and process REACTANTS cards.

(4) Reads OMIT and INSERT cards and stores species names.

(5) Initializes variables in namelist INPT2.

(6) Reads and writes namelist INPT2.

(7) Converts assigned densities, if any, (RHO(i) in INPT2) to specific volumes: VLM(i) = 1/RHO(i).

(8) Stores the number of pressures or volumes in NP.

(9) Stores values of o/f in OXF array. If o/f values have not been inputted directly, they are calculated as follows:

Values in MIX (table VIII)	Code (table VIII)	o/f calculation in main program
Oxidant to fuel weight ratio, o/f	OF = .TRUE.	OXF(i) = o/f
Fuel to air weight ratio, f/a	FA = .TRUE.	OXF(i) = 1/(f/a)
Percent fuel, %F	FPCT = .TRUE.	OXF(i) = (100-%F)/(%F)
Equivalence ratio, r	ERATIO = .TRUE.	$OXF(i) = \frac{-rV^{-(2)} - V^{+(2)}}{rV^{-(1)} + V^{+(1)}}$
Not specified		$OXF(i) = \frac{WP(1)}{WP(2)}$

Values of WP(1) and WP(2) are defined in appendix B.

(10) Makes necessary adjustments to consider charge balance if IONS = .TRUE.. This is done by adding 1 to NLM and E to LLMT array.

(11) Calls SEARCH to pull required THERMO data from tape and to store the data in core.

(12) Sets initial estimates for compositions. These estimates are set with each INPT2 read. They are used only for the first point in the lists of variables in namelist (e.g., the first o/f and the first T and P in a TP problem). All succeeding points use results from a previous point for estimates.

For the first point the program assigns an estimate of 0.1 for n, the total number of kilogram-moles per kilogram. The initial estimate of number of moles of each gaseous species per kilogram of mixture n_j is set equal to 0.1/m where m is the total number

of gaseous species. Condensed species are assigned zero moles. (See Initial Estimates, p. 24)).

(13) Sets IUSE(j) positive for condensed species listed on INSERT cards (see IUSE array).

(14) Calls THERMP if TP, HP, SP, TV, UV, or SV is true.

(15) Calls DETON if DETN is true.

(16) Calls SHCK if SHOCK is true.

(17) Calls ROCKET if RKT is true.

Subroutine REACT

The purpose of subroutine REACT is to read and process the data on the REACTANTS cards. The subroutine is called from the main program after a REACTANTS code card has been read. The data on these cards are described in the REACTANTS Cards section (p. 62).

The reactants may be divided into two groups according to card column 72 on the REACTANTS cards. The two groups are oxidants (O in cc 72) and fuels (cc 72 $\neq$ O). We generally keypunch F in card column 72 for fuels even though this is not necessary. The contents of card column 72 are read into FOX. Depending on the contents of FOX, program variables relating to oxidants or fuels are subscripted 1 for oxidants and 2 for fuels.

The FORTRAN symbols for the properties read from the REACTANTS cards and their associated properties discussed in INPUT CALCULATIONS (p. 55) are as follows:

Property	FORTRAN symbol
$a_{ij}^{(k)}$	ANUM(j, m)[a]
$W_j^{(k)}$	PECWT(j) (if no M in cc 53)
$N_j^{(k)}$	PECWT(j) (if M in cc 53)
$\left(H_T^o\right)_j^{(k)}$	ENTH(j) (if not UV problem and 00 not in cc 37 and 38)
$\left(U_T^o\right)_j^{(k)}$	ENTH(j) (if UV problem and 00 not in cc 37 and 38)
$\rho_j^{(k)}$	DENS(j)

[a]Each of the j REACTANTS cards contains from 1 to 5 stoichiometric coefficients read (indicated by subscript m) into ANUM(j, m) and their corresponding chemical symbols read into NAME(j, m). In relating an ANUM(j, m) with $a_{ij}^{(k)}$, the index i associated with a particular chemical element is determined from the chemical symbol in NAME(j, m).

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If there are several oxidants their properties are combined by subroutine REACT into properties of a total oxidant using the relative proportion of each oxidant given on the REACTANTS cards. Similarly, if there are several fuels, their properties are combined into properties of a total fuel. The total oxidant and total fuel properties discussed in INPUT CALCULATIONS and their associated FORTRAN symbols are as follows:

Property	FORTRAN symbol	Equation
$b_i^{(k)}$	B0P(i,k)	(187)
$M_j^{(k)}$	RMW(j)	(190)
$\mathcal{H}^{(k)}{}_T$	HPP(k) (if not UV problem and 00 not in cc 37 and 38)	(192)
$\mathcal{U}^{(k)}{}_T$	HPP(k) (if UV problem and 00 not in cc 37 and 38)	(194)
$M^{(k)}$	AM(k)	(196)
$\rho^{(k)}$	RH(k)	(198)
$V^{+(k)}$	VPLS(k)	(200)
$V^{-(k)}$	VMIN(k)	(201)
$W_j^{(k)} \Big/ \sum_{j=1}^{NREAC} W_j^{(k)}$	PECWT(j)	

If any of the $\rho_j^{(k)}$ are zero then RH(1) = RH(2) = 0.

These total oxidant and total fuel properties are subsequently combined into total reactant properties by using the values of oxidant-fuel mixture ratios obtained from the main program. This is done in NEWOF, an entry in SAVE.

Other common variables set by REACT are LLMT, NAME, ANUM, ENTH, FAZ, RTEMP, FOX, DENS, RMW, MOLES, NLM, NEWR, and NREAC.

A provision is made for eliminating a second tape search when two consecutive sets of REACTANTS cards contain the same elements. This is done by saving the element symbols (LLMT(l)) in LLMTS(l), the kilogram-atoms per kilogram (B0P(l,k)) in SB0P(l,k), and the number of elements (NLM) in NLS.

Atomic weights M_i used in equation (190) are stored in ATOM(2,i). The corresponding chemical symbols are stored in ATOM(1,i). The oxidation states of the chemical elements V_i^+ or V_i^- used in equations (200) and (201) are stored in ATOM(3,i). The ATOM array is stored by BLOCK DATA.

Subroutine SEARCH

Subroutine SEARCH reads the THERMO data which have been stored on tape 4 and stores the appropriate data in core.

A check is made near the beginning of the routine to prevent THERMO data from exceeding their storage allotments These variables are all in labeled common SPECIES and are currently dimensioned for 150 species (appendix B) However, this dimension may be reduced to save storage (see Changing Numer of Possible Reaction Species, p. 91).

SEARCH is called from the main program when the logical variable NEWR is true (see fig. 1). NEWR is set true in REACT to indicate a new chemical system. REACT also stores chemical element symbols for the current chemical system in the LLMT array. SEARCH stores THERMO data in core for each species whose elements are included in the LLMT array (unless the species name was listed on an OMIT card).

The THERMO data are stored in common variables TLOW, TMID, THIGH, SUB, A, COEF, and TEMP. SEARCH writes out the names and dates of species whose data are stored in core.

SEARCH initializes the IUSE array. IUSE(j) for gaseous species are set equal to zero. IUSE(j) for condensed species are set equal to negative integers. For the chemical system under consideration, the first possible condensed species is set equal to -1, the second to -2, and so on, with one exception. In the event there are two or more condensed phases of the same species, each phase is given the same negative integer. Thus, if IUSE(j) for $B_2O_3(\ell)$ is set equal to -4, for example, IUSE(j) for $B_2O_3(s)$ will also be set equal to -4. A description of the IUSE array is given in the next section.

The various condensed phases of a species are expected to be adjacent in the THERMO data as they are read from tape 4. These phases must be either in increasing or decreasing order according to their temperature intervals.

NS contains the total number of species stored in core. NC contains the total number of condensed species (counting each condensed phase of a species as a separate species).

<u>IUSE array</u>. - Each value in the IUSE array is associated with a species. These values of IUSE serve two purposes:

(1) They indicate which species are to be included in the current iteration (IUSE(j) < 0 for excluded species and IUSE(j) ≥ 0 for included species).

(2) They indicate multiple phases of the same species if absolute values of IUSE(j) are equal.

The IUSE(j) are initialized in subroutine SEARCH and the main program as follows:

(1) IUSE(j) = 0 for all gaseous species.

(2) IUSE(j) = n for all condensed species whose names have been listed on INSERT cards. The number n indicates the species was the nth condensed species whose THERMO data were read from tape 4.

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(3) IUSE(j) = -n for all condensed species not listed on INSERT cards where n is defined in (2).

These initial values of IUSE(j) may be adjusted later in subroutine EQLBRM. For condensed species, the sign is adjusted as species are included or excluded in the current iteration.

For the IONS option, IUSE(j) values for ionic species are set to -10000 when the mole fractions of all ionic species are less than 10^{-8}.

Subroutine HCALC

The purpose of HCALC is to calculate thermodynamic properties for reactants under certain circumstances. HCALC is called from NEWOF (see "Entry NEWOF"), SHCK, and DETON.

HCALC is called from NEWOF when CALCH is set true. CALCH is set true in the main program when zeros have been punched in card columns 37 and 38 on one or more REACTANTS cards. The zeros are a code indicating that the enthalpy (or internal energy for UV problems) for the reactant should be calculated from the THERMO data at the temperature punched on the card. This temperature has been stored in the RTEMP array. CPHS is called to calculate the enthalpy. The value is stored in the ENTH array and printed in the final tables.

The properties calculated in subroutine HCALC, their FORTRAN symbols, and the conditions for which they are used are as follows:

Property	FORTRAN symbol	Equation	Conditions
$\mathscr{H}^{(k)}{}_T$	HPP(k)	(192)	SHOCK problem. DETN problem with T schedule. HP, RKT, or DETN problem if 00 in cc 37 and 38
h_o/R	HSUB0	(193)	SHOCK problem. DETN problem with T schedule. HP, RKT, or DETN problem if 00 in cc 37 and 38
$\mathscr{U}^{(k)}{}_T$	HPP(k)	(194)	UV problem if 00 in cc 37 and 38
u'_o/R	HSUB0	(195)	UV problem if 00 in cc 37 and 38
M_o	AM1	(197)	SHOCK or DETN problem
m_i	EN(j)	(205)	SHOCK problem
$\mathscr{C}_o$	CPR1	(206)	SHOCK problem
$\mathscr{S}_o$	S0	(207)	SHOCK problem

The quantity m_i was deliberately subscripted differently from EN(j) to allow for the fact that the same compound may have a different index as a reactant than as a reaction species. Thus, for example, O_2(g) might be the third reactant read in from REACTANTS

cards and also the tenth species read in by SEARCH. In this case m_3 would be stored in EN(10).

Subroutine SAVE

This subroutine has several functions, all of which are concerned with saving some information from a completed calculation for subsequent use in later calculations. The primary purpose is to save computer time by having good initial estimates for compositions.

These estimates for the next point, NPT, come from either the point just completed, ISV, or some other previous point. The flow of the routine is directed by ISV as follows:

(1) ISV positive. Transfer compositions for point just completed for use as initial estimates for next point (transfer EN(j,ISV) to EN(j,NPT)).

(2) ISV negative. Save values of ENLN(j) for gases and EN(j) for condensed in SLN(j), ENN in ENSAVE, ENNL in ENLSAV, IQ1 in IQSAVE, JSOL in JSOLS, JLIQ in JLIQS, and NLM in LL1. (These values are saved because they are to be used as initial estimates for some future point and they may be overwritten in the meantime.) Make ISV positive and transfer EN(j,ISV) to EN(j,NPT).

(3) ISV zero. Use the data previously saved (as discussed in (2)) as initial estimates for current point. Restore IUSE codes and inclusion or exclusion of "E" as an element for IONS option.

Entry NEWOF. - NEWOF combines the properties of total oxidant and total fuel calculated in subroutine REACT with an o/f value to give properties for the total reactant. NEWOF is called for each mixture assigned in the MIX array in INPT2 namelist. It is called from either THERMP, ROCKET, SHCK, or DETON. The calculated properties and corresponding FORTRAN symbols are as follows:

Property	FORTRAN symbol	Equation
b_i^o	B0(i)	(191)
h_o/R	HSUB0 (if not UV problem)	(193)
u_o'/R	HSUB0 (if UV problem)	(195)
ρ_o	RHOP	(199)
r	EQRAT	(204)

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Subroutine HCALC is called by Entry NEWOF to calculate the enthalpies for each reactant that has zeros keypunched in card columns 37 and 38 in its REACTANTS card (see table VI).

Values of HPP(2), HPP(1), HSUB0, B0P(i,2), B0P(i,1), and B0(i) are printed out.

Subroutine EQLBRM

EQLBRM is the control routine for the equilibrium module which calculates equilibrium compositions and thermodynamic properties for a particular point. The subroutine flow diagram is given in figures 4(a) to (c). Figure 4(a) is a diagram of the complete routine. Figure 4(b) is an expansion of the block labeled 85 in figure 4(a). It gives the details for obtaining and applying corrections in subroutine EQLBRM. Figure 4(c) is the expansion of the block between blocks labeled 160 and 143 in figure 4(a). Figure 4(c) is the flow diagram for adding and removing condensed species.

Several common variables must be set before EQLBRM is called. These variables and the modules setting them are summarized as follows:

Module	Variables
Input	ENN, ENNL, IQ1, IUSE(j), JSOL, JLIQ, EN(j,NPT), ENLN(j) } for first iteration, first point only COEF(k,i,j), TEMP(j,k), IONS, LIMT(l), RR, NS NLM, NC, SHOCK, IDEBUG, TRACE, and TMID. For TP, HP, SP, TV, UV, and SV problems, TP, HP, SP, VOL, and S0 (if SP is true) are all set.
Application	TT, PP, NPT, VLM(NPT) (if VOL is true). In addition, if not previously set in Input: VOL, TP, HP, SP, and S0 (if SP is true).
Additional input processing	B0, EQRAT, and HSUB0

Common variables set by EQLBRM include TTT(NPT), PPP(NPT), SSUM(NPT), HSUM(NPT), CPR(NPT), GAMMAS(NPT), VLM(NPT), WM(NPT), DLVPT(NPT), DLVTP(NPT), TOTN(NPT), ENN, EN(j,NPT), ENLN(j), IUSE(j), JLIQ, and JSOL.

Subroutine CPHS

Subroutine CPHS calculates thermodynamic properties using equations (90), (91), and (92) for species numbering from 1 to NS for an assigned temperature TT. It uses either one of two sets of coefficients: COEF(2,i,j) for the temperature interval TLOW to TMID and COEF(1,i,j) for the interval TMID to THIGH. The index j is the the jth species and the index i (i = 1 to 7) refers to the ith coefficient.

The properties calculated and their corresponding FORTRAN symbols are as follows:

Property	FORTRAN symbol
$\left(S_T^o/R\right)_j$	S(j) j = JS1, . . ., NS
$\left(H_T^o/RT\right)_j$	H0(j) j = JS1, . . ., NS
$\sum_{j=JS1}^{NS} n_j \left(C_p^o/R\right)_j$	CPSUM (one of the terms in eq. (59))
$n_j \left(C_p^o/R\right)_j$	CPSUM (when CPHS is called by HCALC)

The index JS1 is always set equal to 1 in all routines calling CPHS except HCALC. In the latter event JS1 and NS are both set equal to the index j of a particular species.

Subroutine MATRIX

This subroutine sets up the matrices corresponding to tables I to IV. The assigned thermodynamic state being set up (tables I and II) is specified by the following codes:

Assigned thermodynamic state	Codes
TP	TP = .TRUE. VOL = .FALSE. CONVG = .FALSE.
HP	HP = .TRUE. VOL = .FALSE. CONVG = .FALSE.
SP	SP = .TRUE. VOL = .FALSE. CONVG = .FALSE.
TV	TP = .TRUE. VOL = .TRUE. CONVG = .FALSE.
UV	HP = .TRUE. VOL = .TRUE. CONVG = .FALSE.
SV	SP = .TRUE. VOL = .TRUE. CONVG = .FALSE.

After convergence of any of the previous six problems, setup of the derivative matrices (tables III and IV) is specified by the following codes:

Derivative	Codes
DLVTP	CONVG = .TRUE. LOGV = .FALSE.
DLVPT	CONVG = .TRUE. LOGV = .TRUE.

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Subroutine GAUSS

Subroutine GAUSS is used to solve the set of simultaneous linear iteration equations constructed by subroutine MATRIX. The solution is effected by performing a Gauss reduction using a modified pivot technique. In this modified pivot technique only rows are interchanged. The row to be used for the elimination of a variable is selected on the basis that the largest of its elements, after division by the leading element, must be smaller than the largest element of the other rows after division by their leading elements.

The solution vector is stored in X(k). In the event of a singularity, IMAT (which is equal to the number of rows) is set equal to IMAT - 1. IMAT is tested later in subroutine EQLBRM.

Subroutine OUT1

This subroutine, together with entries OUT2 and OUT3, writes statements common to all problems. OUT1 writes statements giving the data on REACTANTS and on o/f, percent fuel, equivalence ratio, and density.

Entry OUT2. - This entry writes the statements for printing values of pressure, temperature, density, enthalpy, entropy, molecular weight, $(\partial \ln V/\partial \ln P)_T$ (if equilibrium), $(\partial \ln V/\partial \ln T)_P$ (if equilibrium), heat capacity, γ_S, and sonic velocity. These variables and corresponding labels are printed with a variable format described in BLOCK DATA.

Entry OUT3. - Entry OUT3 writes statements giving the equilibrium mole fractions of reaction species.

Subroutine VARFMT

Subroutine VARFMT (variable format) adjusts the number of decimal places printed in F-format in the variable format, FMT, according to the size of the number. It is used for P_c/P_e, P, and A_e/A_t. Variable format is described in BLOCK DATA.

Subroutine EFMT

Subroutine EFMT (E-format) writes statements in a special exponent form. This form is similar to the standard FORTRAN E-format, but the letter E and some of the

spaces have been removed for compactness. It is used to write density and mole fractions with the TRACE option.

Subroutine THERMP

This subroutine is the application module for TP, HP, SP, TV, UV, and SV problems. Common variables which must be set according to the assigned thermodynamic states are given in the section Application Modules (p. 76). For these problems, the variables TP, HP, SP, S0, and VOL are set or read in in the main program. HSUB0 is set either in NEWOF or HCALC. The general flow of the routine is given in figure 3.

Indices run from 1 to NP (NP $\leq$ 26) both for assigned pressures P and assigned volumes (V in INPT2 and VL in THERMP). Indices run from 1 to NT (NT $\leq$ 26) for assigned temperature T. NP and NT are set in the main program.

Subroutine ROCKET

This subroutine is the control program for the RKT problem (rocket performance calculations discussed in section ROCKET PERFORMANCE). A flow diagram for this subroutine is given in figure 5. Subroutine ROCKET obtains the required thermodynamic properties for equilibrium performance by calling subroutine EQLBRM. For frozen performance, subroutine ROCKET calls subroutine FROZEN to obtain the required thermodynamic properties. Rocket performance parameters are then obtained by calling subroutine RKTOUT. In addition to calling RKTOUT and FROZEN, and in addition to using controls common to all problems (discussed in section MODULAR FORM OF THE PROGRAM, p. 75), subroutine ROCKET also does the following:

(1) It reads and processes the input data in RKTINP namelist.

(2) It calculates estimates for throat pressure ratios.

(3) It calculates estimates for pressure ratios corresponding to assigned area ratios (if any).

Subroutine RKTOUT

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This subroutine calculates various rocket performance parameters from previously calculated thermodynamic properties.

It is also the control program for writing rocket performance output. It contains the WRITE statements that apply specifically to rocket parameters and it calls subroutine

OUT1 and entries OUT2 and OUT3 for the WRITE statements common to all problems. The rocket parameters are printed with the variable format, FMT, described in BLOCK DATA.

Subroutine RKTOUT is called from subroutine ROCKET.

Subroutine FROZEN

Subroutine FROZEN is called from ROCKET to calculate the temperature and thermodynamic properties for the following assigned conditions:

(1) Composition frozen at combustion conditions (NFZ = 1)

(2) An assigned exit pressure (PP)

(3) An assigned entropy equal to the entropy at combustion conditions (S0 = SSUM(1))

The iteration procedure used for obtaining the exit temperature is discussed in the section Procedure for Obtaining Frozen Rocket Performance (p. 40).

If a temperature is reached 50 K below the range of a condensed combustion species (TEMP(j, 1) to TEMP(j, 2)), calculations are stopped. TT is set to zero and control is returned to ROCKET where a message is printed and data for all preceding points are listed.

The variables which must be set in common before calling FROZEN include NFZ, NPT, TT, PP, IUSE(j), COEF(k,i,j), S0, NS, NC, TEMP(j,k), TMID, WM(1), EN(j,1), RR, and TOTN(1). The variables which are set by FROZEN include TTT(NPT), PPP(NPT), SSUM(NPT), HSUM(NPT), CPR(NPT), GAMMAS(NPT), VLM(NPT), WM(NPT), DLVPT(NPT), DLVTP(NPT), and TOTN(NPT). Many of these variables are the same as are required by or set by EQLBRM.

Subroutine SHCK

Subroutine SHCK is the application module for the SHOCK problems. It calculates the shock parameters discussed in the section "INCIDENT AND REFLECTED SHOCKS". It reads and processes the input data in SHKINP namelist. Depending on which options are specified, it calculates incident shock conditions based on compositions frozen at initial conditions and/or based on equilibrium compositions after shock. It also calculates, based on specified options, frozen and/or equilibrium reflected shock conditions relative to equilibrium and/or frozen incident shock conditions.

Subroutine DETON

This subroutine does the calculations required to obtain Chapman-Jouguet detonation properties as described in the section CHAPMAN-JOUGUET DETONATIONS. Detonation calculations are limited to gaseous reactants only. When no T schedule is included in the namelist input INPT2, enthalpies for the reactants may be either punched on the cards or calculated by subroutine HCALC where the zeros are punched in card columns 37 and 38 as usual. However, if a T schedule is used, all enthalpies will be calculated by the program regardless of the punches on the cards. In this case, of course, all reactants must be in the THERMO data.

BLOCK DATA

BLOCK DATA contains atomic data stored in ATOM(i, j) and many of the variables used with the variable format, FMT. The ATOM variables are defined in appendix B. The format variables are stored in the common labeled OUPT and are described here.

A variable format was used so that one format, FMT, could be used in the final output with changes in the number of decimal places according to the sizes of the numbers. The format is used to print a label and from 1 to 13 associated numbers. The labels contain 14 alphameric characters stored in four words and printed with 3A4, A2. The numbers are all printed in a field of 9. FMT is initially set in BLOCK DATA as follows:

```
FMT (1)  (2)   (3)   (4)   (5)  (6)   (7)  (8)   (9)  (10)  (11)  (12)  (13)  (14)  (15)
     (1H ,3A4 ,A2, F9. 0, F9. 0, F9. 0, F9. 0, F9. 0, F9. 0,
FMT (16) (17) (18) (19) (20) (21) (22) (23) (24) (25) (26) (27) (28) (29) (30)
     F9. 0,  F9. 0,  F9. 0,  F9. 0,  F9. 0,  F9. 0,  F9. 0   )
```

where the spaces are stored as blanks.

Some variables set in BLOCK DATA to modify FMT are as follows:

Variable:	F0	F1	F2	F3	F4	F5	FB	FMT13	FMT9X	FMTI9
Storage:	0,	1,	2,	3,	4,	5,		13	9X,	I9,

The following is a list of variables used as labels and printed with 3A4, A2 in FMT:

Variable	Stored label
FP	P, ATM
FT	T, DEG K
FH	H, CAL/G
FS	S, CAL/(G)(K)
FM	M, MOL WT
FV	(DLV/DLP)T
FD	(DLV/DLT)P
FC	CP, CAL/(G)(K)
FG	GAMMA (S)
FL	SON VEL, M/SEC
FR1	PC/P
FC1	CF
FN	MACH NUMBER
FR	CSTAR, FT/SEC
FI	ISP, LB-SEC/LB
FA	IVAC, LB-SEC/LB
FA1, FA2	AE/AT

MODIFICATION OF THE PROGRAM

Changing Number of Possible Reaction Species

All variables dimensioned for the number of possible reaction species are in the common labeled SPECES which takes two cards. These variables are dimensioned for 150 species in the main program and subroutines SEARCH, SAVE, HCALC, MATRIX, CPHS, EQLBRM, OUT1, THERMP, ROCKET, RKTOUT, FROZEN, SHCK, and DETON. The two cards are the same in all of these routines. The 150 number may be either increased or decreased, to any number as required. No other program changes are necessary.

Actually the number 150 is considerably larger than necessary for most chemical systems. Since each species requires 51 storages, an obvious way to reduce storage is to decrease the size of this number. This procedure might be desirable if a new application were added and additional storage were required.

Eliminating an Application

Any application module may be removed simply by removing the statement calling the controlling subroutine (THERMP, ROCKET, SHCK, or DETON) and removing the

subroutine(s) in the application module. The calling statements are near the end of the main program (see MODULAR FORM OF THE PROGRAM, p. 75).

Adding an Application

An application may be added by doing the following:

(1) Giving the type of problem a name and including the name in the main program in the following places:

(a) Namelist INPT2

(b) Logical statement

(c) Statement setting it to false before the INPT2 read

(2) Programming an application module as described in the section Application Module (p. 76).

(3) Calling the module when the name variable is true after the INPT2 namelist data have been processed in the main program.

Modifying Input and Output Modules

The input modules may be modified as long as the common variables used by EQLBRM are properly set. These variables are indicated in the description of the modules.

The listed output may be modified. Labeled common variables which are calculated by the equilibrium module and which are used in subroutine OUT2 and OUT3 include HSUM, SSUM, CPR, DLVTP, DLVPT, GAMMAS, PPP, TTT, VLM, TOTN, and EN. (Variables are defined in appendix B.)

The units in the output may be changed in OUT2 and RKTOUT. Either a variable format (FMT) or a special E-format (subroutine EFMT) is used for all output. The variable format (FMT) is described in the section "BLOCK DATA" and the adjustments in number of decimal places may be easily reset in the output routines. The parameter labels may be adjusted in the DATA statements in BLOCK DATA, the output routines, or in the application module itself.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, February 23, 1971,
129-01.

APPENDIX A

SYMBOLS

A	area, m^2
A_e/A_t	ratio of nozzle exit area to throat area, eq. (106)
a	velocity of sound, m/sec, eqs. (67) and (74)
$a_{S,T}$	velocity of sound, m/sec, defined by eq. (85)
a_{ij}	stoichiometric coefficients, kg-atoms of element i per kg-mole of species j, $(\text{kg-atom})_i/(\text{kg-mole})_j$
$a_{ij}^{(k)}$	stoichiometric coefficients, kg-atoms of element i per kg-mole of reactant j (oxidant if k = 1, fuel if k = 2), $(\text{kg-atom})_i^{(k)}/(\text{kg-mole})_j^{(k)}$
a_i(i=1 to 7)	least squares coefficients, eqs. (90), (91), and (92)
b_i	kg-atoms of element i per kg of mixture, $(\text{kg-atom})_i/\text{kg}$, eq. (7b)
$b_i^{(k)}$	assigned kg-atoms of element i per kilogram of total oxidant (k = 1) or total fuel (k = 2), $(\text{kg-atom})_i^{(k)}/\text{kg}^{(k)}$, eq. (187)
b_i^o	assigned kg-atoms of element i per kg of total reactant, $(\text{kg-atom})_i/\text{kg}$, eq. (191)
C_F	coefficient of thrust, eq. (105)
$\left(C_p^o\right)_j$	standard state constant pressure specific heat for species or reactant j, $J/(\text{kg-mole})_j(K)$
$\left(C_v^o\right)_j$	standard state constant volume specific heat for species j, $J/(\text{kg-mole})_j(K)$
$\mathscr{C}_o$	constant pressure specific heat of total reactant, kg-mole/kg, eq. (206)
$\mathscr{C}_j$	$\left(C_p^o\right)_j/R$, dimensionless constant pressure specific heat for species j
$\left(\mathscr{C}_v\right)_j$	$\left(C_v^o\right)_j/R$, dimensionless constant volume specific heat for species j
c^*	characteristic velocity, m/sec, eq. (103)
c_p	constant pressure specific heat of mixture, J/(kg)(K), eqs. (49), (59), or (121)

c_v	constant volume specific heat of mixture, J/(kg)(K), eq. (70) or (124)
F	Helmholtz free energy of mixture with constraints, defined by eq. (33), J/kg; or force N, eq. (98)
%F	percent of total fuel in total reactant by weight (or mass)
f	Helmholtz free energy of mixture, J/kg, eqs. (30) and (31)
f/a	fuel to air weight (or mass) ratio or fuel to oxidant weight (or mass) ratio
G	Gibbs free energy of mixture with constraints, J/kg, defined by eq. (8)
$\mathscr{g}_j$	μ_j/RT, dimensionless Gibbs free energy for species j
g	Gibbs free energy of mixture, J/kg, eq. (5)
g_c	conversion factor
$\left(H_T^o\right)_j$	standard state enthalpy for species j, J/(kg-mole)$_j$
$\left(H_T^o\right)_j^{(k)}$	enthalpy of reactant j (k = 1 for oxidant, k = 2 for fuel), J/(kg-mole)$_j^{(k)}$, eq. (192)
$\left(\Delta H_f^o\right)_T$	heat of formation at temperature T, J/(kg-mole)
$\mathscr{h}$	h/RT, enthalpy of mixture, (kg-mole)/kg
$\mathscr{h}_j$	$\left(H_T^o\right)_j \Big/ RT$, dimensionless enthalpy for species j
$\mathscr{h}_o$	enthalpy of total reactant, kg-mole/kg, eq. (193)
$\mathscr{h}^{(k)}$	enthalpy of total oxidant (k = 1) or total fuel (k = 2), (kg-mole/kg)^k, eq. (192)
h	enthalpy of mixture, J/kg, eq. (14)
h_o	enthalpy of total reactants, J/kg, eq. (193)
h'	term defined by right side of eq. (156)
h''	term defined by right side of eq. (171)
h*	term defined by right side of eq. (131)
I	specific impulse, N/(kg/sec) or m/sec, eq. (99)
I_{sp}	specific impulse with exit and ambient pressures equal, N/(kg/sec) or m/sec, eq. (100)
I_{vac}	vacuum specific impulse, N/(kg/sec) or m/sec, eq. (101)
M	molecular weight of mixture, kg/kg-mole, eq. (2)

M_i	atomic weight of chemical element i, $(kg/kg\text{-}atom)_i$, eq. (190)
M_o	molecular weight of total reactant, kg/kg-mole, eq. (197)
$M^{(k)}$	molecular weight of total oxidant (k = 1) or total fuel (k = 2), $(kg/kg\text{-}mole)^{(k)}$, eq. (196)
$M_j^{(k)}$	molecular weight of reactant j (oxidant if k = 1, fuel if k = 2), $(kg/kg\text{-}mole)_j^{(k)}$, eq. (190)
$\mathscr{M}$	Mach number, eq. (102)
m_j	moles of reactant j per kilogram of total reactant, $(kg\text{-}mole)_j/kg$, eq. (205)
$\dot{m}$	mass flow rate, kg/sec, eq. (96)
$N_j^{(k)}$	kg-moles of reactant j (oxidant if k = 1, fuel if k = 2), $(kg\text{-}mole)_j^{(k)}$
n	moles of mixture, kg-mole/kg, eq. (3)
n_j	kg-moles of species j per kg of mixture, $(kg\text{-}mole)_j/kg$
$n_j^{(k)}$	kg-moles of reactant j per kg of total oxidant (k = 1) or total fuel (k = 2), $(kg\text{-}mole)_j^{(k)}/kg^{(k)}$, eq. (188) or (189)
o/f	oxidant to fuel weight (or mass) ratio
P	pressure, N/m^2
P_{atm}	pressure, atm (see eqs. (11) and (17))
P_c/P_e	ratio of combustion pressure to exit pressure
P_o	assigned or initial pressure, N/m^2
P'	term defined by right side of eq. (155)
P''	term defined by right side of eq. (170)
P*	term defined by right side of eq. (130)
R	universal gas constant, 8314.3 J/(kg-mole)(K)
r	equivalence ratio, eq. (204)
S_j	entropy of species j, $J/(kg\text{-}mole)_j(K)$, eq. (17)
$(S_T^o)_j$	standard state entropy for species j, $J/(kg\text{-}mole)_j(K)$
$\mathscr{S}$	s/R, entropy of mixture, (kg-mole)/kg

$\mathscr{S}_j$	S_j/R, dimensionless entropy for species j
$\mathscr{S}_o$	entropy of total reactants, (kg-mole)/kg, eq. (207)
s	entropy of mixture, J/(kg)(K), eq. (16)
s_o	entropy of total reactants, J/(kg)(K), eq. (207)
T	temperature, K
$\left(U_T^o\right)_j$	standard state internal energy for species j, J/(kg-mole)$_j$
$\left(U_T^o\right)_j^{(k)}$	internal energy of reactant j (oxidant if k = 1, fuel if k = 2), (J/kg-mole)$_j^{(k)}$, eq. (194)
$\mathscr{U}_j$	$\left(U_T^o\right)_j \Big/ RT$, dimensionless internal energy for species j
$\mathscr{U}_o$	internal energy of total reactant, (kg-mole)/kg, eq. (195)
$\mathscr{U}^{(k)}$	internal energy of total oxidant (k = 1) or total fuel (k = 2), (kg-mole/kg)$^{(k)}$, eq. (194)
u	velocity (in shock problems, velocity relative to incident or reflected shock front), m/sec
u_1	velocity at station 1 (in shock problems, velocity of unshocked gas relative to incident shock front), m/sec
u_2	velocity at station 2 (in shock problems, velocity of incident-shocked gas relative to incident shock front), m/sec
u_2^*	velocity of incident-shocked gas relative to reflected shock front, m/sec, eq. (128)
u_5	velocity of reflected-shocked gas relative to reflected shock front, m/sec, eq. (129)
u'	internal energy of mixture, J/kg, eq. (38)
u_o'	internal energy of total reactant, J/kg, eq. (195)
V	specific volume, m^3/kg
V^+	positive oxidation state of total reactant, eq. (202)
V^-	negative oxidation state of total reactant, eq. (203)
$V^{+(k)}$	positive oxidation state of total oxidant (k = 1) or total fuel (k = 2), eq. (200)

$V^{-(k)}$	negative oxidation state of total oxidant (k = 1) or total fuel (k = 2), eq. (201)
V_i^+	positive oxidation state of chemical element i
V_i^-	negative oxidation state of chemical element i
v	actual velocity of shocked or unshocked gases in fixed coordinates, m/sec, eq. (125)
v_1	actual velocity of unshocked gases in fixed coordinates ($v_1 = 0$), eq. (126)
v_2	actual velocity of incident-shocked gases in fixed coordinates, m/sec, eq. (127)
v_5	actual velocity of reflected-shocked gases in fixed coordinates (v_5 assumed to be zero), m/sec, eq. (129)
$W_j^{(k)}$	weight of reactant j (oxidant if k = 1, fuel if k = 2), $kg_j^{(k)}$, eq. (188)
w	shock front velocity, m/sec, eq. (125)
w_R	reflected shock front velocity, m/sec, eq. (128)
w_S	incident shock front velocity, m/sec, eq. (126)
γ	ratio of specific heats, eq. (72)
γ_S	isentropic exponent, eqs. (71) and (73)
$\gamma_{S,T}$	special isentropic exponent defined by eq. (84)
λ	control factor defined by eq. (78) or (146)
λ_i	Lagrangian multiplier for chemical element i, $J/(kg\text{-atom})_i$
λ_1	control factor defined by eq. (76)
λ_2	control factor defined by eq. (77)
λ_3	control factor defined by eq. (144)
λ_4	control factor defined by eq. (145)
μ_j	chemical potential of species j, $J/(kg\text{-mole})_j$, eq. (6)
μ_j^o	standard state chemical potential for species j, $J/(kg\text{-mole})_j$
π_i	$-\lambda_i/RT$, Lagrangian multiplier for chemical element i, $kg\text{-mole}/(kg\text{-atom})_i$
ρ	density of mixture, kg/m^3, eq. (1)
ρ_o	density of total reactant, kg/m^3, eq. (199)

$\rho^{(k)}$	density of total oxidant (k = 1) or total fuel (k = 2), $(kg/m^3)^{(k)}$, eq. (198)
$\rho_j^{(k)}$	density of reactant j (oxidant if k = 1, fuel if k = 2), $(kg/m^3)_j^{(k)}$, eq. (198)

Subscripts:

a	ambient
c	combustion; condensed
e	exit
g	gas
k	iteration k
m	melting temperature
o	total reactant; zeroth iteration
t	throat
1, 2, 5	stations

Superscripts:

o	an assigned or initial condition
k	1 if oxidant, 2 if fuel

Indices:

l	number of chemical elements (if ions are considered, number of chemical elements plus one)
m	number of possible gaseous species
n	number of possible species, gases and condensed
NREAC	number of reactants

APPENDIX B

COMMON VARIABLES

All common variables are given in this appendix except those with common label OUPT. These latter variables are discussed in section BLOCK DATA (p. 90).

Variable	Dimension	Common label	Routines where used	Description and comments
A	15,150	SPECES	SEARCH MATRIX EQLBRM HCALC	a_{ij}, stoichiometric coefficient of ith element in j^{th} species.
AC	2	MISC	SAVE	Saves JSOL (AC(1)) and JLIQ (AC(2)).
AEAT	13	PERF	ROCKET RKTOUT SHCK DETON	In RKTOUT, area ratios A_e/A_t to be printed out. In SHCK, M2M1, molecular weight ratio. In DETON, GM1, γ for unburned gas.
AM	2	MISC	REACT HCALC	$AM(k) \equiv M^{(k)}$, molecular weight of total oxidant (k = 1) or total fuel (k = 2).
ANUM	15,5	MISC	REACT HCALC OUT1 SHCK	Stoichiometric coefficients of reactants. First subscript refers to the reactant, the second, the element on the card. (See section Subroutine REACT).
APP	13	PERF	ROCKET RKTOUT SHCK	P_c/P_e, ratio of chamber pressure to exit pressure. In SHCK, RRHO, a density ratio.
AREA	1	PERF	ROCKET	Logical variable indicating (if true) area ratios have been assigned.

Variable	Dimension	Common label	Routines where used	Description and comments
ATOM	3,101	MISC	REACT BLOCK DATA	For j^{th} atom: ATOM (1,j) ≡ atomic symbol (H, HE, . . .). ATOM (2,j) ≡ atomic weight. ATOM (3,j) ≡ atomic valence.
AWT	1	PERF	ROCKET	nT/Pu at throat. AWT is used in obtaining area ratios, eq. (106).
E0	15	MISC	NEWOF MATRIX	b_i^o, assigned kg-atoms of element i per kg of total reactant.
B0P	15,2	MISC	Main REACT NEWOF	B0P(i,1) ≡ $b_i^{(1)}$, kg-atoms of ith element per kg of total oxidant. B0P(i,2) ≡ $b_i^{(2)}$, kg-atoms of ith element per kg of total fuel, eq. (187).
CALCH	1	INDX	Main SAVE HCALC THERMP ROCKET SHCK	Logical variable indicating (if true) zeros were punched in card columns 37 and 38 of at least one REACTANTS card.
COEF	2,7,150	SPECES	SEARCH CPHS	Constants in empirical equations for thermodynamic functions. COEF(i,j,k): i = 1 for upper temperature interval and i = 2 for the lower one; j = 1, . . . 7, for the 7 coefficients, a_j; k = 1, . . . 150 for the number of species, eqs. (90) to (92).
CONVG	1	INDX	EQLBRM MATRIX FROZEN	Logical variable indicating convergence is true.

Variable	Dimension	Common label	Routines where used	Description and comments
CPCVEQ	1	INDX	EQLBRM MATRIX	Equivalenced to LOGV in EQLBRM and MATRIX (see LOGV)
CPCVFR	1	INDX	--------	Temporary storage.
CPR	13	POINTS	EQLBRM OUT2 DETON SHCK ROCKET FROZEN	c_p/R, constant pressure specific heat, kg-mole/kg (eq. (59) or (121)).
CPSUM	1	MISC	EQLBRM CPHS MATRIX HCALC ROCKET FROZEN SHCK	c_p/R, frozen constant pressure specific heat, kg-mole/kg, eq. (121).
CR	1	MISC	-----	Not used.
CSTR	1	PERF	RKTOUT	c*, characteristic velocity, ft/sec.
DATA	22	MISC	Main HCALC REACT SHCK DETON	Temporary storage.
DELN	150	SPECES	EQLBRM Main	In EQLBRM: Corrections to $\ln n_j$ for gases or n_j for condensed. In Main: Equivalent to ENSERT, an array of names read from INSERT cards.
DENS	15	MISC	REACT OUT1	Density of reactant read from input card.

Variable	Dimension	Common label	Routines where used	Description and comments
DLVPT	13	POINTS	EQLBRM OUT2 DETON SHCK FROZEN	$\left(\frac{\partial \ln V}{\partial \ln P}\right)_T$, eq. (51) or (123).
DLVTP	13	POINTS	EQLBRM OUT2 DETON SHCK ROCKET FROZEN	$\left(\frac{\partial \ln V}{\partial \ln T}\right)_P$, eq. (50) or (122).
EN	150,13	SPECES	Main EQLBRM CPHS MATRIX SAVE OUT3 SEARCH SHCK HCALC RKTOUT FROZEN	n_j, kg-moles of jth species/kg of mixture ($j \leq 150$). The second subscript is for point number for output. In SEARCH, EN is equivalenced to DATE, the dates read from THERMO data.
ENLN	150	SPECES	Main SEARCH EQLBRM MATRIX SAVE	$\ln n_j$ (see EN). In the main program ENLN is equivalenced to OMIT, an array for storing names on OMIT cards.
ENLSAV	1	MISC	SAVE	ln n, saved for a particular point (see ENN).
ENN	1	MISC	Main EQLBRM MATRIX SAVE ROCKET	n, moles of mixture, kg-mole/kg (eq. (3) for assigned volume problems or eq. (79) for assigned pressure problems).

Variable	Dimension	Common label	Routines where used	Description and comments
ENNL	1	MISC	Main EQLBRM SAVE	ln n, (see ENN).
ENSAVE	1	MISC	SAVE	n, saved for a particular point (see ENN).
ENTH	15	MISC	REACT HCALC OUT1	For assigned pressure problems, $\left(H_T^o\right)_j$, assigned enthalpy of a reactant in calories per mole. For assigned volume (or density) problems, $\left(U_T^o\right)_j$, assigned internal energy of a reactant in calories per mole.
EQL	1	PERF	Main ROCKET OUT3 RKTOUT SHCK DETON	Logical variable indicating (if true) equilibrium calculations rather than frozen.
EQRAT	1	MISC	Main NEWOF OUT1	r, equivalence ratio (eq. (204)).
FAZ	15	MISC	Main REACT HCALC OUT1	Alphameric letter read from reactant cards. The letter G indicates gas; any other letter indicates condensed phase.
FOX	15	MISC	REACT HCALC OUT1	Alphameric letter, F or O, read from reactant cards indicating reactant is a fuel (F or blank) or oxidant (O).
FPCT	1	MISC	Main	Logical variable in namelist INPT2 (see table VIII).

Variable	Dimension	Common label	Routines where used	Description and comments
FROZ	1	PERF	ROCKET	Logical variable in namelist RKTINP. If true, rocket performance is desired with frozen composition.
G	20, 21 (Double precision)	DOUBLE	EQLBRM MATRIX GAUSS SHCK	Matrix region.
GAMMAS	13	POINTS	EQLBRM OUT2 DETON SHCK ROCKET RKTOUT FROZEN	γ_S or $\gamma_{S,T}$ isentropic exponent exponent (eq. (71), (73), or (84)).
H0	150	SPECES	EQLBRM CPHS MATRIX HCALC FROZEN RKTOUT SHCK OUT3	$\mathscr{H}_j$, dimensionless enthalpy for species j. H0 is used as a temporary storage in OUT3.
HP	1	INDX	Main EQLBRM MATRIX THERMP DETON ROCKET	Logical variable indicating (if true) either enthalpy and pressure or internal energy and volume (or density) have been assigned.
HPP	2	MISC	REACT HCALC NEWOF	$\mathscr{H}^{(k)}T$ or $\mathscr{U}^{(k)}T$, enthalpy or internal energy of total oxidant (k = 1) and total fuel (k = 2) (eqs. (192) and (194)).

Variable	Dimension	Common label	Routines where used	Description and comments
HSUB0	1	MISC	NEWOF HCALC MATRIX DETON SHCK THERMP	h_0/R or u_0'/R assigned enthalpy or zero internal energy of total reactant (eqs. (193) and (195)).
HSUM	13	POINTS	EQLBRM MATRIX OUT2 DETON SHCK ROCKET RKTOUT FROZEN	$\mathscr{H}$ in MATRIX and h/R at the end of EQLBRM and in the other routtines (eqs. (29) and (14)).
IC	1	INDX	--------	Not used.
IDEBUG	1	INDX	Main EQLBRM DETON SHCK ROCKET THERMP	When set to a value i (i > 0), intermediate output is printed for all points ≥ i.
IMAT	1	INDX	EQLBRM MATRIX GAUSS	Number of rows in matrix setup.
IONS	1	INDX	Main EQLBRM SAVE	Logical variable indicating (if true) ionic species are to be considered.
IP	1	INDX	THERMP DETON ROCKET	Index for pressure or specific volume values.

Variable	Dimension	Common label	Routines where used	Description and comments
IQ1	1	INDX	Main EQLBRM SAVE MATRIX	Number of elements plus the number of condensed species included in matrix equations plus 1.
IQSAVE	1	INDX	SAVE	IQ1 saved for a particular point when ISV is negative.
ISUB	1	INDX	ROCKET	Index for SUBAR values (see SUBAR).
ISUP	1	INDX	ROCKET	Index for SUPAR values (see SUPAR).
ISV	1	INDX	SAVE THERMP DETON SHCK ROCKET	ISV > 0: Use compositions from last point (numbered ISV) as estimates for current point (numbered NPT). ISV < 0: Store compositions in SLN array to use as estimates for future points. Make ISV positive and proceed as with ISV > 0. ISV = 0: Use compositions stored in SLN array as estimates for current point (numbered NPT).
IT	1	INDX	Main THERMP ROCKET RKTOUT DETON	Index for T values (see T).
ITM	1	INDX	ROCKET FROZEN	Integer 1.
ITNUM	1	INDX	ROCKET	Iteration number for converging to assigned area ratio.

Variable	Dimension	Common label	Routines where used	Description and comments
IUSE	150	SPECES	Main EQLBRM CPHS MATRIX HCALC SAVE SEARCH FROZEN SHCK	See section "IUSE array".
JLIQ	1	INDX	EQLBRM SAVE	Index of condensed species which is included simultaneously with another condensed phase of the same species. JLIQ is the index for the phase in the higher temperature range; JSOL is the index for the phasc in the lower temperature range. Otherwise JLIQ = JSOL = 0.
JS1	1	INDX	CPHS EQLBRM FROZEN HCALC SHCK	Index for species for which thermodynamic functions are to be calculated in CPHS.
JSOL	1	INDX	EQLBRM ROCKET SAVE	See JLIQ.
KASE	1	INDX	Main OUT1	Optional identifying case number for a set of reactants. The variable is part of namelist INPT2.
KMAT	1	INDX	EQLBRM MATRIX	Number of columns in matrix setup. KMAT = IMAT + 1.

Variable	Dimension	Common label	Routines where used	Description and comments
LLMT	15	MISC	Main REACT SEARCH HCALC EQLBRM SAVE NEWOF	Alphameric symbols for elements in the chemical system being processed.
LOGV	1	INDX	EQLBRM MATRIX	Logical variable indicating (if true) matrix setup given in table IV. LOGV is equivalenced to CPCVEQ which appears in common INDX.
LSAVE	1	INDX	SAVE	LLMT(NLM), the last element symbol is saved in LSAVE for use at some future point. If IONS is true and LSAVE is not "E", then ionic species were removed.
MOLES	1	INDX	Main REACT OUT1 HCALC	Logical variable indicating (if true) that the relative amounts of the reactants have been specified in terms of moles.
NAME	15,5	MISC	Main REACT HCALC DETON SHCK OUT1	Alphameric symbols for elements as given on the reactant cards. Allowance is made for up to 5 symbols and 15 reactants.
NC	1	INDX	Main SEARCH EQLBRM FROZEN	Number of condensed species in thermodynamic data for a particular system.

Variable	Dimension	Common label	Routines where used	Description and comments
NEWR	1	INDX	Main REACT SEARCH	Logical variable indicating (if true) that the search of tape 4 has not yet been made for thermodynamic data for species in a new chemical system.
NFZ	1	INDX	ROCKET FROZEN RKTOUT	Index of point where equilibrium composition is to be frozen. NFZ = 1 for rocket problems.
NLM	1	INDX	Main REACT SEARCH HCALC NEWOF EQLBRM MATRIX	Number of elements in the chemical system.
NOF	1	INDX	Main THERMP DETON SHCK ROCKET	Number of o/f values. Note: mixture values given in the form of equivalence ratio, percent fuel, or fuel-air ratio are converted to o/f values in the main program.
NOMIT	1	INDX	Main SEARCH EQLBRM MATRIX REACT	Number of species to be omitted.
NP	1	INDX	Main THERMP DETON ROCKET	Number of pressure values in the P array in namelist INPT2.
NPP	1	INDX	ROCKET	Number of P_c/P_e values. This is equal to the number of PCP values in namelist RKTINP plus 2 to include chamber and throat.

Variable	Dimension	Common label	Routines where used	Description and comments
NPT	1	INDX	All routines except Main, REACT, GAUSS, and SEARCH	Index for the data saved for output ($1 \leq NPT \leq 13$).
NREAC	1	INDX	Main REACT HCALC OUT1 DETON SHCK	Number of reactants.
NS	1	INDX	Main SEARCH HCALC OUT3 EQLBRM CPHS MATRIX FROZEN SHCK RKTOUT SAVE	Number of species considered in a particular chemical system.
NSERT	1	INDX	Main	Number of condensed species listed on INSERT cards.
NSUB	1	INDX	ROCKET	Number of SUBAR values (see SUBAR).
NSUP	1	INDX	ROCKET	Number of SUPAR values (see SUPAR).
NT	1	INDX	Main THERMP DETON ROCKET	Number of temperature values listed in T schedule in namelist INPT2.

Variable	Dimension	Common label	Routines where used	Description and comments
OF	1	MISC	Main HCALC NEWOF OUT1 DETON SHCK ROCKET THERMP	o/f, oxidant to fuel weight ratio for current point.
OXF	15	MISC	Main THERMP DETON SHCK ROCKET	o/f, oxidant to fuel weight ratios. In the main program, OXF is equivalenced to MIX, an INPT2 namelist variable.
P	26	POINTS	Main THERMP DETON SHCK ROCKET	Assigned pressure schedule in namelist INPT2. Values are converted to atmosphere units in the main program. For TV, UV, and SV problems, assigned volumes, VL, in cm^3/g are stored in the P array in the main program.
PCP	22	PERF	ROCKET SHCK DETON	Pressure ratios read in with RKTINP namelist. Storage is used as temporary storage in SHCK and DETON.
PECWT	15	MISC	REACT HCALC OUT1	Relative weight or number of moles of reactants as read from card columns 46 to 52 on the reactant cards.
PP	1	MISC	HCALC EQLBRM THERMP DETON SHCK ROCKET FROZEN	Assigned pressure in atmospheres for current point.

Variable	Dimension	Common label	Routines where used	Description and comments
PPP	13	POINTS	EQLBRM OUT2 DETON SHCK RKTOUT FROZEN	Static pressure in atmospheres stored for output.
R	1	MISC	Main REACT HCALC OUT2 THERMP DETON	Universal gas constant, 1.987165 cal/(g-mole)(K).
RH	2	MISC	REACT NEWOF	$\rho^{(1)}$, density of total oxidant and $\rho^{(2)}$, density of total fuel, eq. (198).
RHOP	1	MISC	Main OUT1 NEWOF	ρ_o, density of total reactant, eq. (199).
RMW	15	MISC	REACT HCALC	Molecular weight of individual reactants.
RR	1	MISC	Main OUT2 EQLBRM DETON SHCK ROCKET RKTOUT FROZEN	Universal gas constant, 8314.3 J/(kg-mole)(K).
RTEMP	15	MISC	REACT HCALC OUT1 DETON SHCK	Temperatures read from reactant card columns 64 to 71.

Variable	Dimension	Common label	Routines where used	Description and comments
S	150	SPECES	HCALC EQLBRM CPHS MATRIX FROZEN SHCK	$\left(s_T^o\right)_j / R$, dimensionless entropy calculated from coefficients for reaction species. See appendix A for definition.
SHOCK	1	INDX	Main HCALC EQLBRM	Logical variable indicating (if true) SHOCK problem.
SLN	150	SPECES	SAVE	$\ln n_j$ for gases and n_j for condensed species for a particular point (see ISV with negative value).
S0	1	MISC	Main EQLBRM MATRIX ROCKET FROZEN	In INPT2 namelist for SP and SV problem, entropy in cal/(g)(K). For SHOCK problems S0 = $\mathcal{S}_o$, eq. (207). For RKT problems, S0 = s/R, eq. (16), for the combustion point (NPT = 1).
SONVEL	13	POINTS	OUT2 DETON RKTOUT	a, velocity of sound, eq. (74), or $a_{S,T}$, eq. (85).
SP	1	INDX	Main EQLBRM MATRIX THERMP ROCKET	Logical variable indicating (if true) entropy and either pressure (VOL is false) or volume (VOL is true) have been assigned. In namelist INPT2, SP indicates an SP problem.
SPIM	13	PERF	DETON SHCK RKTOUT	In RKTOUT, I_{sp}, specific impulse with ambient and exit pressures equal, (lb-force)(sec)/lb-mass. Storage is used for other variables in SHCK and DETON.
SS0	1	PERF	-----	Not used.

Variable	Dimension	Common label	Routines where used	Description and comments
SSUM	13	POINTS	HCALC EQLBRM OUT2 ROCKET FROZEN SHCK	s/R, entropy of mixture, (kg-mole)/kg.
SUB	150,3	SPECES	Main SEARCH EQLBRM OUT1 RKTOUT SHCK	Alphameric names of species read from THERMO data. Each name takes 3 words, 4 characters each.
SUBAR	13	PERF	DETON SHCK ROCKET	In ROCKET and RKTINP namelist, subsonic area ratios. SUBAR is equivalenced to other variables in SHCK and DETON.
SUMN	1	MISC	Main EQLBRM MATRIX	$\sum_{j=1}^{m} n_j$, moles of mixture, kg-mole/kg.
SUPAR	13	PERF	DETON SHCK ROCKET	In ROCKET and RKTINP namelist, supersonic area ratios. SUPAR is equivalenced to other variables in SHCK and DETON.
T	26	POINTS	Main THERMP DETON SHCK ROCKET RKTOUT	T, assigned temperature schedule in namelist INPT2. Values are in degrees Kelvin.
TEMP	50,2	SPECES	SEARCH HCALC EQLBRM GAUSS FROZEN	Temperature ranges of individual condensed species. The lower value is in TEMP(j,1).

Variable	Dimension	Common label	Routines where used	Description and comments
THIGH	1	MISC	Main SEARCH HCALC EQLBRM SHCK	Highest temperature in temperature range of species in the THERMO data.
TLN	1	MISC	EQLBRM CPHS HCALC SHCK FROZEN	ln T.
TLOW	1	MISC	Main SEARCH HCALC EQLBRM FROZEN SHCK	Lowest temperature in temperature range of species in the THERMO data.
TM	1	MISC	HCALC EQLBRM MATRIX	$\ln(P_{atm}/n)$.
TMID	1	MISC	Main SEARCH CPHS	Common temperature of two temperature ranges of the THERMO data.
TOTN	13	POINTS	EQLBRM OUT3 FROZEN RKTOUT	$\sum_{j=1}^{NS} n_j$, used in the calculation of mole fractions.
TP	1	INDX	Main EQLBRM MATRIX THERMP DETON SHCK ROCKET	Logical variable indicating (if true) temperature and either pressure (VOL is false) or volume (VOL is true) have been assigned. The assignments may be for a complete problem (TP) or a particular point.

Variable	Dimension	Common label	Routines where used	Description and comments
TRACE	1	MISC	Main EQLBRM OUT3 RKTOUT SHCK	If TRACE > 0, print mole fractions $\geq$ TRACE in special E-format. TRACE is namelist INPT2 variable.
TT	1	MISC	NEWOF HCALC EQLBRM CPHS MATRIX THERMP DETON SHCK ROCKET FROZEN	Current temperature.
TTT	13	POINTS	EQLBRM OUT2 DETON SHCK ROCKET RKTOUT FROZEN	Temperature stored for printout.
V	13	POINTS	Main REACT OUT2 OUT3 VARFMT THERMP DETON SHCK RKTOUT EFMT	Temporary storage. Assigned volume in INPT2 namelist.

Variable	Dimension	Common label	Routines where used	Description and comments
VACI	13	PERF	RKTOUT DETON SHCK	In RKTCUT, I_{vac}, (lb force) (sec)/(lb mass) Storage is used for other variables in SHCK and DETCN.
VLM	13	POINTS	EQLBRM THERMP SHCK FROZEN OUT2	Volume, cm^3/g, stored for output.
VMIN	2	MISC	Main REACT NEWOF	$V^{-(k)}$, negative oxidation state of total oxidant (if k = 1) or total fuel (if k = 2), eq. (201).
VMOC	13	PERF	RKTOUT DETON	$\mathcal{M}$, Mach number, eq. (102). Used as temporary storage in DETON.
VOL	1	INDX	Main HCALC NEWOF EQLBRM MATRIX THERMP	Logical variable indicating (if true) volume has been assigned.
VPLS	2	MISC	Main REACT NEWOF	$V^{+(k)}$, positive oxidation state of total oxidant (if k = 1) or total fuel (if k = 2), eq. (200).
WM	13	POINTS	OUT2 EQLBRM DETON SHCK ROCKET RKTOUT FROZEN	M, molecular weight of the mixture, kg/kg-mole, eq. (2).

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Variable	Dimension	Common label	Routines where used	Description and comments
WP	2	MISC	Main REACT HCALC	$WP(k) = \sum_{j=1}^{NREAC} W_j^{(k)}$.
X	20 (Double precision)	DOUBLE	EQLBRM GAUSS MATRIX SHCK	Answer region for matrix solution.

APPENDIX D

THERMO DATA (FORMAT AND LISTING)

The order and format of the input data cards in this appendix are given in the following table:

Card order	Contents	Format	Card column
1	THERMO	3A4	1 to 6
2	Temperature ranges for 2 sets of coefficients: lowest T, common T, and highest T	3F10.3	1 to 30
3	Species name	3A4	1 to 12
	Date	2A3	19 to 24
	Atomic symbols and formula	4(A2, F3.0)	25 to 44
	Phase of species (S, L, or G for solid, liquid, or gas, respectively)	A1	45
	Temperature range	2F10.3	46 to 65
	Integer 1	I15	80
4	Coefficients a_i(i = 1 to 5) in equations (90) to (92) (for upper temperature interval)	5(E15.8)	1 to 75
	Integer 2	I5	80
5	Coefficients in equations (90) to (92) (a_6, a_7 for upper temperature interval, and a_1, a_2, and a_3 for lower)	5(E15.8)	1 to 75
	Integer 3	I5	80
6	Coefficients in equations (90) to (92) (a_4, a_5, a_6, a_7 for lower temperature interval)	4(E15.8)	1 to 60
	Integer 4	I20	80
(a)	Repeat cards numbered 1 to 4 in cc 80 for each species		
(Final card)	END (Indicates end of thermodynamic data)	3A4	1 to 3

[a]Gaseous species and condensed species with only one condensed phase can be in any order. However, the sets for two or more condensed phases of the same species must be adjacent. If there are more than two condensed phases of a species, their sets must be either in increasing or decreasing order according to their temperature intervals.

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The program writes the THERMO data on tape 4 as the cards are read. The data are written on tape with the same formats as the cards with two minor exceptions. The THERMO code card is omitted and the card numbers in card colunn 80 are also omitted.

A listing of the THERMO data cards included with the program follows. These cards were made by the program described in reference 15.

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TABLE I. - ITERATION EQUATIONS TO DETERMINE EQUILIBRIUM COMPOSITIONS FOR EITHER ASSIGNED TEMPERATURE AND PRESSURE, ENTHALPY AND PRESSURE, OR ENTROPY AND PRESSURE

Equation \ Variables	z_1	z_2	---	z_l	Δn_{m+1}	---	Δn_n	$\Delta \ln n$	$\Delta \ln T$ (a)	Right side
(24)	$\sum_{j=1}^{m} a_{1j}a_{1j}n_j$	$\sum_{j=1}^{m} a_{1j}a_{2j}n_j$	---	$\sum_{j=1}^{m} a_{1j}a_{lj}n_j$	$a_{1,m+1}$	---	a_{1n}	$\sum_{j=1}^{m} a_{1j}n_j$	$\sum_{j=1}^{m} a_{1j}n_j\mathscr{X}_j$	$(b_1^o - b_1) + \sum_{j=1}^{m} a_{1j}n_j\mathscr{G}_j$
	$\sum_{j=1}^{m} a_{2j}a_{1j}n_j$	$\sum_{j=1}^{m} a_{2j}a_{2j}n_j$	---	$\sum_{j=1}^{m} a_{2j}a_{lj}n_j$	$a_{2,m+1}$	---	a_{2n}	$\sum_{j=1}^{m} a_{2j}n_j$	$\sum_{j=1}^{m} a_{2j}n_j\mathscr{X}_j$	$(b_2^o - b_2) + \sum_{j=1}^{m} a_{2j}n_j\mathscr{G}_j$
	---	---	---	---	---	---	---	---	---	---
	$\sum_{j=1}^{m} a_{lj}a_{1j}n_j$	$\sum_{j=1}^{m} a_{lj}a_{2j}n_j$	---	$\sum_{j=1}^{m} a_{lj}a_{lj}n_j$	$a_{l,m+1}$	---	a_{ln}	$\sum_{j=1}^{m} a_{lj}n_j$	$\sum_{j=1}^{m} a_{lj}n_j\mathscr{X}_j$	$(b_l^o - b_l) + \sum_{j=1}^{m} a_{lj}n_j\mathscr{G}_j$
(25)	$a_{1,m+1}$	$a_{2,m+1}$	---	$a_{l,m+1}$	0	---	0	0	$\mathscr{X}_{m+1}$	$\mathscr{G}_{m+1}$
	---	---	---	---	---	---	---	---	---	---
	a_{1n}	a_{2n}	---	a_{ln}	0	---	0	0	$\mathscr{X}_n$	$\mathscr{G}_n$
(26)	$\sum_{j=1}^{m} a_{1j}n_j$	$\sum_{j=1}^{m} a_{2j}n_j$	---	$\sum_{j=1}^{m} a_{lj}n_j$	0	---	0	0	$\sum_{j=1}^{m} n_j\mathscr{X}_j$	$n - \sum_{j=1}^{m} n_j + \sum_{j=1}^{m} n_j\mathscr{G}_j$
(27) (b)	$\sum_{j=1}^{m} a_{1j}n_j\mathscr{X}_j$	$\sum_{j=1}^{m} a_{2j}n_j\mathscr{X}_j$	---	$\sum_{j=1}^{m} a_{lj}n_j\mathscr{X}_j$	$\mathscr{X}_{m+1}$	---	$\mathscr{X}_n$	$\sum_{j=1}^{m} n_j\mathscr{X}_j$	$\sum_{j=1}^{n} n_j\mathscr{G}_j + \sum_{j=1}^{m} n_j\mathscr{X}_j\mathscr{X}_j$	$\mathscr{X}_o - \mathscr{X} + \sum_{j=1}^{m} n_j\mathscr{X}_j\mathscr{G}_j$
(28) (c)	$\sum_{j=1}^{m} a_{1j}n_j\mathscr{S}_j$	$\sum_{j=1}^{m} a_{2j}n_j\mathscr{S}_j$	---	$\sum_{j=1}^{m} a_{lj}n_j\mathscr{S}_j$	$\mathscr{S}_{m+1}$	---	$\mathscr{S}_n$	$\sum_{j=1}^{m} n_j\mathscr{S}_j$	$\sum_{j=1}^{n} n_j\mathscr{G}_j + \sum_{j=1}^{m} n_j\mathscr{X}_j\mathscr{S}_j$	$\mathscr{S}_o - \mathscr{S} + n - \sum_{j=1}^{m} n_j + \sum_{j=1}^{m} n_j\mathscr{S}_j\mathscr{G}_j$

[a]Column not used for assigned temperature and pressure.
[b]Row used only for assigned enthalpy and pressure.
[c]Row used only for assigned entropy and pressure.

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TABLE II. - ITERATION EQUATIONS TO DETERMINE EQUILIBRIUM COMPOSITIONS FOR EITHER ASSIGNED TEMPERATURE AND VOLUME, INTERNAL ENERGY AND VOLUME, OR ENTROPY AND VOLUME

Equation \ Variables	π_1	π_2	---	π_l	Δn_{m+1}	---	Δn_n	$\Delta \ln T$ (a)	Right side
(45)	$\sum_{j=1}^{m} a_{1j}a_{1j}n_j$	$\sum_{j=1}^{m} a_{1j}a_{2j}n_j$	---	$\sum_{j=1}^{m} a_{1j}a_{lj}n_j$	$a_{1,m+1}$	---	a_{1n}	$\sum_{j=1}^{m} a_{1j}n_j\mathscr{T}_j$	$\left(b_1^o - b_1\right) + \sum_{j=1}^{m} a_{1j}n_j\,\mathscr{G}_j$
	$\sum_{j=1}^{m} a_{2j}a_{1j}n_j$	$\sum_{j=1}^{m} a_{2j}a_{2j}n_j$	---	$\sum_{j=1}^{m} a_{2j}a_{lj}n_j$	$a_{2,m+1}$	---	a_{2n}	$\sum_{j=1}^{m} a_{2j}n_j\mathscr{T}_j$	$\left(b_2^o - b_2\right) + \sum_{j=1}^{m} a_{2j}n_j\,\mathscr{G}_j$
	---	---	---	---	---	---	---	---	---
	$\sum_{j=1}^{m} a_{lj}a_{1j}n_j$	$\sum_{j=1}^{m} a_{lj}a_{2j}n_j$	---	$\sum_{j=1}^{m} a_{lj}a_{lj}n_j$	$a_{l,m+1}$	---	a_{ln}	$\sum_{j=1}^{m} a_{lj}n_j\mathscr{T}_j$	$\left(b_l^o - b_l\right) + \sum_{j=1}^{m} a_{lj}n_j\,\mathscr{G}_j$
(46)	$a_{1,m+1}$	$a_{2,m+1}$	---	$a_{l,m+1}$	0	---	0	$\mathscr{T}_{m+1}$	$\mathscr{G}_{m+1}$
	---	---	---	---	---	---	---	---	---
	a_{1n}	a_{2n}	---	a_{ln}	0	---	0	$\mathscr{T}_n$	$\mathscr{G}_n$
(47) (b)	$\sum_{j=1}^{m} a_{1j}n_j\mathscr{T}_j$	$\sum_{j=1}^{m} a_{2j}n_j\mathscr{T}_j$	---	$\sum_{j=1}^{m} a_{lj}n_j\mathscr{T}_j$	$\mathscr{T}_{m+1}$	---	$\mathscr{T}_n$	$\sum_{j=1}^{n} n_j\left(\mathscr{C}_v\right)_j + \sum_{j=1}^{m} n_j\mathscr{T}_j\mathscr{T}_j$	$\mathscr{T}_o - \mathscr{T} + \sum_{j=1}^{m} n_j\mathscr{T}_j\,\mathscr{G}_j$
(48) (c)	$\sum_{j=1}^{m} a_{1j}n_j(\mathscr{S}_j - 1)$	$\sum_{j=1}^{m} a_{2j}n_j(\mathscr{S}_j - 1)$	---	$\sum_{j=1}^{m} a_{lj}n_j(\mathscr{S}_j - 1)$	$\mathscr{S}_{m+1}$	---	$\mathscr{S}_n$	$\sum_{j=1}^{n} n_j\left(\mathscr{C}_v\right)_j + \sum_{j=1}^{m} n_j\mathscr{T}_j(\mathscr{S}_j - 1)$	$\mathscr{S}_o - \mathscr{S} + \sum_{j=1}^{m} n_j(\mathscr{S}_j - 1)\,\mathscr{G}_j$

[a]Column not used for assigned temperature and volume.

[b]Row used only for assigned internal energy and volume.

[c]Row used only for assigned entropy and volume.

TABLE III. - EQUATIONS FOR EVALUATING DERIVATIVES WITH RESPECT TO LOGARITHM OF TEMPERATURE AT CONSTANT PRESSURE

Equation \ Variables	$\frac{\partial \pi_1}{\partial \ln T}$	$\frac{\partial \pi_2}{\partial \ln T}$	---	$\frac{\partial \pi_l}{\partial \ln T}$	$\frac{\partial n_{m+1}}{\partial \ln T}$	---	$\frac{\partial n_n}{\partial \ln T}$	$\frac{\partial \ln n}{\partial \ln T}$	Right side
(56)	$\sum_{j=1}^{m} a_{1j}a_{1j}n_j$	$\sum_{j=1}^{m} a_{1j}a_{2j}n_j$	---	$\sum_{j=1}^{m} a_{1j}a_{lj}n_j$	$a_{1,m+1}$	---	a_{1n}	$\sum_{j=1}^{m} a_{1j}n_j$	$-\sum_{j=1}^{m} a_{1j}n_j\mathscr{X}_j$
	$\sum_{j=1}^{m} a_{2j}a_{1j}n_j$	$\sum_{j=1}^{m} a_{2j}a_{2j}n_j$	---	$\sum_{j=1}^{m} a_{2j}a_{lj}n_j$	$a_{2,m+1}$	---	a_{2n}	$\sum_{j=1}^{m} a_{2j}n_j$	$-\sum_{j=1}^{m} a_{2j}n_j\mathscr{X}_j$
	---	---	---	---	---	---	---	---	---
	$\sum_{j=1}^{m} a_{lj}a_{1j}n_j$	$\sum_{j=1}^{m} a_{lj}a_{2j}n_j$	---	$\sum_{j=1}^{m} a_{lj}a_{lj}n_j$	$a_{l,m+1}$	---	a_{ln}	$\sum_{j=1}^{m} a_{lj}n_j$	$-\sum_{j=1}^{m} a_{lj}n_j\mathscr{X}_j$
(57)	$a_{1,m+1}$	$a_{2,m+1}$	---	$a_{l,m+1}$	0	---	0	0	$-\mathscr{X}_{m+1}$
	---	---	---	---	---	---	---	---	---
	a_{1n}	a_{2n}	---	a_{ln}	0	---	0	0	$-\mathscr{X}_n$
(58)	$\sum_{j=1}^{m} a_{1j}n_j$	$\sum_{j=1}^{m} a_{2j}n_j$	---	$\sum_{j=1}^{m} a_{lj}n_j$	0	---	0	0	$-\sum_{j=1}^{m} n_j\mathscr{X}_j$

TABLE IV. - EQUATIONS FOR EVALUATING DERIVATIVES WITH RESPECT TO LOGARITHM OF PRESSURE AT CONSTANT TEMPERATURE

Equation \ Variables	$\frac{\partial \pi_1}{\partial \ln P}$	$\frac{\partial \pi_2}{\partial \ln P}$	---	$\frac{\partial \pi_l}{\partial \ln P}$	$\frac{\partial n_{m+1}}{\partial \ln P}$	---	$\frac{\partial n_n}{\partial \ln P}$	$\frac{\partial \ln n}{\partial \ln P}$	Right side
(64)	$\sum_{j=1}^{m} a_{1j}a_{1j}n_j$	$\sum_{j=1}^{m} a_{1j}a_{2j}n_j$	---	$\sum_{j=1}^{m} a_{1j}a_{lj}n_j$	$a_{1,m+1}$	---	a_{1n}	$\sum_{j=1}^{m} a_{1j}n_j$	$\sum_{j=1}^{m} a_{1j}n_j$
	$\sum_{j=1}^{m} a_{2j}a_{1j}n_j$	$\sum_{j=1}^{m} a_{2j}a_{2j}n_j$	---	$\sum_{j=1}^{m} a_{2j}a_{lj}n_j$	$a_{2,m+1}$	---	a_{2n}	$\sum_{j=1}^{m} a_{2j}n_j$	$\sum_{j=1}^{m} a_{2j}n_j$
	---	---	---	---	---	---	---	---	---
	$\sum_{j=1}^{m} a_{lj}a_{1j}n_j$	$\sum_{j=1}^{m} a_{lj}a_{2j}n_j$	---	$\sum_{j=1}^{m} a_{lj}a_{lj}n_j$	$a_{l,m+1}$	---	a_{ln}	$\sum_{j=1}^{m} a_{lj}n_j$	$\sum_{j=1}^{m} a_{lj}n_j$
(65)	$a_{1,m+1}$	$a_{2,m+1}$	---	$a_{l,m+1}$	0	---	0	0	0
	---	---	---	---	---	---	---	---	---
	a_{1n}	a_{2n}	---	a_{ln}	0	---	0	0	0
(66)	$\sum_{j=1}^{m} a_{1j}n_j$	$\sum_{j=1}^{m} a_{2j}n_j$	---	$\sum_{j=1}^{m} a_{lj}n_j$	0	---	0	0	$\sum_{j=1}^{m} n_j$

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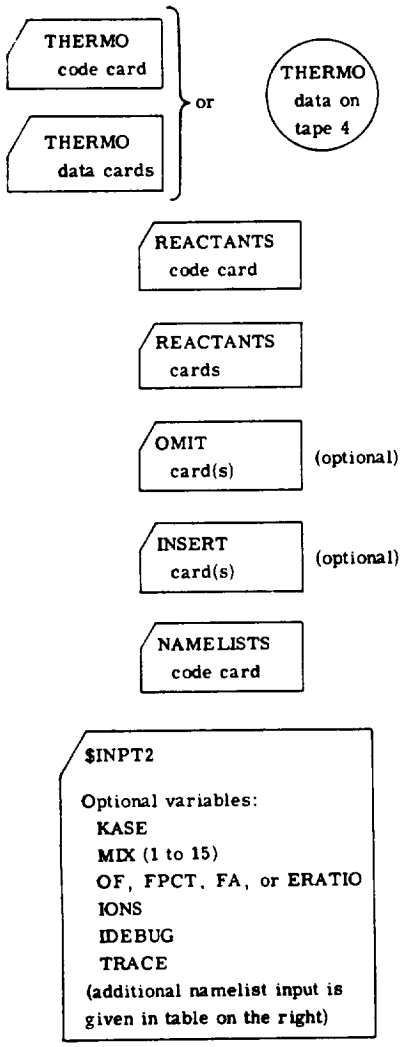

TABLE V - PROGRAM INPUT

Problem	Namelist	Variables	
		Required	Optional
Assigned temperature and pressure (TP)	INPT2	TP = .TRUE. T(1 to 26) P(1 to 26)	NSQM, PSIA, or MMHG
Assigned enthalpy and pressure (HP)	INPT2	HP = .TRUE. P(1 to 26)	NSQM, PSIA, or MMHG
Assigned entropy and pressure (SP)	INPT2	SP = .TRUE. S0(1) P(1 to 26)	NSQM, PSIA, or MMHG
Assigned temperature and volume or density (TV)	INPT2	TV = .TRUE. T(1 to 26) V(1 to 26) or RHO(1 to 26)	
Assigned internal energy and volume or density (UV)	INPT2	UV = .TRUE. V(1 to 26) or RHO(1 to 26)	
Assigned entropy and volume or density (SV)	INPT2	SV = .TRUE. V(1 to 26) or RHO(1 to 26) S0(1)	
Detonation (DETN)	INPT2	DETN = .TRUE. P(1 to 26) [initial gas]	NSQM, PSIA, or MMHG T(1 to 26) [initial gas]
Shock (SHOCK)	INPT2	SHOCK = .TRUE. P(1 to 13) [initial gas] T(1 to 13) [initial gas]	NSQM, PSIA, or MMHG
	SHKINP	U1(1 to 13) or MACH1 (1 to 13)	INCDEQ = .FALSE. or INCDFZ = .FALSE.
Rocket (RKT)	INPT2	RKT = .TRUE. P(1 to 26)(chamber pressures)	T(1 to 26)(chamber) NSQM, PSIA, or MMHG
	RKTINP		EQL = .FALSE. or FROZ = .FALSE. PCP(1 to 22) SUPAR(1 to 13) SUBAR(1 to 13)

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TABLE VI. - REACTANTS CARDS

Order	Contents	Format	Card columns
First	REACTANTS	3A4	1 to 9
Any	One card for each reactant species (maximum 15). Each card contains:		
	(1) Atomic symbols and formula numbers (maximum 5 sets)[a]	5(A2, F7.5)	1 to 45
	(2) Relative weight[b] or number of moles	F7.5	46 to 52
	(3) Blank if (2) is relative weight or M if (2) is number of moles	A1	53
	(4) Enthalpy or internal energy[a], cal/mole	F9.5	54 to 62
	(5) State: S, L, or G for solid, liquid or gas, respectively	A1	63
	(6) Temperature associated with enthalpy in (4)	F7.0	64 to 70
	(6a) J if (4) is in units of kJ/kg-mole and blank if (4) is in units of cal/g-mole	A1	71
	(7) F if fuel or O if oxidant	A1	72
	(8) Density in g/cm^3 (optional)	F8.5	73 to 80
Last	Blank		

[a]Program will calculate the enthalpy or internal energy (4) for species in the THERMO data at the temperature (6) if zeros are punched in card columns 37 and 38. (See section Reactant enthalpy for additional information.)

[b]Relative weight of fuel in total fuels or oxidant in total oxidants. All reactants must be given either all in relative weights or all in number of moles.

TABLE VII. - LIST OF REACTANTS CARDS FOR SOME OXIDANTS AND FUELS

Chemical	Chemical formula (card columns 1 to 45)	Percent (cc 46-52)	Assigned enthalpy, cal/mole (cc 54-62)	(a)	Temperature, K (cc 64-71)	(b)	Density, g/cm^3 (cc 73-80)	References for assigned enthalpy	References for density
Acetonitrile	C 2. H 3. N 1.	100.	12800.	L	298.15	F	.7857	19	20
Acetylene	C 2. H 2.	100.	49270.	L	192.60	F	.610	14 (series E)	14 (series E)
Air	N 1.561760 .41559 AR.009324C .000300	100.	-28.2	G	298.15	O		(c)	----------
Aluminum	AL1.	100.	0.	S	298.15	F	2.702	reference element	20
Ammonia(g)	N 1. H 3.	100.	-10970.	G	298.15	F		8	----------
Ammonia(l)	N 1. H 3.	100.	-17090.	L	239.72	F	.676	14 (series E)	14 (series E)
Ammonium perchlorate	N 1. H 4. CL1. O 4.	100.	-70690.	S	298.15	F	1.95	14 (series A)	14 (series A)
Aniline	C 6. H 7. N 1.	100.	7100.	L	298.15	F	1.02173	21	20
Argon	AR1.	100.	0.0	G	298.15	F		reference element	----------
Benzene	C 6. H 6.	100.	+11715.	L	298.15	F	.8737	22	22
Beryllium	BE1.	100.	0.0	S	298.15	F	1.85	reference element	20
Butane	C 4. H 10.	100.	-36080.	L	272.65	F	.6012	22	20
1-butene	C 4. H 8.	100.	-5800.	L	266.9	F	.6263	22	22
Chlorine(g)	CL2.	100.	0.	G	298.15	O		reference element	----------
Chlorine(l)	CL2.	100.	-5391.	L	239.09	O	1.56	14 (series E)	14 (series E)
Chlorine trifluoride(g)	CL1. F 3.	100.	-39000.	G	298.15	O		19	----------
Chlorine trifluoride(l)	CL1. F 3.	100.	-45680.	L	284.55	O	1.8517	23	24
Cyanogen(g)	C 2. N 2.	100.	+73840.	G	298.15	F		19	----------
Cyanogen(l)	C 2. N 2.	100.	67655.	L	252.01	F	.9537	8, 15, 19, 25	26
Diborane	B 2. H 6.	100.	4970.	L	180.59	F	.4371	14 (series E)	14 (series E)
Ethane	C 2. H 6.	100.	-25008.	L	184.52	F	.5464	21, 22	22
Ethyl alcohol	C 2. H 6. O 1.	100.	-66370.	L	298.15	F	.7893	19	20
Ethylene	C 2. H 4.	100.	8100.	L	169.44	F	.5688	14 (series E)	14 (series E)
Ethylene oxide	C 2. H 4. O 1.	100.	-18840.	L	283.72	F	.8824	19, 21, 25	20
Ethylene polymer	C 1. H 2.	100.	-6100.	S[d]	298.15	F	.935	(d)	27
Fluorine(g)	F 2.	100.	0.	G	298.15	O		reference element	----------
Fluorine(l)	F 2.	100.	-3098.	L	85.02	O	1.505	14 (series D)	14 (series D)
Graphite	C 1.	100.	0.	S	298.15	F	2.25	reference element	20
Helium	HE1.	100.	0.	G	298.15	F		reference element	----------
Heptane	C 7. H 16.	100.	-53630.	L	298.15	F	.67951	22	22
Hydrazine	N 2. H 4.	100.	12100.	L	298.15	F	1.0036	19	28

[a]Phase: S, solid; L, liquid; G, gas.
[b]Fuel, F; oxidant, O.
[c]Based on the following molar percents: N_2 = 78.0881, O_2 = 20.9495, Ar = 0.9324, CO_2 = 0.0300.
[d]Estimate based on paraffin hydrocarbon series.

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TABLE VII. - Concluded. LIST OF REACTANTS CARDS FOR SOME OXIDANTS AND FUELS

Chemical	Chemical formula (card columns 1 to 45)	Percent (cc 46-52)	Assigned enthalpy, cal/mole (cc 54-62)	(a)	Temperature, K (cc 64-71)	(b)	Density, g/cm^3 (cc 73-80)	References for assigned enthalpy	References for density
Hydrogen(g)	H 2.	100.	0.	G	298.15	F		reference element	----------
Hydrogen(l)	H 2.	100.	-2154.	L	20.27	F	.0709	14 (series D)	14 (series D)
Hydrogen peroxide	H 2. O 2.	100.	-44880.	L	298.15	O	1.407	14 (series C)	14 (series C)
IRFNA	H 1.572168 1.629450 4.695058 .02499	100.	-64960.	L	298.15	O	1.48	(e)	(e)
JP-5, ASTMA1	C 1. H 1.9185	100.	-5300.	L	298.15	F	.807	(f)	(f)
JP-4, RP-1	C 1. H 1.9423	100.	-5430.	L	298.15	F	.773	(g)	20
Lithium(l)	LI1.	100.	1714.1	L	453.69	F	.512	8	30
Lithium(s)	LI1.	100.	0.	S	298.15	F	.534	reference element	20
Lithium perchlorate	LI1. CL1. O 4.	100.	-90880.	S	298.15	O	2.43	14 (series A)	14 (series A)
Methane(g)	C 1. H 4.	100.	-17895.	G	298.15	F		8	----------
Methane(l)	C 1. H 4.	100.	-21390.	L	111.66	F	.4239	14 (series E)	14 (series E)
Methyl alcohol	C 1. H 4. O 1.	100.	-57040.	L	298.15	F	.78659	19	31
Monomethyl hydrazine	C 1. H 6. N 2.	100.	12900.	L	298.15	F	.874	19	32
Nitric acid	H 1. N 1. O 3.	100.	-41460.	L	298.15	O	1.5327	14 (series C)	14 (series C)
Nitrogen(g)	N 2.	100.	0.0	G	298.15	F		reference element	----------
Nitrogen(l)	N 2.	100.	-2939.	L	77.35	F	.808	14 (series D)	14 (series D)
Nitrogen tetroxide	N 2. O 4.	100.	-4680.	L	298.15	O	1.431	14 (series C)	14 (series C)
Nitrogen trifluoride	N 1. F 3.	100.	-34100.	L	144.14	O	1.531	14 (series E)	14 (series E)
Nitromethane	C 1. H 3. N 1. O 2.	100.	-27030.	L	298.15	F	1.1371	14 (series A)	20
Octane	C 8. H 18.	100.	-59740.	L	298.15	F	.69869	22	22
Oxygen(g)	O 2.	100.0	0.0	G	298.15	O		reference element	----------
Oxygen(l)	O 2.	100.	-3107.	L	90.18	O	1.149	14 (series D)	14 (series D)
Oxygen difluoride	O 1. F 2.	100.	1869.	L	127.88	O	1.571	8, 14 (series E)	14 (series E)
Ozone(g)	O 3.	100.	34100.	G	298.15	O		8	----------
Ozone(l)	O 3.	100.	30310.	L	162.64	O	1.449	14 (series E)	14 (series E)
Pentaborane	B 5. H 9.	100.	7740.	L	298.15	F	.6183	14 (series A)	14 (series A)
Perchloryl fluoride	CL1. O 3. F 1.	100.	-11350.	L	226.48	O	1.392	15, 19, 21	20
Propane	C 3. H 8.	100.	-30372.	L	231.08	F	.5808	21, 22	22
n-propyl nitrate	C 3. H 7. N 1. O 3.	100.	-51270.	L	298.15	F	1.0538	21	20
Toluene	C 7. H 8.	100.	2867.	L	298.15	F	.86230	22	22
Unsymmetrical dimethylhydrazine	C 2. H 8. N 2.	100.	+11900.	L	298.15	F	.783	14 (series A)	33

[a]Phase: S, solid; L, liquid; G, gas.
[b]Fuel, F; oxidant, O.
[e]Inhibited red fuming nitric acid based on following weight percents: $HNO_3(l)$ = 83.5, $N_2O_4(l)$ = 14, $H_2O(l)$ = 2, $HF(g)$ = 0.5
[f]Typical jet fuel having following properties: H/C weight ratio = 0.161, heat of combustion = 18 800 Btu/lb.
[g]Typical jet fuel having following properties: H/C weight ratio = 0.163, heat of combustion = 18 840 Btu/lb.

TABLE VIII. - VARIABLES IN INPT2 NAMELIST

Variable	Dimension	Type	Common label	Value before read	Definition and comments
KASE	1	I	INDX	0	Optional assigned number associated with case
P	26	R	POINTS	0	Assigned pressures; chamber pressures for rocket problems; values in atm unless PSIA, NSQM or MMHG = T (see below)
NSQM	1	L	-------	False	[a]Values in P array are in N/m^2
PSIA	1	L	-------	False	[a]Values in P array are in psia units
MMHG	1	L	-------	False	[a]Values in P array are in mm Hg units
V	26	R	POINTS	0	Volume, cm^3/g
RHO	26	R	POINTS[b](P)	0	Density, g/cm^3
T	26	R	POINTS	0	Assigned temperature, K
MIX	15	R	MISC[b](OXF)	0	Values of equivalence ratios if ERATIO = T; oxidant to fuel weight ratio if OF = T; percent fuel by weight if FPCT = T; and fuel to air weight ratio if FA = T
ERATIO	1	L	MISC	False	Equivalence ratios are given in MIX[a]
OF	1	L	MISC	False	Oxidant to fuel weight ratios are given in MIX[a]
FPCT	1	L	MISC	False	Percent fuel by weight are given in MIX[a]
FA	1	L	-----	False	Fuel to air weight ratios are given in MIX[a]
TRACE	1	R	MISC	0 (5.E-9 for SHOCK problem)	Option to print mole fractions ≥ TRACE in special E-format
IONS	1	L	INDX	False	Consider ionic species[a]
IDEBUG	1	I	INDX	0	Print intermediate output for all points indexed ≥ integer value
TP	1	L	INDX	False	Assigned temperature and pressure problem[a]
HP	1	L	INDX	False	Assigned enthalpy and pressure problem[a]
SP	1	L	INDX	False	Assigned entropy (S0) and pressure problem[a]
S0	1	R	MISC	0	Assigned entropy, cal/(g)(K)
TV	1	L	INDX	False	Assigned temperature and volume (or density) problem[a]
UV	1	L	INDX	False	Assigned internal energy and volume (or density) problem[a]
SV	1	L	INDX	False	Assigned entropy (S0) and volume (or density) problem[a]
RKT	1	L	----------	False	Rocket problem[a]
DETN	1	L	----------	False	Detonation problem[a]
SHOCK	1	L	INDX	False	Shock problem[a]
SIUNIT	1	L	----------	False	If true, the output tables will be in SI units

[a]If variable is set to be true.
[b]Equivalenced to variable given in parentheses.

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TABLE IX. - VARIABLES IN RKITINP NAMELIST[a]

Variable	Dimension	Type	Common label	Value before read	Definition and comments
EQL	1	L	PERF	TRUE	Calculate rocket performance assuming equilibrium composition during expansion[b]
FROZ	1	L	PERF	TRUE	Calculate rocket performance assuming frozen composition during expansion[b]
PCP	22	R	PERF	0	Ratio of chamber pressure to exit pressure; list should not include values for the chamber and throat; storage allows for 22 values
SUBAR	13	R	PERF	0	Subsonic area ratios
SUPAR	13	R	PERF	0	Supersonic area ratios
TCEST	1	R	-----	3800	Optional initial chamber temperature estimate K. May be necessary when condensed species have been inserted on INSERT cards and 3800 K is far outside the range of the data for the inserted species
NFZ	1	I	-----	1	Option for freezing composition at throat (NFZ = 2) or a supersonic point (NFZ > 2) when FROZ = .true. An extra table is printed with equilibrium composition through point NFZ and frozen thereafter with the composition of point NFZ assumed. If NFZ > 2, only 13-NFZ additional exit points are allowed.

[a]Required for rocket problems only.
[b]Set variable false if these calculations are not desired.

TABLE X. - VARIABLES IN SHKINP NAMELIST[a]

Variable	Dimension	Type	Value before read	Definition and comments
INCDEQ	1	L	TRUE	Calculate incident shock parameters assuming equilibrium compositions[b]
INCDFZ	1	L	TRUE	Calculate incident shock parameters assuming frozen compositions[b]
REFLEQ	1	L	FALSE	Calculate reflected shock parameters assuming equilibrium composition[c]
REFLFZ	1	L	FALSE	Calculate reflected shock parameters assuming composition frozen at incident composition[c]
U1	13	R	0	Shock velocity in m/sec (not required if values of MACH1 are listed)
MACH1	13	R	0	Ratio of shock velocity to the velocity of sound in the unshocked gas (not required if values of U1 are listed)

[a]Required for shock problems only.
[b]Set variable false if these calculations are not desired.
[c]If variable is set to be true.

TABLE XI. - SAMPLE OF INTERMEDIATE OUTPUT, ITERATION DETAILS

ITERATION 1 MATRIX

0.775000E-01	0.375000E-01	0.325000E-01	0.175000E-01	0.525000E-01	0.748120E+00	-0.149261E+01
0.375000E-01	0.222500E+00	0.675000E-01	0.500000E-02	0.825000E-01	0.960824E+00	-0.253549E+01
0.325000E-01	0.675000E-01	0.250000E+00	0.625000E-01	0.110000E+00	0.225254E+01	-0.299947E+01
0.175000E-01	0.500000E-02	0.625000E-01	0.180000E+00	0.700000E-01	-0.432686E-01	-0.360210E+01
0.525000E-01	0.825000E-01	0.110000E+00	0.700000E-01	0.	0.129548E+01	-0.282170E+01
0.748120E+00	0.960824E+00	0.225254E+01	-0.432686E-01	0.129548E+01	0.320091E+02	-0.220327E+02

PI	N	H	C	F		
-0.114597E+02	-0.830788E+01	-0.670916E+01	-0.163577E+02	0.229937E+00	0.270542E+00	

T= 0.38000000E+04 ENN= 0.09999999E+00 ENNL=-0.23025851E+01 PP= 0.10000000E+03 LN P/N= 0.69077552E+01 AMBDA= 0.22699746E+00

	NJ	LN NJ	DEL LN NJ	HOJ/RT	SOJ/R	-COJ/RT	-GJ/RT
C(S)	0.	0.	0.106756E-15	0.255670E+01	0.682884E+01	0.427214E+01	0.427214E+01
C	0.250000E-02	-0.599146E+01	-0.192088E+00	0.249787E+02	0.254243E+02	0.445652E+00	-0.470039E+00
CF	0.250000E-02	-0.599146E+01	0.375930E+01	0.121579E+02	0.363812E+02	0.242233E+02	0.233070E+02
CF2	0.250000E-02	-0.599146E+01	0.457011E+01	0.424252E+00	0.449905E+02	0.445663E+02	0.436500E+02
CF3	0.250000E-02	-0.599146E+01	0.226640E+01	-0.619128E+01	0.542188E+02	0.604101E+02	0.594938E+02
CF4	0.250000E-02	-0.599146E+01	0.724818E+00	-0.182767E+02	0.602191E+02	0.784958E+02	0.775795E+02
CH	0.250000E-02	-0.599146E+01	0.658594E-01	0.229680E+02	0.325235E+02	0.955544E+01	0.863514E+01
CH2	0.250000E-02	-0.599146E+01	-0.872760E+00	0.182137E+02	0.364246E+02	0.182110E+02	0.173947E+02
CH3	0.250000E-02	-0.599146E+01	0.489968E+00	0.122663E+02	0.417569E+02	0.294906E+02	0.285743E+02
CH4	0.250000E-02	-0.599146E+01	-0.144617E+01	0.726030E+01	0.444770E+02	0.372167E+02	0.363004E+02
CN	0.250000E-02	-0.599146E+01	0.294569E+01	0.179497E+02	0.349345E+02	0.169847E+02	0.160685E+02
CN2	0.250000E-02	-0.599146E+01	-0.423552E+01	0.248664E+02	0.442984E+02	0.194320E+02	0.185157E+02
C2	0.250000E-02	-0.599146E+01	-0.913843E+00	0.308414E+02	0.356883E+02	0.484694E+01	0.393065E+01
C2F2	0.250000E-02	-0.599146E+01	-0.993611E+00	0.978809E+01	0.529665E+02	0.431784E+02	0.422621E+02
C2F4	0.250000E-02	-0.599146E+01	-0.282405E+01	-0.700585E+01	0.716010E+02	0.786068E+02	0.776906E+02
C2H	0.250000E-02	-0.599146E+01	0.269689E+01	0.214693E+02	0.407704E+02	0.193011E+02	0.183848E+02
C2HF	0.250000E-02	-0.599146E+01	0.200451E+01	0.127050E+02	0.500426E+02	0.373375E+02	0.364212E+02
C2H2	0.250000E-02	-0.599146E+01	0.304606E+01	0.158335E+02	0.453164E+02	0.294829E+02	0.285666E+02
C2H4	0.250000E-02	-0.599146E+01	-0.276457E+01	0.138135E+02	0.546480E+02	0.408345E+02	0.399182E+02
C2N	0.250000E-02	-0.599146E+01	0.204201E+01	0.242775E+02	0.453558E+02	0.210783E+02	0.201620E+02
C2N2	0.250000E-02	-0.599146E+01	0.126559E+01	0.187255E+02	0.520291E+02	0.333036E+02	0.323873E+02
C3	0.250000E-02	-0.599146E+01	-0.131610E+01	0.314394E+02	0.424314E+02	0.109921E+02	0.100758E+02
C4	0.250000E-02	-0.599146E+01	-0.626311E+01	0.396707E+02	0.501980E+02	0.105273E+02	0.961100E+01
C5	0.250000E-02	-0.599146E+01	-0.713524E+01	0.424425E+02	0.580569E+02	0.156144E+02	0.146981E+02
F	0.250000E-02	-0.599146E+01	0.507517E+01	0.483716E+01	0.256477E+02	0.208106E+02	0.198943E+02
FCN	0.250000E-02	-0.599146E+01	0.303237E+01	0.759720E+01	0.438271E+02	0.362299E+02	0.353136E+02
F2	0.250000E-02	-0.599146E+01	-0.855432E+00	0.425524E+01	0.356504E+02	0.313951E+02	0.304788E+02
H	0.250000E-02	-0.599146E+01	0.443929E+01	0.920306E+01	0.201468E+02	0.109437E+02	0.100274E+02
HCN	0.250000E-02	-0.599146E+01	0.487249E+01	0.104605E+02	0.397061E+02	0.292456E+02	0.283293E+02
HF	0.250000E-02	-0.599146E+01	0.881067E+01	-0.490616E+01	0.305838E+02	0.354899E+02	0.345737E+02
H2	0.250000E-02	-0.599146E+01	0.541631E+01	0.376914E+01	0.254679E+02	0.216987E+02	0.207824E+02
N	0.250000E-02	-0.599146E+01	0.140463E-01	0.172759E+02	0.248022E+02	0.752623E+01	0.660994E+01
NF	0.250000E-02	-0.599146E+01	-0.487857E+00	0.120067E+02	0.368143E+02	0.248076E+02	0.238913E+02
NF2	0.250000E-02	-0.599146E+01	-0.403916E+01	0.754265E+01	0.463644E+02	0.388217E+02	0.379054E+02
NF3	0.250000E-02	-0.599146E+01	-0.103071E+02	0.465937E+01	0.543509E+02	0.496915E+02	0.487752E+02
NH	0.250000E-02	-0.599146E+01	0.614820E+00	0.145689E+02	0.317362E+02	0.171673E+02	0.162510E+02
NH2	0.250000E-02	-0.599146E+01	0.229329E+00	0.107633E+02	0.368825E+02	0.261192E+02	0.252029E+02
NH3	0.250000E-02	-0.599146E+01	-0.566411E+00	0.612052E+01	0.410080E+02	0.348874E+02	0.339711E+02
N2	0.250000E-02	-0.599146E+01	0.663143E+01	0.387959E+01	0.331472E+02	0.292676E+02	0.283513E+02
N2C	0.250000E-02	-0.599146E+01	-0.519863E+00	0.202300E+02	0.446320E+02	0.244026E+02	0.234863E+02
N2H4	0.250000E-02	-0.599146E+01	-0.100827E+02	0.153115E+02	0.580036E+02	0.426922E+02	0.417759E+02

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T DERIV MATRIX

0.256969E-01	0.666043E-03	0.198388E-02	0.865496E-04	0.136700E-01	0.715742E-01	0.
0.666043E-03	0.384154E-01	0.189197E-02	0.320738E-01	0.368480E-01	-0.678682E-01	0.
0.198388E-02	0.189197E-02	0.696977E-02	0.175341E-02	0.475402E-02	0.717455E-01	0.
0.865496E-04	0.320738E-01	0.175341E-02	0.382665E-01	0.375972E-01	-0.788308E-01	0.
0.136700E-01	0.368480E-01	0.475402E-02	0.375972E-01	0.	0.285781E-02	0.

PI	N	H	C	F	
0.227109E+01	-0.412088E+00	0.105453E+02	-0.167927E+01	-0.533033E+00	

P DERIV MATRIX

0.256969E-01	0.666043E-03	0.198388E-02	0.865496E-04	0.136700E-01	0.136700E-01	0.
0.666043E-03	0.384154E-01	0.189197E-02	0.320738E-01	0.368480E-01	0.368480E-01	0.
0.198388E-02	0.189197E-02	0.696977E-02	0.175341E-02	0.475402E-02	0.475402E-02	0.
0.865496E-04	0.320738E-01	0.175341E-02	0.382665E-01	0.375972E-01	0.375972E-01	0.
0.136700E-01	0.368480E-01	0.475402E-02	0.375972E-01	0.	0.484072E-01	0.

PI	N	H	C	F	
0.515006E+00	0.441740E+00	0.279985E+00	0.631931E+00	-0.342684E-01	

POINT= 1 P= 0.100000E+03 T= 0.453457E+04 H/R= 0.129590E+02 S/R= 0.136009E+01

MW= 0.206581E+02 CP/R= 0.636139E+00 DLVPT=-0.103427E+01 DLVTP= 0.153303E+01 GAMMA(S)= 0.116900E+01 V= 0.180117E+03

TABLE XII. - INTERMEDIATE OUTPUT, TEST FOR CONDENSED PHASES

```
AL(S)            300.000    933.000    IUSE=  -1  0.
GO-SUM(AIJ*PII) =  0.7170131E+02              MAX NEG DELTA G =  0.

AL(L)            933.000   5000.000    IUSE=  -1  0.

ALCL3(S)         300.000    465.700    IUSE=  -2  0.

ALCL3(L)         465.700   3000.000    IUSE=  -2  0.
GO-SUM(AIJ*PII) =  0.3785759E+02              MAX NEG DELTA G =  0.

ALN(S)           300.000   3000.000    IUSE=  -3  0.
GO-SUM(AIJ*PII) =  0.3137253E+02              MAX NEG DELTA G =  0.

AL2O3(S)         300.000   2315.000    IUSE=   4  0.1657809E-02

AL2O3(L)        2315.000   5000.000    IUSE=  -4  0.

C(S)             300.000   5000.000    IUSE=  -5  0.
GO-SUM(AIJ*PII) = -0.1317053E+01              MAX NEG DELTA G =  0.

H2O(S)           200.000    273.150    IUSE=  -6  0.

H2O(L)           273.150    373.150    IUSE=  -6  0.

MG(S)            300.000    922.000    IUSE=  -7  0.
GO-SUM(AIJ*PII) =  0.4137586E+02              MAX NEG DELTA G = -0.1317053E+01

MG(L)            922.000   5000.000    IUSE=  -7  0.

MGCL2(S)         300.000    987.000    IUSE=  -8  0.
GO-SUM(AIJ*PII) = -0.1033547E+02              MAX NEG DELTA G = -0.1317053E+01

MGCL2(L)         987.000   5000.000    IUSE=  -8  0.

MGO(S)           300.000   3098.000    IUSE=  -9  0.
GO-SUM(AIJ*PII) = -0.1368991E+02              MAX NEG DELTA G = -0.1033547E+02

MGO(L)          3098.000   5000.000    IUSE=  -9  0.

S(S)             300.000    388.360    IUSE= -10  0.

S(L)             388.360   2000.000    IUSE= -10  0.
GO-SUM(AIJ*PII) =  0.1291119E+02              MAX NEG DELTA G = -0.1368991E+02
```

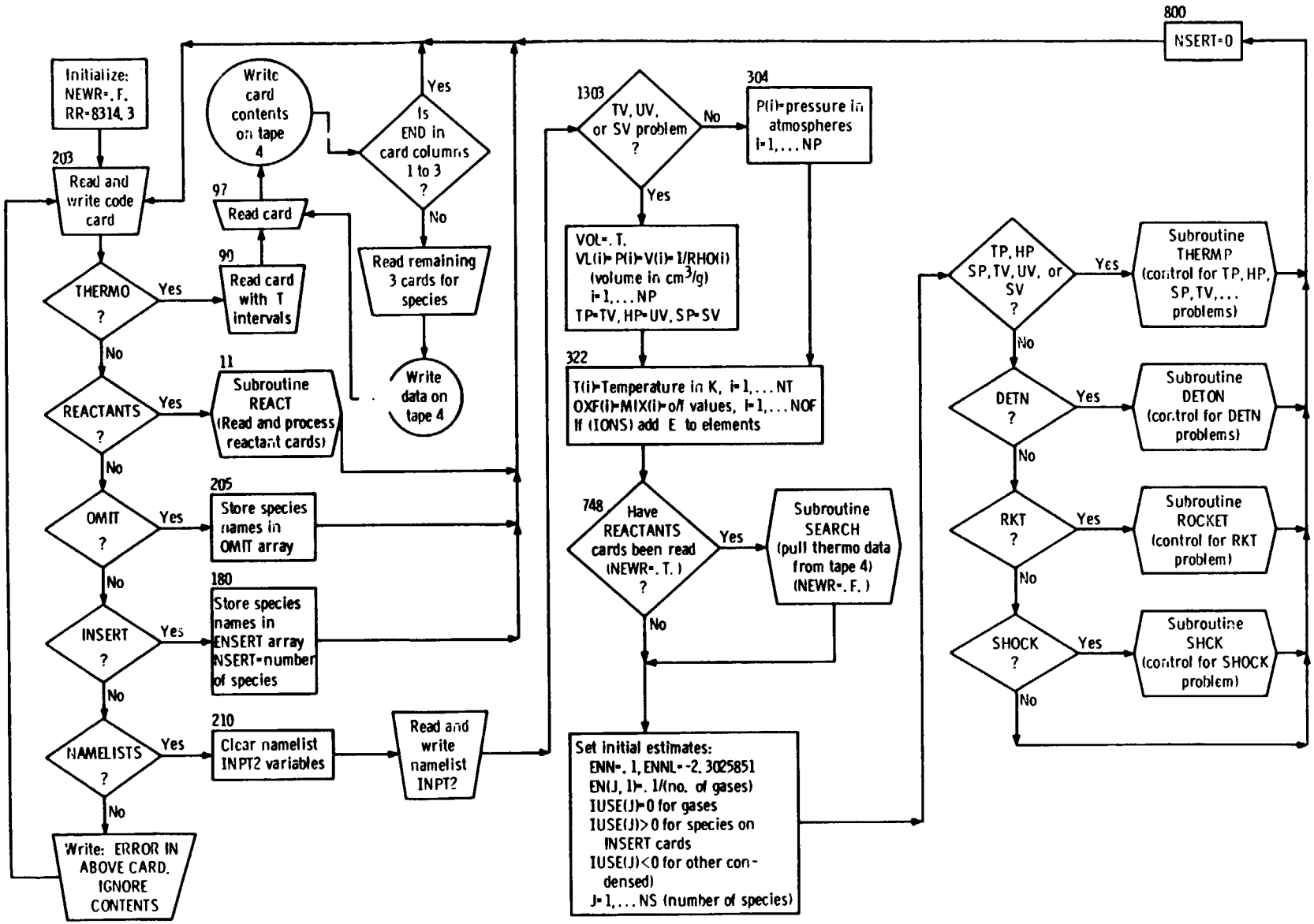

Figure 1. - Flow diagram for main routine.

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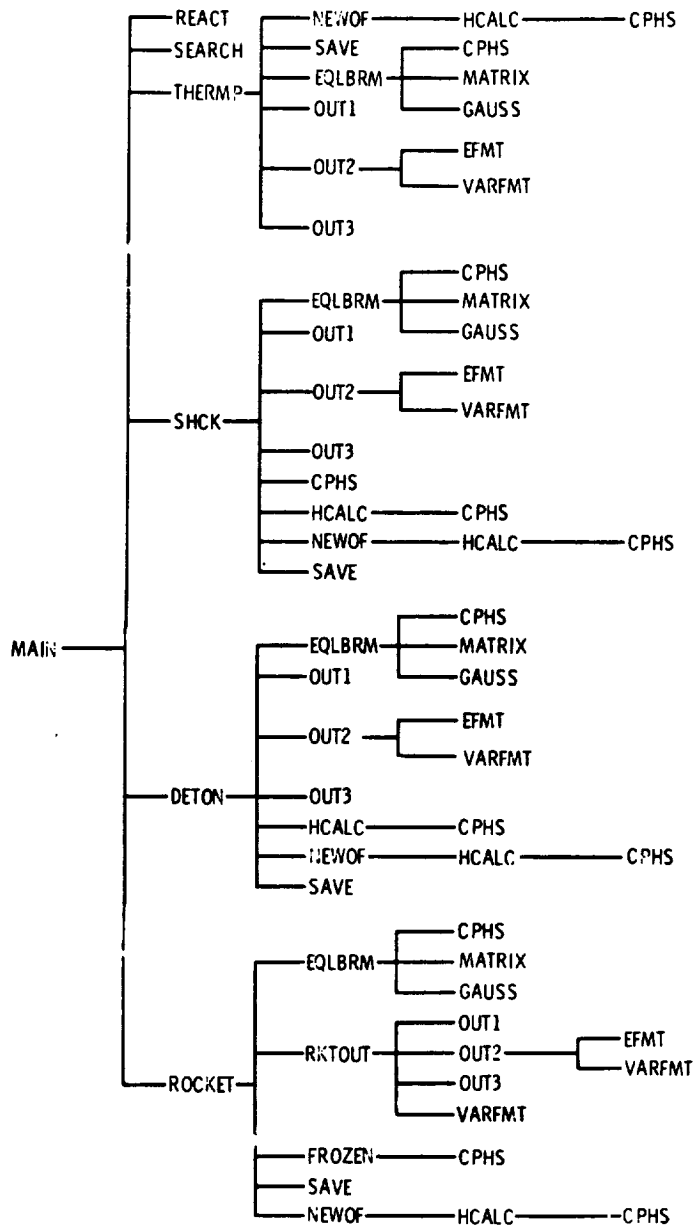

Figure 2. - Subroutine tree diagram.

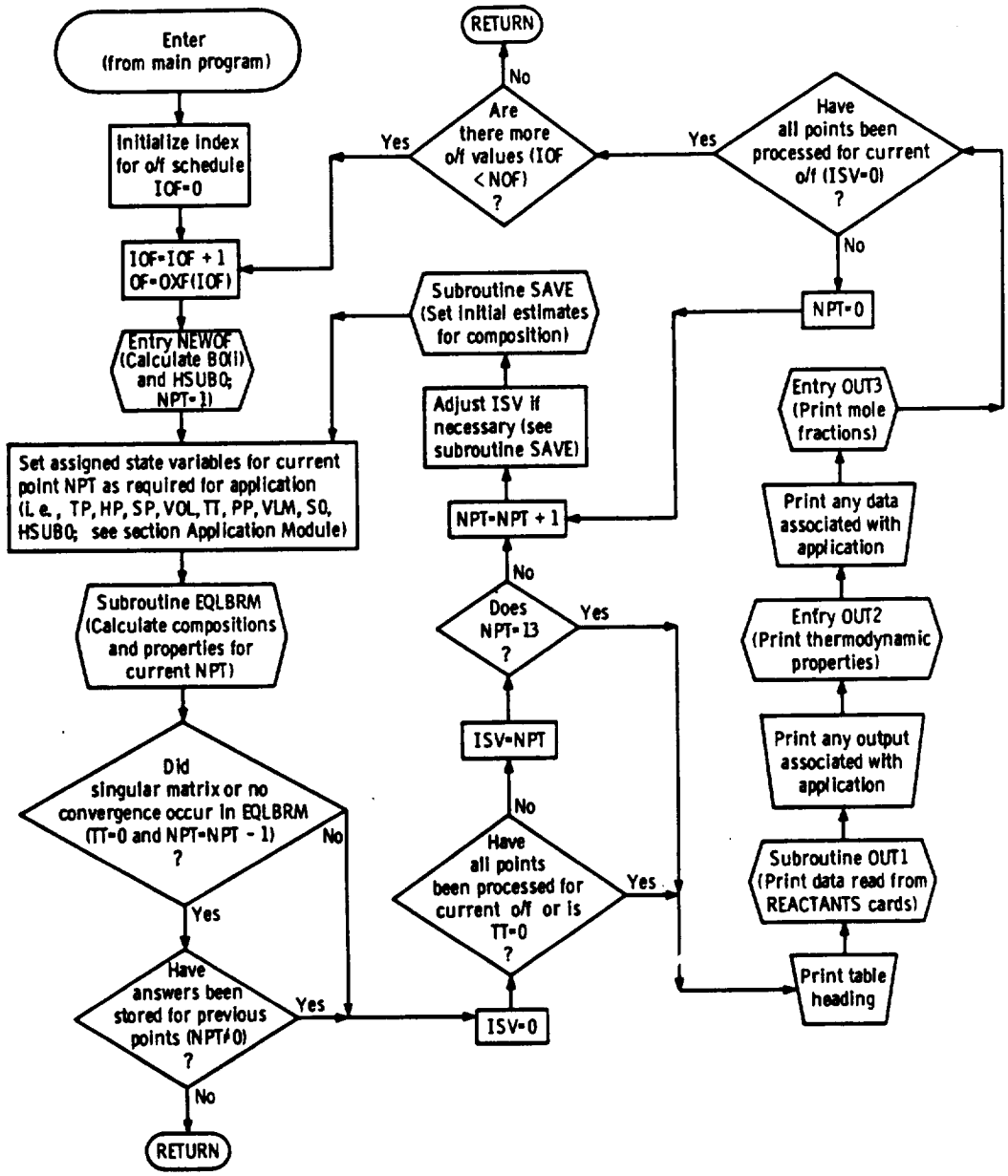

Figure 3. - Flow diagram of an application module.

*USGPO: 1976 — 660-384/58 Region 5-11