Computer Program for Calculation of Complex Chemical Equilibrium Compositions and Applications

I. Analysis

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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 over more than 40 years. These programs have changed over the years to include additional features and improved calculation techniques and to take advantage of constantly improving computer capabilities. The minimization-of-free-energy approach to chemical equilibrium calculations has been used in all versions of the program since 1967.

The two principal purposes of this report are presented in two parts. The first purpose, which is accomplished here in part I, is to present in detail a number of topics of general interest in complex equilibrium calculations. These topics include mathematical analyses and techniques for obtaining chemical equilibrium; formulas for obtaining thermodynamic and transport mixture properties and thermodynamic derivatives; criteria for inclusion of condensed phases; calculations at a triple point; inclusion of ionized species; and various applications, such as constant-pressure or constant-volume combustion, rocket performance based on either a finite- or infinite-chamber-area model, shock wave calculations, and Chapman-Jouguet detonations.

The second purpose of this report, to facilitate the use of the computer code, is accomplished in part II, entitled "Users Manual and Program Description." Various aspects of the computer code are discussed, and a number of examples are given to illustrate its versatility.

Contents

Chapter 1
Introduction

Knowing the 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.

For more than 40 years the NASA Lewis Research Center has been involved in developing methods and computer programs for calculating complex chemical equilibrium compositions and thermodynamic properties of the equilibrium mixtures and in applying these properties to a number of problems (Gordon et al., 1959, 1962, 1963, 1970, 1976, 1984, 1988; Huff et al., 1951; Svehla and McBride, 1973; and Zeleznik and Gordon, 1960, 1962a,b, 1968). Earlier versions of the chemical equilibrium computer program (Zeleznik and Gordon, 1962a; and Gordon and McBride, 1976) have had wide acceptance. Since the last publication this program has been under continuous revision and updating, including several substantial additions. One addition is an option for obtaining the transport properties of complex mixtures (Gordon et al., 1984) by methods simpler than those of Svehla and McBride (1973). A second addition is an option to calculate rocket performance for a rocket motor with a finite-area combustor (Gordon and McBride, 1988). The present report documents these and other additions and revisions to the program since 1976. The revised program is called CEA (Chemical Equilibrium and Applications).

The program can now do the following kinds of problems:

(1) Obtaining chemical equilibrium compositions for assigned thermodynamic states. These states may be specified by assigning two thermodynamic state functions as follows:

(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) Calculating theoretical rocket performance for a finite- or infinite-area combustion chamber
(3) Calculating Chapman-Jouguet detonations
(4) Calculating shock tube parameters for both incident and reflected shocks

Some problems handled by the program use just one combination of assigned states—namely, the tp, hp, sp, tv, uv, and sv problems. For example, the tp problem, which consists of a schedule of one or more assigned temperatures and pressures, might be used to construct Mollier diagrams. The hp problem gives constant-pressure combustion properties and the uv problem gives constant-volume combustion properties. Other problems make use of more than one combination of assigned thermodynamic states. For example, the shock and detonation problems use hp and tp; the rocket problem uses hp or tp and also sp.

This report consists of two parts. Part I, containing the analysis, includes

(1) The equations describing chemical equilibrium and the applications previously mentioned (i.e., rocket performance, shocks, and Chapman-Jouguet detonations)
(2) The reduction of these equations to forms suitable for mathematical solution by means of iterative procedures
(3) Equations for obtaining thermodynamic and transport properties of mixtures

Part II, a program description and users manual, discusses the modular form of the program and briefly

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describes each subroutine. It also discusses the preparation of input, various permitted options, output tables, and error messages. A number of examples are also given to illustrate the versatility of the program.

In addition to the work in chemical equilibrium calculations and applications over the past 40 years, progress in computer programs, data generation, and data fitting has also been made at NASA Lewis for the thermodynamic and thermal transport properties of individual species required for the equilibrium calculations. Some examples of this effort are Burcat et al. (1985), McBride et al. (1961, 1963, 1967, 1992, 1993a,b),

Svehla (1962), and Zeleznik and Gordon (1961). In addition to data calculated by us, other thermodynamic data included in our files are taken from sources such as Chase et al. (1985), Garvin et al. (1987), Gurvich et al. (1989), and Marsh et al. (1988). Files distributed with the computer program are described in part II.

Various versions of the equilibrium program or modifications of the program have been incorporated into a number of other computer codes. An example is Radhakrishnan and Bittker (1994) for kinetics calculations.

Chapter 2
Equations Describing Chemical Equilibrium

Chemical equilibrium is usually described by either of two equivalent formulations—equilibrium constants or minimization of free energy. Reports by Zeleznik and Gordon (1960, 1968) compare the two formulations. Zeleznik and Gordon (1960) shows that, if a generalized method of solution is used, the two formulations reduce to the same number of iteration equations. However, with the minimization-of-free-energy method each species can be treated independently without specifying a set of reactions a priori, as is required with equilibrium constants. Therefore, the minimization-of-free-energy formulation is used in the CEA program.

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

Zeleznik and Gordon (1960) presents equations based on minimization of Gibbs energy. Some of these equations are repeated and expanded herein for convenience. In addition, a set of equations based on minimization of Helmholtz energy is also presented. However, because only ideal gases and pure condensed phases are being considered, the general notation of Zeleznik and Gordon (1960) is not used.

2.1 Units

The International System of Units (SI) used in this report is

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

The numerical values of a number of fundamental contants are taken from Cohen and Taylor (1987). For example, the value of the gas constant R taken from this reference is 8314.51 J/(kg-mole)(K). In those sections dealing with the computer program, other units are used in addition to or instead of SI units.

2.2 Equation of State

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

$$PV = nRT \qquad (2.1a)$$

or

$$\frac{P}{\rho} = nRT \qquad (2.1b)$$

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where P is pressure (in newtons per square meter), V specific volume (in cubic meters per kilogram), n moles per unit mass of mixture (in kilograms-mole per kilogram), T temperature (in kelvin), and ρ density (in kilograms per cubic meter). Symbols used in this report are defined in the appendix. For a reacting chemical system the number of moles n is generally not constant.

Equation (2.1) 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 relative to the gaseous species. An example given in part II of this report illustrates the validity of this assumption. In the variables V, n, and ρ the volume and mole number refer to gases only, but the mass is for the entire mixture including condensed species. The word "mixture" is used in this report to refer to mixtures of reaction products as distinguished from mixtures of reactants, which are referred to as "total reactants."

On the basis of this definition, n can be written as

$$n = \sum_{j=1}^{NG} n_j \qquad (2.2)$$

where n_j is the number of kilogram-moles of species j per kilogram of mixture and the index NG refers to the number of gases in the mixture. The molecular weight of the mixture M is defined as

$$M = \frac{1}{n} \qquad (2.3a)$$

or equivalently as

$$M = \frac{\sum_{j=1}^{NS} n_j M_j}{\sum_{j=1}^{NG} n_j} \qquad (2.3b)$$

where M_j is the molecular weight of species j and the index NS refers to the number of species in the mixture. In the CEA computer program, among the NS species, gases are indexed from 1 to NG and condensed species from NG + 1 to NS.

More conventionally, molecular weight is defined as

$$MW = \frac{\sum_{j=1}^{NS} n_j M_j}{\sum_{j=1}^{NS} n_j} \qquad (2.4a)$$

Molecular weight is given the symbol MW in equation (2.4a) to differentiate it from M. The two different definitions of molecular weight, M and MW, give different results only in mixtures of products containing condensed as well as gaseous species. Only M is given in the output, but MW may be obtained from M by means of

$$MW = M\left(1 - \sum_{j=NG+1}^{NS} x_j\right) \qquad (2.4b)$$

where x_j is the mole fraction of species j relative to all species in the mixture. Some additional discussion of the differences in these molecular weights is given in part II of this report.

2.3 Minimization of Gibbs Energy

For a mixture of NS species the Gibbs energy per kilogram of mixture g is given by

$$g = \sum_{j=1}^{NS} \mu_j n_j \qquad (2.5)$$

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

$$\mu_j = \left(\frac{\partial g}{\partial n_j}\right)_{T,P,n_{i \neq j}} \qquad (2.6)$$

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:

$$\sum_{j=1}^{NS} a_{ij} n_j - b_i^\circ = 0 \qquad (i = 1,...,\ell) \qquad (2.7a)$$

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or

$$b_i - b_i^\circ = 0 \qquad (i = 1,...,\ell) \qquad (2.7b)$$

where the stoichiometric coefficients a_{ij} are the number of kilogram-atoms of element i per kilogram-mole of species j, the index ℓ is the number of chemical elements (if ions are considered, the number of chemical elements plus one), b_i° is the assigned number of kilogram-atoms of element i per kilogram of total reactants (see eq. (9.5)), and

$$b_i = \sum_{j=1}^{NS} a_{ij} n_j \qquad (i = 1,...,\ell) \qquad (2.7c)$$

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

Defining a term G to be

$$G = g + \sum_{i=1}^{\ell} \lambda_i (b_i - b_i^\circ) \qquad (2.8)$$

where λ_i are Lagrangian multipliers, the condition for equilibrium becomes

$$\delta G = \sum_{j=1}^{NS} \left(\mu_j + \sum_{i=1}^{\ell} \lambda_i a_{ij} \right) \delta n_j + \sum_{i=1}^{\ell} (b_i - b_i^\circ) \delta \lambda_i = 0 \qquad (2.9)$$

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

$$\mu_j + \sum_{i=1}^{\ell} \lambda_i a_{ij} = 0 \qquad (j = 1,...,NS) \qquad (2.10)$$

and also gives the mass-balance equation (2.7b).

From the assumptions in section 2.2 the chemical potential can be written as

$$\mu_j = \begin{cases} \mu_j^\circ + RT \ln \dfrac{n_j}{n} + RT \ln P & (j = 1,...,NG) \\[2mm] \mu_j^\circ & (j = NG+1,...,NS) \end{cases} \qquad (2.11)$$

where μ_j° for gases ($j = 1$ to NG) and for condensed phases ($j > NG$) is the chemical potential in the standard

state. For a gas the standard state is the hypothetical ideal gas at the standard-state pressure. For a pure solid or liquid the standard state is the substance in the condensed phase at the standard-state pressure. Historically, the defined standard-state pressure has been 1 atmosphere (101 325 Pa). Most early tabulations of thermodynamic data were based on this pressure. However, in 1982 the International Union of Pure and and Applied Chemistry (Cox, 1982) recommended that the standard-state pressure should be defined as 1 bar (10^5 Pa). Most recent compilations have used 1 bar as the standard pressure (e.g., Chase et al. (1985), Garvin et al. (1987), Gurvich et al. (1989), Marsh et al. (1988), and McBride et al. (1993a,b)). The unit of pressure in equation (2.11) should be consistent with the unit of pressure in the thermodynamic data being used.

The term μ_j° and other thermodynamic terms that appear later in the text, such as $C_{p,j}^\circ$, H_j°, S_j°, $C_{v,j}^\circ$, and U_j°, are all functions of temperature. However, including T as part of the symbol notation, such as $H_j^\circ(T)$ or $H^\circ(T)$, is done only when needed for clarity. For example, sensible heat for species j between a temperature T and a temperature of 298.15 K can be written as $H_j^\circ(T) - H_j^\circ(298.15)$.

Equations (2.7a) and (2.10) permit the determination of equilibrium compositions for thermodynamic states specified by an assigned temperature T_0 and pressure P_0. That is, in addition to equations (2.7a) and (2.10), we have the pair of trivial equations

$$T = T_0 \qquad (2.12a)$$

$$P = P_0 \qquad (2.12b)$$

However, the thermodynamic state can be specified by assigning any two state functions. For example, the thermodynamic state corresponding to a constant-pressure combustion is specified, instead of by equations (2.12), by

$$h = h_0 \qquad (2.13a)$$

$$P = P_0 \qquad (2.13b)$$

where h is the specific enthalpy of the mixture and h_0 a constant equal to the specific enthalpy of the reactants (see eq. (9.7)). The expression for h is

$$h = \sum_{j=1}^{NS} n_j H_j^o \qquad (2.14)$$

where H_j^o is the standard-state molar enthalpy for species j at temperature T.

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

$$s = s_0 \qquad (2.15a)$$

$$P = P_0 \qquad (2.15b)$$

where s is the specific entropy of the mixture and s_0 the assigned specific entropy, or the specific entropy of the total reactant (see eq. (9.22)). The expression for s is

$$s = \sum_{j=1}^{NS} n_j S_j \qquad (2.16)$$

where

$$S_j = \begin{cases} S_j^o - R \ln \dfrac{n_j}{n} - R \ln P & (j = 1,...,NG) \\[2ex] S_j^o & (j = NG + 1,...,NS) \end{cases} \qquad (2.17)$$

and S_j^o is the standard-state molar entropy for species j. Equation (2.17) is similar to equation (2.11), and the same discussion concerning standard-state pressure that applied to equation (2.11) also applies to equation (2.17).

2.3.1 Gibbs Iteration Equations

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 to be described it will be convenient to treat n as an independent variable. A descent Newton-Raphson method is used to solve for corrections to initial estimates of compositions n_j, Lagrangian multipliers λ_j, moles of gaseous species n, and (when required) temperature T. This method involves a Taylor series ex-

pansion of the appropriate equations with all terms truncated that contain derivatives higher than the first. The correction variables used are $\Delta \ln n_j$ ($j = 1,...,NG$), Δn_j ($j = NG+1,...,NS$), $\Delta \ln n$, $\pi_i = -\lambda_i/RT$, and $\Delta \ln T$. As Zeleznik and Gordon (1968) points out, 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 (2.10). After making dimensionless those equations containing thermodynamic functions, the Newton-Raphson equations obtained from equations (2.10), (2.7), (2.13a), and (2.15a) are

$$\Delta \ln n_j - \sum_{i=1}^{\ell} a_{ij} \pi_i - \Delta \ln n - \frac{H_j^o}{RT} \Delta \ln T$$
$$= -\frac{\mu_j}{RT} \qquad (j = 1,...,NG) \qquad (2.18)$$

$$-\sum_{i=1}^{\ell} a_{ij} \pi_i - \frac{H_j^o}{RT} \Delta \ln T = -\frac{\mu_j}{RT}$$
$$(j = NG + 1,...,NS) \qquad (2.19)$$

$$\sum_{j=1}^{NG} a_{kj} n_j \Delta \ln n_j + \sum_{j=NG+1}^{NS} a_{kj} \Delta n_j = b_k^o - b_k$$
$$(k = 1,...,\ell) \qquad (2.20)$$

$$\sum_{j=1}^{NG} n_j \Delta \ln n_j - n \Delta \ln n = n - \sum_{j=1}^{NG} n_j \qquad (2.21)$$

$$\sum_{j=1}^{NG} \frac{n_j H_j^o}{RT} \Delta \ln n_j + \sum_{j=NG+1}^{NS} \frac{H_j^o}{RT} \Delta n_j$$
$$+ \left(\sum_{j=1}^{NS} \frac{n_j C_{p,j}^o}{R} \right) \Delta \ln T = \frac{h_0 - h}{RT} \qquad (2.22)$$

$$\sum_{j=1}^{NG} \frac{n_j S_j}{R} \Delta \ln n_j + \sum_{j=NG+1}^{NS} \frac{S_j^o}{R} \Delta n_j + \left(\sum_{j=1}^{NS} \frac{n_j C_{p,j}^o}{R}\right) \Delta \ln T$$

$$= \frac{S_0 - S}{R} + n - \sum_{j=1}^{NG} n_j \qquad (2.23)$$

where $C_{p,j}^o$ is the standard-state specific heat at constant pressure for species j at temperature T.

2.3.2 Reduced Gibbs Iteration Equations

For problems with assigned thermodynamic states tp, hp, or sp, various combinations of equations (2.18) to (2.23) 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. The expression for $\Delta \ln n_j$ obtained from equation (2.18) is substituted into equations (2.20) to (2.23). When equation (2.19) written with signs reversed is included, the resulting reduced equations are

$$\sum_{i=1}^{\ell} \sum_{j=1}^{NG} a_{kj} a_{ij} n_j \pi_i + \sum_{j=NG+1}^{NS} a_{kj} \Delta n_j + \left(\sum_{j=1}^{NG} a_{kj} n_j\right) \Delta \ln n$$

$$+ \left(\sum_{j=1}^{NG} \frac{a_{kj} n_j H_j^o}{RT}\right) \Delta \ln T = b_k^o - b_k + \sum_{j=1}^{NG} \frac{a_{kj} n_j \mu_j}{RT}$$

$$(k = 1,...,\ell) \qquad (2.24)$$

$$\sum_{i=1}^{\ell} a_{ij} \pi_i + \frac{H_j^o}{RT} \Delta \ln T = \frac{\mu_j}{RT} \qquad (j = NG + 1,...,NS)$$

$$(2.25)$$

$$\sum_{i=1}^{\ell} \sum_{j=1}^{NG} a_{ij} n_j \pi_i + \left(\sum_{j=1}^{NG} n_j - n\right) \Delta \ln n + \left(\sum_{j=1}^{NG} \frac{n_j H_j^o}{RT}\right) \Delta \ln T$$

$$= n - \sum_{j=1}^{NG} n_j + \sum_{j=1}^{NG} \frac{n_j \mu_j}{RT} \qquad (2.26)$$

$$\sum_{i=1}^{\ell} \left(\sum_{j+1}^{NG} \frac{a_{ij} n_j H_j^o}{RT}\right) \pi_i + \sum_{j=NG+1}^{NS} \frac{H_j^o}{RT} \Delta n_j + \left(\sum_{j=1}^{NG} \frac{n_j H_j^o}{RT}\right) \Delta \ln n$$

$$+ \left[\sum_{j=1}^{NG} \frac{n_j C_{p,j}^o}{R} + \sum_{j=1}^{NG} \frac{n_j (H_j^o)^2}{R^2 T^2}\right] \Delta \ln T = \frac{h_0 - h}{RT} + \sum_{j=1}^{NG} \frac{n_j H_j^o \mu_j}{R^2 T^2}$$

$$(2.27)$$

$$\sum_{i=1}^{\ell} \left(\sum_{j=1}^{NG} \frac{a_{ij} n_j S_j}{R}\right) \pi_i + \sum_{j=NG+1}^{NS} \frac{S_j}{R} \Delta n_j + \left(\sum_{j=1}^{NG} \frac{n_j S_j}{R}\right) \Delta \ln n$$

$$+ \left(\sum_{j=1}^{NS} \frac{n_j C_{p,j}^o}{R} + \sum_{j=1}^{NG} \frac{n_j H_j^o S_j}{R^2 T}\right) \Delta \ln T = \frac{S_0 - S}{R} + n$$

$$- \sum_{j=1}^{NG} n_j + \sum_{j=1}^{NG} \frac{n_j S_j \mu_j}{R^2 T} \qquad (2.28)$$

Equations (2.24) to (2.28) are given in table 2.1 in a form that permits a direct comparison with other sets of simultaneous equations presented in later sections (tables 2.2 to 2.4). (Note that tables 2.1 to 2.4 appear at the end of this document.) In a previous report (Gordon and McBride, 1976), some special script symbols were used for the sake of compactness in preparing tables 2.1 to 2.4, as for example,

$$\mathcal{H} = \frac{h}{RT} \qquad (2.29)$$

These script symbols are no longer used in this report.

The correction equations required for several types of constant-pressure problems are summarized as follows, where $i = 1,...,\ell$ and $j = NG + 1,...,NS$:

Type of problem	Equations required	Correction variables
Assigned temperature and pressure, tp	(2.24), (2.25), (2.26)	π_i, Δn_j, $\Delta \ln n$
Assigned enthalpy and pressure, hp	(2.24), (2.25), (2.26), (2.27)	π_i, Δn_j, $\Delta \ln n$, $\Delta \ln T$
Assigned entropy and pressure, sp	(2.24), (2.25), (2.26), (2.28)	π_i, Δn_j, $\Delta \ln n$, $\Delta \ln T$

After obtaining the correction variables shown above, the corrections for gaseous species $\Delta \ln n_j$ ($j = 1,...,NG$) are then obtained from equation (2.18). Section 3.3 discusses controlling the size of corrections before they are applied to obtain improved estimates.

2.4 Minimization of Helmholtz Energy

The equations presented in this section are similar to those in section 2.3. Whatever differences appear are due to the different forms of the chemical potential μ_j ($j = 1,...,NG$). In section 2.3 pressure was one of the assigned thermodynamic states, and consequently Gibbs energy was minimized. In this section volume (or density) is one of the assigned thermodynamic states, and consequently Helmholtz energy is minimized.

The two energies (Gibbs and Helmholtz) have the following thermodynamic relationship:

$$f = g - PV \qquad (2.30)$$

where f is the Helmholtz energy per kilogram of mixture. After substituting Gibbs energy g as given by equation (2.5), equation (2.30) becomes

$$f = \sum_{j=1}^{NS} \mu_j n_j - PV \qquad (2.31)$$

The chemical potential μ_j can be expressed as a thermodynamic derivative in several ways (Kirkwood and Oppenheim, 1961). One way is given by equation (2.6). Another expression is

$$\mu_j = \left(\frac{\partial f}{\partial n_j} \right)_{T,V,n_{i \neq j}} \qquad (2.32)$$

If

$$F = f + \sum_{i=1}^{\ell} \lambda_i \left(b_i - b_i^o \right) \qquad (2.33)$$

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

$$\delta F = \sum_{j=1}^{NS} \left(\mu_j + \sum_{i=1}^{\ell} \lambda_i a_{ij} \right) \delta n_j + \sum_{i=1}^{\ell} \left(b_i - b_i^o \right) \delta \lambda_i = 0 \qquad (2.34)$$

Treating δn_j and $\delta \lambda_i$ as independent again gives, as in section 2.3, equations (2.7) and (2.10). Now, however, instead of equation (2.11),

$$\mu_j = \begin{cases} \mu_j^o + RT \ln \dfrac{n_j R' T}{V} & (j = 1,...,NG) \\[2mm] \mu_j^o & (j = NG + 1,...,NS) \end{cases} \qquad (2.35)$$

where $R' = R \times 10^{-5}$.

Equations (2.7) and (2.10), with μ_j given by equation (2.35), permit the determination of equilibrium compositions for thermodynamic states specified by an assigned temperature T_0 and volume V_0; that is, in addition to equations (2.7) and (2.10), we have the pair of trivial equations

$$T = T_0 \qquad (2.36a)$$

$$V = V_0 \qquad (2.36b)$$

Analogous to equation (2.13) for a constant-pressure combustion process, we can set down the following conditions for constant-volume combustion:

$$u' = u_0' \qquad (2.37a)$$

$$V = V_0 \qquad (2.37b)$$

where u' is the specific internal energy of the mixture and u_0' a constant equal to the specific internal energy of the reactants. The expression for u' is

$$u' = \sum_{j=1}^{NS} n_j U_j^o \qquad (2.38)$$

where U_j^o is the standard-state molar internal energy for species j.

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Analogous to equation (2.15), for assigned entropy and volume (such as for an isentropic compression or expansion to a specified volume), the thermodynamic state is specified by

$$s = s_0 \qquad (2.39a)$$

$$V = V_0 \qquad (2.39b)$$

Iteration equations are derived in section 2.4.1 that permit solution of the composition variables for constant-volume problems.

2.4.1 Helmholtz Iteration Equations

Correction equations are obtained in a manner similar to that described in section 2.3.1. In this case, however, the expression for μ_j is equation (2.35) rather than equation (2.11). Because n does not appear explicitly as a variable in equation (2.35), $\Delta\ln n$ no longer appears as a correction variable. The Newton-Raphson equations obtained from equations (2.10), (2.7), (2.37a), and (2.39a) are

$$\Delta\ln n_j - \sum_{i=1}^{\ell} a_{ij}\pi_i - \frac{U_j^o}{RT}\Delta\ln T = -\frac{\mu_j}{RT} \qquad (j = 1,...,NG)$$

$$(2.40)$$

$$-\sum_{i=1}^{\ell} a_{ij}\pi_i - \frac{U_j^o}{RT}\Delta\ln T = -\frac{\mu_j}{RT} \qquad (j = NG+1,...,\mathbb{N})$$

$$(2.41)$$

$$\sum_{j=1}^{NG} a_{kj}n_j\Delta\ln n_j + \sum_{j=NG+1}^{NS} a_{kj}\Delta n_j = b_k^o - b_k \qquad (k = 1,...,\ell)$$

$$(2.42)$$

$$\sum_{j=1}^{NG} \frac{n_j U_j^o}{RT}\Delta\ln n_j + \sum_{j=NG+1}^{NS} \frac{U_j^o}{RT}\Delta n_j$$

$$+ \left(\sum_{j=1}^{NS} \frac{n_j C_{v,j}^o}{R}\right)\Delta\ln T = \frac{u_0' - u'}{RT} \qquad (2.43)$$

$$\sum_{j=1}^{NG} n_j\left(\frac{S_j}{R} - 1\right)\Delta\ln n_j + \sum_{j=NG+1}^{NS} \frac{S_j}{R}\Delta n_j$$

$$+ \left(\sum_{j=1}^{NS} \frac{n_j C_{v,j}^o}{R}\right)\Delta\ln T = \frac{s_0 - s}{R} \qquad (2.44)$$

where $C_{v,j}^o$ is the standard-state specific heat at constant volume for species j at temperature T.

2.4.2 Reduced Helmholtz Iteration Equations

Equations (2.40) to (2.44) may be reduced to a much smaller set of working correction equations by eliminating $\Delta\ln\ n_j$, obtained from equation (2.40), from equations (2.42) to (2.44). When equation (2.41) written with the signs reversed is included, the resulting reduced set of equations is

$$\sum_{i=1}^{\ell}\sum_{j=1}^{NG} a_{kj}a_{ij}n_j\pi_i + \sum_{j=NG+1}^{NS} a_{kj}\Delta n_j + \left(\sum_{j=1}^{NG} \frac{a_{kj}n_j U_j^o}{RT}\right)\Delta\ln T$$

$$= b_k^o - b_k + \sum_{j=1}^{NG} \frac{a_{kj}n_j\mu_j}{RT} \qquad (k = 1,...,\ell) \qquad (2.45)$$

$$\sum_{i=1}^{\ell} a_{ij}\pi_i + \frac{U_j^o}{RT}\Delta\ln T = \frac{\mu_j}{RT} \qquad (j = NG+1,...,NS)$$

$$(2.46)$$

$$\sum_{i=1}^{\ell}\left(\sum_{j=1}^{NG} \frac{a_{ij}n_j U_j^o}{RT}\right)\pi_i + \sum_{j=NG+1}^{NS} \frac{U_j^o}{RT}\Delta n_j$$

$$+ \left[\sum_{j=1}^{NS} \frac{n_j C_{v,j}^o}{R} + \sum_{j=1}^{NG} \frac{n_j(U_j^o)^2}{R^2 T^2}\right]\Delta\ln T$$

$$= \frac{u_0' - u'}{RT} + \sum_{j=1}^{NG} \frac{n_j U_j^o\mu_j}{R^2 T^2}$$

$$(2.47)$$

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$$\sum_{i=1}^{\ell} \left(\sum_{j=1}^{NG} a_{ij} n_j \frac{S_j - R}{R} \right) \pi_i + \sum_{j=NG+1}^{NS} \frac{S_j}{R} \Delta n_j$$

$$+ \left[\sum_{j=1}^{NS} \frac{n_j C_{v,j}^o}{R} + \sum_{j=1}^{NG} \frac{n_j U_j^o (S_j - R)}{R^2 T} \right] \Delta \ln T$$

$$= \frac{S_0 - s}{R} + \sum_{j=1}^{NG} \frac{n_j (S_j - R) \mu_j}{R^2 T} \qquad (2.48)$$

Equations (2.45) to (2.48) are given in table 2.2 in a form that permits direct comparison with the iteration equations in table 2.1 and the derivative equations in tables 2.3 and 2.4.

The correction equations required for several types of constant-volume problems are summarized as follows, where $i = 1,...,\ell$ and $j = NG + 1,...,NS$:

Type of problem	Equations required	Correction variables
Assigned temperature and volume, tv	(2.45), (2.46)	$\pi_i, \Delta n_j$
Assigned internal energy and volume, uv	(2.45), (2.46), (2.47)	$\pi_i, \Delta n_j, \Delta \ln T$
Assigned entropy and volume, sv	(2.45), (2.46), (2.48)	$\pi_i, \Delta n_j, \Delta \ln T$

After obtaining the correction variables the corrections for gaseous species $\Delta \ln n_j$ ($j=1,...,NG$) are then obtained from equation (2.40). (See section 3.3 for discussion on controlling size of corrections before applying them to obtain improved estimates.)

2.5 Thermodynamic Derivatives From Matrix Solutions

All thermodynamic first derivatives can be expressed in terms of any three independent first derivatives. The Bridgman tables, as tabulated, for example, in Lewis and Randall (1961), 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 use the logarithmic form of the volume derivatives because it gives an indication of the extent of chemical reaction occurring among the reaction species. These derivatives may have more than one value depending on what is assumed occurs to composition in a thermodynamic process from one condition to another. If, for example,

composition is assumed to reach its equilibrium value instantaneously, the derivatives are referred to as "equilibrium" derivatives. If, on the other hand, reaction times are assumed to be infinitely slow, composition remains fixed (frozen) and the derivatives are referred to as "frozen." Special subscripts are used to differentiate these different conditions only for c_p, thermal conductivity, and Prandtl number. The equilibrium value of c_p may be expressed as the the sum of a "frozen" contribution and a "reaction" contribution as follows:

$$c_{p,e} = c_{p,f} + c_{p,r} \qquad (2.49a)$$

where

$$c_{p,f} = \sum_{j=1}^{NS} n_j C_{p,j}^o \qquad (2.49b)$$

and

$$c_{p,r} = \sum_{j=1}^{NG} n_j \frac{H_j^o}{T} \left(\frac{\partial \ln n_j}{\partial \ln T} \right)_P + \sum_{j=NG+1}^{NS} \frac{H_j^o}{T} \left(\frac{\partial n_j}{\partial \ln T} \right)_P \qquad (2.49c)$$

The expressions in equations (2.49b) and (2.49c) were obtained by differentiating equation (2.14). (Subscripts different from those used in equation (2.49a) are used in transport property calculations. See section 5.2.3).

From equation (2.1)

$$\left(\frac{\partial \ln V}{\partial \ln T} \right)_P = 1 + \left(\frac{\partial \ln n}{\partial \ln T} \right)_P \qquad (2.50)$$

$$\left(\frac{\partial \ln V}{\partial \ln P} \right)_T = -1 + \left(\frac{\partial \ln n}{\partial \ln P} \right)_T \qquad (2.51)$$

2.5.1 Derivatives With Respect to Temperature

The derivatives of n_j and n with respect to temperature are needed to evaluate equations (2.49c) and (2.50). These may be obtained by differentiating equations (2.10), (2.7), and (2.3), which gives the following:

$$\left(\frac{\partial \ln n_j}{\partial \ln T} \right)_P - \sum_{i=1}^{\ell} a_{ij} \left(\frac{\partial \pi_i}{\partial \ln T} \right)_P - \left(\frac{\partial \ln n}{\partial \ln T} \right)_P = \frac{H_j^o}{RT}$$

$$(j = 1,...,NG) \qquad (2.52)$$

$$-\sum_{i=1}^{\ell} a_{ij} \left(\frac{\partial \pi_i}{\partial \ln T} \right)_P = \frac{H_j^o}{RT} \qquad (j = NG + 1,...,NS) \qquad (2.53)$$

$$\sum_{j=1}^{NG} a_{kj} n_j \left(\frac{\partial \ln n_j}{\partial \ln T}\right)_P + \sum_{j=NG+1}^{NS} a_{kj} \left(\frac{\partial n_j}{\partial \ln T}\right)_P = 0$$

$$(k = 1,...,\ell) \qquad (2.54)$$

$$\sum_{j=1}^{NG} n_j \left(\frac{\partial \ln n_j}{\partial \ln T}\right)_P - n\left(\frac{\partial \ln n}{\partial \ln T}\right)_P = 0 \qquad (2.55)$$

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 (2.52), from equations (2.54) and (2.55). When equation (2.53) written with the sign reversed is included, the resulting reduced number of temperature derivative equations is

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

$$+ \sum_{j=1}^{NG} a_{kj} n_j \left(\frac{\partial \ln n}{\partial \ln T}\right)_P = -\sum_{j=1}^{NG} \frac{a_{kj} n_j H_j^o}{RT}$$

$$(k = 1,...,\ell) \qquad (2.56)$$

$$\sum_{i=1}^{\ell} a_{ij}\left(\frac{\partial \pi_i}{\partial \ln T}\right)_P = -\frac{H_j^o}{RT} \qquad (j = NG+1,...,NS) \qquad (2.57)$$

$$\sum_{i=1}^{\ell}\sum_{j=1}^{NG} a_{ij} n_j \left(\frac{\partial \pi_i}{\partial \ln T}\right)_P = -\sum_{j=1}^{NG} \frac{n_j H_j^o}{RT} \qquad (2.58)$$

Equations (2.56) to (2.58) are given in table 2.3 in a form that simplifies the comparison of derivative equations with the iteration equations in tables 2.1 and 2.2. The values of the derivatives obtained from equations (2.56) to (2.58) could be used in equation (2.52) to obtain derivatives for the gaseous species $(\partial \ln n_j/\partial \ln T)_P$ ($j = 1,...,NG$) and all of the temperature derivatives could then be used to evaluate c_p from equations (2.49). However, there is an alternative and much simpler procedure for obtaining c_p. Substituting $\partial \ln n_j/\partial \ln T)_P$ obtained from equation (2.52) into equations (2.49) and dividing by R yield

$$\frac{c_{p,e}}{R} = \sum_{i=1}^{\ell} \left(\sum_{j=1}^{NG} \frac{a_{ij} n_j H_j^o}{RT}\right)\left(\frac{\partial \pi_i}{\partial \ln T}\right)_P + \sum_{j=NG+1}^{NS} \frac{H_j^o}{RT}\left(\frac{\partial n_j}{\partial \ln T}\right)_P$$

$$+ \left(\sum_{j=1}^{NG} \frac{n_j H_j^o}{RT}\right)\left(\frac{\partial \ln n}{\partial \ln T}\right)_P + \sum_{j=1}^{NS} \frac{n_j C_{p,j}^o}{R} + \sum_{j=1}^{NG} \frac{n_j (H_j^o)^2}{R^2 T^2}$$

$$(2.59)$$

In equation (2.59) only the temperature derivatives obtained directly from solution of equations (2.56) to (2.58) are required. Furthermore, all the coefficients in equation (2.59) are exactly the coefficients appearing in the reduced-enthalpy equation (2.27). The second-last term in equation (2.59) is the frozen contribution to specific heat (eq. (2.49b)); the remainder of the terms are the reaction contribution (eq. (2.49c)).

2.5.2 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. Differentiating equations (2.10), (2.7), and (2.3) gives

$$\left(\frac{\partial \ln n_j}{\partial \ln P}\right)_T - \sum_{i=1}^{\ell} a_{ij}\left(\frac{\partial \pi_i}{\partial \ln P}\right)_T - \left(\frac{\partial \ln n}{\partial \ln P}\right)_T = -1$$

$$(j = 1,...,NG) \qquad (2.60)$$

$$-\sum_{i=1}^{\ell} a_{ij}\left(\frac{\partial \pi_i}{\partial \ln P}\right)_T = 0 \qquad (j = NG+1,...,NS) \qquad (2.61)$$

$$\sum_{j=1}^{NG} a_{kj} n_j \left(\frac{\partial \ln n_j}{\partial \ln P}\right)_T + \sum_{j=NG+1}^{NS} a_{kj}\left(\frac{\partial n_j}{\partial \ln P}\right)_T = 0$$

$$(k = 1,...,\ell) \qquad (2.62)$$

$$\sum_{j=1}^{NG} n_j \left(\frac{\partial \ln n_j}{\partial \ln P}\right)_T - n\left(\frac{\partial \ln n}{\partial \ln P}\right)_T = 0 \qquad (2.63)$$

Equations (2.60) to (2.63) can be reduced to a smaller set by eliminating $(\partial \ln n_j/\partial \ln P)_T$, obtained from equation (2.60), from equations (2.62) and (2.63). When equation (2.61) written with the sign reversed is included, the results are

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

$$+ \sum_{j=1}^{NG} a_{kj}n_j\left(\frac{\partial \ln n}{\partial \ln P}\right)_T = \sum_{j=1}^{NG} a_{kj}n_j \quad (k = 1,...,\ell) \quad (2.64)$$

$$\sum_{i=1}^{\ell} a_{ij}\left(\frac{\partial \pi_i}{\partial \ln P}\right)_T = 0 \quad (j = NG + 1,...,NS) \quad (2.65)$$

$$\sum_{i=1}^{\ell}\sum_{j=1}^{NG} a_{ij}n_j\left(\frac{\partial \pi_i}{\partial \ln P}\right)_T = \sum_{j=1}^{NG} n_j \quad (2.66)$$

Equations (2.64) to (2.66) are given in table 2.4 for comparison with tables 2.1, 2.2, and 2.3. The only derivative obtained from solution of equations (2.64) to (2.66) that is used is $(\partial \ln n/\partial \ln P)_T$ (see eq. (2.51).

2.6 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 Lewis and Randall (1961)). Velocity of sound a, a frequently used parameter, is defined by

$$a^2 = \left(\frac{\partial P}{\partial \rho}\right)_S = \frac{P}{\rho}\left(\frac{\partial \ln P}{\partial \ln \rho}\right)_S = -\frac{P}{\rho}\left(\frac{\partial \ln P}{\partial \ln V}\right)_S \quad (2.67)$$

From Bridgman tables

$$\left(\frac{\partial \ln P}{\partial \ln V}\right)_S = \frac{c_p}{c_p\left(\frac{\partial \ln V}{\partial \ln P}\right)_T + \frac{PV}{T}\left(\frac{\partial \ln V}{\partial \ln T}\right)_P^2} \quad (2.68)$$

This may be written as

$$\left(\frac{\partial \ln P}{\partial \ln V}\right)_S = \frac{c_p}{c_v\left(\frac{\partial \ln V}{\partial \ln P}\right)_T} \quad (2.69)$$

where

$$c_v \equiv \left(\frac{\partial u'}{\partial T}\right)_V = c_p + \frac{\frac{PV}{T}\left(\frac{\partial \ln V}{\partial \ln T}\right)_P^2}{\left(\frac{\partial \ln V}{\partial \ln P}\right)_T} \quad (2.70)$$

Using the symbols

$$\gamma_s \equiv \left(\frac{\partial \ln P}{\partial \ln \rho}\right)_S \quad (2.71)$$

and

$$\gamma \equiv \frac{c_p}{c_v} \quad (2.72)$$

equation (2.69) may be written as

$$\gamma_s = -\frac{\gamma}{\left(\frac{\partial \ln V}{\partial \ln P}\right)_T} \quad (2.73)$$

Using the equation of state given in equation (2.1), we obtain from equation (2.67) the familiar expression for velocity of sound

$$a = \sqrt{nRT\gamma_s} \quad (2.74)$$

Note that the γ_s defined by equation (2.71) is required in equation (2.74) and not the specific heat ratio γ defined in equation (2.72).

In section 3.5 an alternative expression is derived for γ_s for the special situation of triple phases, where the expressions in equations (2.68), (2.69), and (2.73) are no longer valid.

Gordon and Zeleznik (1962) gives numerous first derivative relations that are of interest in rocket performance calculations. One of these derivatives, which is used in section 6.3.4, is

$$\left(\frac{\partial \ln P}{\partial \ln T}\right)_S = \frac{c_p}{nR\left(\frac{\partial \ln V}{\partial \ln T}\right)_P} \quad (2.75)$$

A numerical example involving this derivative is given in Zeleznik and Gordon (1968).

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Chapter 3
Procedure for Obtaining Equilibrium Compositions

In principle, obtaining equilibrium compositions by means of the Newton-Raphson iteration procedure discussed in sections 2.3.1, 2.3.2, 2.4.1, and 2.4.2 should offer no difficulties. However, a number of practical items require detailed attention in order to avoid numerical difficulties: initial estimates, tests for condensed phases, phase transitions and triple points, convergence, accidental singularities, special handling of ions, and consideration of trace species.

3.1 Initial Estimates

An extremely simple procedure is used in this report to assign estimates for composition. For the first iteration of the first point in a schedule of points, we assign $n = 0.1$, which 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/NG, where NG 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 in the input.

Admittedly, this simple procedure will often give poor initial estimates. However, for a general chemistry program, we find this technique preferable to the alternative 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. 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 question is discussed in section 3.3.

3.2 Magnitude of Species Used During Iteration

Both the linear and logarithmic composition variables are used for gaseous species during the composition iteration process. Only the linear variable is used for condensed species. Corrections to compositions for gases are in the form of logarithmic variables $\Delta \ln n_j$, and therefore the logarithmic values of gaseous compositions $\ln n_j$ are continuously updated from iteration to iteration. The linear values of the compositions n_j are obtained by taking the antilogarithm of $\ln n_j$. However, to save computer time during iteration, n_j are calculated only for those species whose mole fractions are greater than a certain specified size. In a previous version of the program (Gordon and McBride, 1976) this specified size had only one value, namely $n_j/n = 10^{-8}$ (or $\ln n_j/n = -18.420681$). A program variable SIZE was defined as SIZE = 18.420681. Thus, antilogarithms of $\ln n_j$ were obtained only for gases meeting the following condition: $\ln n_j/n \geq -\text{SIZE}$ $(n_j/n > 10^{-8}.)$ For gaseous species not passing this test n_j were set equal to zero. In addition, the maximum number of iterations permitted was 35.

In the present CEA program several additional variables relating to SIZE have been added to handle more demanding situations. Two of the present variables relating to the mole fraction size for which antilogarithms are obtained are TSIZE for non-ionized species and ESIZE for ionized species. TSIZE may be modified for any of the following reasons: inclusion of species in the calculations with mole fractions smaller than 10^{-8} (by means of an input parameter TRACE); a change of

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components; a singular matrix; or the chemical system under consideration containing a chemical element that differs in magnitude from the largest of the other elements by more than 10^5. The purpose of changing TSIZE in the last case is to ensure that not all species containing the trace element will be eliminated during iteration. To aid in testing for trace elements, a parameter BRATIO is defined to be the ratio of the elements with the lowest to highest kilogram-atoms per kilogram of mixture. The following, then, are the conditions under which several parameters relating to species size are set to various values. These conditions are based on extensive practical experience with obtaining solutions for many types of problems:

(1) TSIZE = SIZE until convergence or a singular matrix occurs.

(2) TSIZE = XSIZE if TRACE $\neq$ 0 after first convergence, or if a singular matrix or new components occur.

(3) ITN $\equiv$ maximum number of iterations.

Default:

(1) SIZE = $-\ln 10^{-8}$ = 18.420681
(2) XSIZE = $-\ln 10^{-11}$ = 25.328436
(3) ESIZE = $-\ln 10^{-14}$ = 32.236191
(4) ITN = 50
(5) TRACE = 0

Nondefault:

(1) If TRACE $\neq$ 0, ITN = 50 + NS/2
(2) If TRACE < 10^{-8}, XSIZE = $-\ln$ TRACE and ESIZE = $-\ln$ (TRACE$\times 10^{-3}$) = XSIZE + 6.9077553

(3) If BRATIO < 10^{-5}, SIZE = ln 1000/BRATIO and XSIZE = SIZE + ln 1000 (6.9077553)

(4) If singular matrix, XSIZE = TSIZE = 80.

The use of ESIZE to control the size of ionized species permitted to be present during iteration is discussed in the section 3.7.

3.3 Convergence

The problem of convergence is discussed in Zeleznik and Gordon (1962a) and Gordon and McBride (1976). Zeleznik and Gordon (1962a) points out that the iteration equations sometimes give large corrections that, 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 small amounts. An example of this second situation is given in Zeleznik and Gordon (1962a). In both of these cases a control factor λ is used to restrict the size of the corrections to $\ln n_j$ (j = 1,...,NG) and n_j (j = NG + 1,...,NS) as well as to $\ln n$ and $\ln T$ obtained by solving the equations in tables 2.1 and 2.2.

The numerical value of λ is determined by empirical rules that experience has shown to be satisfactory. For T and n, corrections are limited to a factor of $e^{0.4}$ = 1.4918. For gas-phase species two different correction controls are calculated that depend on the magnitude of the mole fractions. The logarithm of each mole fraction is compared with a parameter called SIZE whose default value is $-\ln 10^{-8}$ = 18.420681. If $\ln(n_j/n) > -$SIZE, corrections to n_j are limited to a factor of e^2 = 7.3891. For these limitations on corrections to T, n, and n_j/n the value of a control factor λ_1 may be calculated as

$$\lambda_1 = \frac{2}{\max(5|\Delta\ln T|, \ 5|\Delta\ln n|, \ |\Delta\ln n_j|)} \quad (3.1)$$

For those gaseous species for which $\ln(n_j/n)$ $\leq -$SIZE and $\Delta\ln n_j \geq 0$, a control factor λ_2 is defined as

$$\lambda_2 = \min\left|\frac{-\ln\frac{n_j}{n} - 9.2103404}{\Delta\ln n_j - \Delta\ln n}\right| \quad (3.2)$$

This prevents a gaseous species with a small mole fraction from increasing to a mole fraction greater than 10^{-4}. The control factor λ to be used in equations (3.4) is defined in terms of λ_1 and λ_2 as

$$\lambda = \min(1, \ \lambda_1, \ \lambda_2) \quad (3.3)$$

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 correction equations

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

$$n_j^{(i+1)} = n_j^{(i)} + \lambda^{(i)}(\Delta n_j)^{(i)} \quad (j = NG + 1,...,NS)$$

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

$$\ln T^{(i+1)} = \ln T^{(i)} + \lambda^{(i)}(\Delta \ln T)^{(i)} \quad (3.4)$$

where the superscript i represents the ith estimate.

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

$$\frac{n_j|\Delta \ln n_j|}{\displaystyle\sum_{j=1}^{NS} n_j} \leq 0.5\times10^{-5} \quad (j = 1,...,NG)$$

$$\frac{|\Delta n_j|}{\displaystyle\sum_{j=1}^{NS} n_j} \leq 0.5\times10^{-5} \quad (j = NG + 1,...,NS)$$

$$\frac{n|\Delta \ln n|}{\displaystyle\sum_{j=1}^{NS} n_j} \leq 0.5\times10^{-5} \quad (3.5)$$

For those chemical elements for which $b_0^i > 1.0\times10^{-6}$, the convergence test for mass balance is

$$\left| b_0^i - \sum_{j=1}^{NS} a_{ij}n_j \right| \leq \left(b_0^i\right)_{max} \times 1.0\times10^{-6} \quad (3.6a)$$

$$(i = 1,...,\ell)$$

where the subscript "max" refers to the chemical element i with the largest value of b_0^i. When temperature is a variable, the convergence test for temperature is

$$|\Delta \ln T| \leq 1.0\times10^{-4} \quad (3.6b)$$

For a constant-entropy problem (sp, sv, or rocket), the following convergence test on entropy is also required:

$$\left| \frac{s_0 - s}{R} \right| \leq 0.5\times10^{-4} \quad (3.6c)$$

When TRACE $\neq$ 0, an additional test is used:

$$\left| \frac{\pi_i^{(k)} - \pi_i^{(k+1)}}{\pi_i^{(k+1)}} \right| \leq 0.001 \quad (i = 1,...,\ell) \quad (3.6d)$$

where the superscript refers to the kth iteration. The convergence tests in equations (3.5) and (3.6) ensure accuracy to five places in composition when expressed as mole fractions.

As pointed out in section 3.2 the maximum number of iterations permitted by the CEA program is 50 + NS/2. For most of the hundreds of different kinds of problems that have been solved by the program, convergence has been obtained in fewer than this number. For the first point, which starts with arbitrary initial estimates, a typical number of iterations is 8 to 20. For succeeding points, which use compositions of a previously calculated point for initial estimates, a typical number of iterations is 3 to 10. In the sample problems given in part II, for example, the number of iterations for the first point was 9 to 15. In some special cases a problem may be singular, and solutions to the correction matrix are then unobtainable. Techniques for handling this situation are discussed in section 3.6.

3.4 Tests for Condensed Phases

For the first point in a schedule of points, unless INSERT records are used (see part II of this report), the program considers only gaseous species during the 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 Gibbs energy. At equilibrium, equation (2.9) 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 Gibbs energy; that is, from equation (2.9)

$$\frac{\partial G}{\partial n_j} = \left(\frac{\mu_j^o}{RT}\right)_c - \sum_{i=1}^{\ell} \pi_i a_{ij} < 0 \quad (3.7)$$

where the subscript c refers to a condensed species. Equation (3.7) is identical to the vapor pressure test used in Zeleznik and Gordon (1962a) when data for the gas

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phase as well for the condensed phase are available. The vapor pressure test is

$$\left(\frac{\mu_j^o}{RT}\right)_c - \left(\frac{\mu_j^o}{RT} + \ln\frac{n_j P}{n}\right)_g < 0 \qquad (3.8)$$

where the subscript g refers to the gas phase of the same species as the solid phase referred to by the subscript c. Equations (3.7) and (3.8) are equivalent. The last term in equation (3.7) is identical for the gas and condensed phases of the same species. From equation (2.10) this term for the gas phase equals $(\mu_j/RT)_g$, which, using the definition of μ_j in equation (2.11), leads directly to equation (3.8). However, the advantage of equation (3.7) over (3.8) is that equation (3.8) can be used only when the gas phase of the species corresponding to the condensed phase to be tested is present, whereas equation (3.7) can always be used. Using equation (3.7) eliminates the need for the extensive programming required in Zeleznik and Gordon (1962a) 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 (3.7), only that species giving the largest negative change to Gibbs 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 (3.7) 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.

3.5 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 because 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 characterization is shown by the fact that the iteration

equations of table 2.1 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 the two or more condensed phases of a species is to be considered. However, when temperature is a variable, such as in combustion or rocket problems, several possibilities 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 second, both liquid and solid might be considered simultaneously and a new convergence obtained. Similar possibilites 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 Zeleznik and Gordon (1962a); the discussion is not repeated herein. In brief, the following criteria are used by the program to determine whether to switch one condensed phase of a species to another or whether to consider both simultaneously:

(1) Liquid present at temperature $T < T_m$:
    (a) If $T_m - T > 50$ K, switch solid for liquid.
    (b) If $T_m - T \leq 50$ K, include solid and liquid.

(2) Solid present at temperature $T > T_m$:
    (a) If $T - T_m > 50$ K, switch liquid for solid.
    (b) If $T - T_m \leq 50$ K, include solid and liquid.

Similar tests apply for two solid phases of a species.

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 (2.73) cannot be used to obtain γ_s.

In Gordon (1970) the following expression was derived for the situation of constant temperature and

entropy:

$$\gamma_{S,T} \equiv \left(\frac{\partial \ln P}{\partial \ln \rho}\right)_{S,T} = -\frac{1}{\left(\frac{\partial \ln V}{\partial \ln P}\right)_T} \qquad (3.9)$$

The velocity of sound for this situation is no longer given by equation (2.74) but rather by

$$a_{S,T} = \sqrt{nRT\gamma_{S,T}} \qquad (3.10)$$

These derivatives will be used in connection with discontinuities in a rocket throat (see section 6.3.4).

3.6 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 several situations involving singularities that would otherwise cause the iteration method to fail. One such situation is a singularity in the coefficient matrix that is caused when all species that contain one of the elements are temporarily eliminated during the iteration process. Another situation resulting in a singularity 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 being considered during the current iteration that contains both elements. That is,

$$\frac{a_{ij}}{a_{kj}} = \frac{b_i^{\,o}}{b_k^{\,o}} \qquad (j = 1,...,NG) \qquad (3.11)$$

One example for which equation (3.11) applies is stoichiometric hydrogen and oxygen at low temperatures and pressures, where the only species with $n_j > 10^{-8}$ is $H_2O(g)$. Another example is stoichiometric lithium and fluorine at low temperatures, where the only species are LiF, Li_2F_2, and Li_3F_3. When either of these two situations occurs, the program will automatically reset all species currently set to zero to $n_j = 10^{-6}$. This reset

feature can be tried twice and will usually take care of these causes of singularity.

If the restart procedure just described is not successful and the situation represented by equation (3.11) is the cause of the singularity, the program will attempt an additional procedure: (1) selecting one of the larger species containing both elements to be one of the new components; (2) reducing the number of components and the size of the coefficient matrix by 1; and (3) switching components for the rest of the chemical system.

Another singularity is caused when several condensed species are currently being considered and one of these species can be formed by some linear combination of the others. An example of this is a chemical system containing iron and oxygen where the current iteration is simultaneously considering FeO(s), $Fe_2O_3(s)$, and $Fe_3O_4(s)$. When this occurs, the program automatically removes one of the species involved with the singularity, prints an error message with this information, and restarts.

3.7 Iteration Procedure and Tests for 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. Plasma textbooks, such as Griem (1964), point out that effects of coulombic interactions do need to be considered in plasmas (by means of the Debye-Huckel approximation, e.g.). However, special programming is needed to take care of these effects. Therefore, because the program does not consider these effects, the results of calculations when ions are considered will be valid only for those conditions where the ionic density is so small that the coulombic effects are unimportant.

For ions to be considered, the charge-balance equation

$$\sum_{j=1}^{NG} a_{ej} n_j = 0 \qquad (3.12)$$

is required, where a_{ej} indicates the excess or deficiency of electrons in the ion relative to the neutral species. For example, in a mole of an ionized species, $a_{ej} = -3$ for Ar^{+++} and $+1$ for O_2^-. To prevent difficulties in matrix

solutions, the program automatically removes the charge-balance equation when, for each ionized species being considered, $\ln n_j/n < -\text{ESIZE}$ (defined in section 3.2).

There are situations when all the previous convergence tests have been passed but the ion balance is still incorrect. A special iteration procedure was developed to obtain the correct ion balance for these situations. It consists of obtaining a value of the Lagrangian multiplier for ions divided by RT, based on the assumption that the magnitude of the ionized species is small relative to the un-ionized species. The initial estimate for π_e is taken to be the value in storage for the current point or from a previous point. The iteration procedure consists of the following steps:

(1) Corrections to π_e are obtained from

$$\Delta\pi_e = \frac{-\sum_{j=1}^{NG} a_{ej} n_j}{\sum_{j=1}^{NG} (a_{ej})^2 n_j} \qquad (3.13)$$

(2) The test for convergence is

$$|\Delta\pi_e| \leq 0.0001 \qquad (3.14)$$

(3) If this convergence test is not met, new estimates for the composition of ionized species are obtained from

$$(\ln n_j)^{i+1} = (\ln n_j)^i + a_{ej}\, \Delta\pi_e \qquad (3.15)$$

where the superscript i refers to the ith iteration. The previous sequence of steps is repeated until equation (3.14) is satisfied. The CEA program allows for a maximum of 80 ion-balance iterations, but generally convergence is reached in about 2 to 10 iterations.

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Chapter 4
Thermodynamic Data

Thermodynamic data are included with the current program for reaction products and reactants. The number of these products and reactants changes over time as new ones are added to the data base. The data are selected from a number of sources, but the principal current sources are Chase et al. (1985), Cox et al. (1989), Gurvich et al. (1989), and Marsh et al. (1988). McBride et al. (1993a) documents the sources and the data for 50 reference elements plus electron gas and deuterium, which are presently included in the thermodynamic data set. These elements are discussed in section 4.1. The data for the atomic gases as well as for a number of diatomic and polyatomic gases were calculated at NASA Lewis by using the PAC91 computer program described in McBride and Gordon (1992).

The thermodynamic data provided with the CEA program are in the form of least-squares coefficients (to be described). These data, in formatted form, are processed by subroutine UTHERM and stored for further use in unformatted form. Subroutine UTHERM and the format for the coefficient data are both described in part II of this report.

4.1 Assigned Enthalpies

For each species heats of formation (and, when applicable, heats of transition) were combined with sensible heats to give assigned enthalpies $H°(T)$. By definition

$$H°(T) \equiv H°(298.15) + [(H°(T) - H°(298.15)] \quad (4.1)$$

We have arbitrarily assumed $H°(298.15) = \Delta_f H°(298.15)$. Equation (4.1) then becomes

$$H°(T) = \Delta_f H°(298.15) + [H°(T) - H°(298.15)] \quad (4.2)$$

In general, $H°(T) \neq \Delta_f H°(T)$ for $T \neq 298.15$ K.

A set of reference elements must be specified in order for heats of formation to be unambiguously related to specific reactions. Included among the species for which thermodynamic data are on a data file are the following 50 reference elements plus deuterium and electron gas: Ag, Al, Ar, B, Ba, Be, Bi, Br_2, C, Ca, Cd, Cl_2, Co, Cr, Cu, D_2, e⁻, F_2, Fe, Ge, H_2, He, Hg, I_2, K, Kr, Li, Mg, Mn, Mo, N_2, Na, Nb, Ne, Ni, O_2, P, Pb, Rb, S, Si, Sn, Sr, Ta, Th, Ti, U, V, W, Xe, Zn, and Zr. The thermodynamic data for these elements are documented in McBride et al. (1993a). For all reference elements $\Delta_f H°(298.15) = H°(298.15) = 0$.

Assigned enthalpies for a number of reactants are in a reactant data file. For noncryogenic reactants assigned enthalpies (heats of formation) are given at 298.15 K. For cryogenic liquids assigned enthalpies are given at their boiling points. These enthalpies are usually obtained by subtracting the following quantities from the heat of formation of the gas phase at 298.15 K: the sensible heat between 298.15 K and the boiling point, the difference in enthalpy between the ideal gas and the real gas at the boiling point, and the heat of vaporization at the boiling point.

4.2 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. The general form of these equations is as follows:

$$\frac{C_p°}{R} = \sum a_i T^{q_i} \quad (4.3)$$

$$\frac{H^\circ}{RT} = \frac{\int C_p^\circ \, dT}{RT} \qquad (4.4)$$

$$\frac{S^\circ}{R} = \int \frac{C_p^\circ}{RT} dT \qquad (4.5)$$

Two sets of least-squares coefficients have been used in the chemical equilibrium program to represent thermodynamic data. The "old" form has been used for the last 25 years (Gordon and McBride, 1976; and McBride et al., 1993b). It consists of a fourth-order polynomial for the C_p°/R function plus integration constants for enthalpy and entropy as follows:

$$\frac{C_p^\circ}{R} = a_1 + a_2 T + a_3 T^2 + a_4 T^3 + a_5 T^4 \qquad (4.6)$$

$$\frac{H^\circ}{RT} = a_1 + \frac{a_2}{2} T + \frac{a_3}{3} T^2 + \frac{a_4}{4} T^3 + \frac{a_5}{5} T^4 + \frac{a_6}{T} \qquad (4.7)$$

$$\frac{S^\circ}{R} = a_1 \ln T + a_2 T + \frac{a_3}{2} T^2 + \frac{a_4}{3} T^3 + \frac{a_5}{4} T^4 + a_7 \qquad (4.8)$$

The "new" form for these functions will be used to represent the thermodynamic data with the program described in part II. This form consists of seven terms for C_p°/R and corresponding terms for enthalpy and entropy as well as the integration constants a_8 and a_9 as follows:

$$\frac{C_p^\circ}{R} = a_1 T^{-2} + a_2 T^{-1} + a_3 + a_4 T$$
$$+ a_5 T^2 + a_6 T^3 + a_7 T^4 \qquad (4.9)$$

$$\frac{H^\circ}{RT} = -a_1 T^{-2} + a_2 T^{-1} \ln T + a_3 + a_4 \frac{T}{2} + a_5 \frac{T^2}{3}$$
$$+ a_6 \frac{T^3}{4} + a_7 \frac{T^4}{5} + \frac{a_8}{T} \qquad (4.10)$$

$$\frac{S^\circ}{R} = -a_1 \frac{T^{-2}}{2} - a_2 T^{-1} + a_3 \ln T + a_4 T$$
$$+ a_5 \frac{T^2}{2} + a_6 \frac{T^3}{3} + a_7 \frac{T^4}{4} + a_9 \qquad (4.11)$$

For gases the temperature intervals for both the old and new functional forms are fixed. These intervals are 200 to 1000 K and 1000 to 6000 K for the old form (i.e., the fourth-order polynomial form for C_p°). The new form uses these same intervals plus an additional interval from 6000 to 20 000 K for some gases. For the condensed species each phase has its own set of coefficients. If possible, the old form uses the same two temperature intervals for condensed species as for the gases, but the intervals are usually limited by transition points. Furthermore, there are two intervals only if the 1000 K common point is within the species temperature range. Otherwise, there is just one. By contrast, the new functional form has a flexible number of intervals in order to fit the selected data more accurately.

Generally, the three functions C_p°/R, H°/RT, and S°/R are fit simultaneously. The fit is constrained to match the functions exactly at $T = 298.15$ K. Thus, the least-squares coefficients reproduce heats of formation at $T = 298.15$ K exactly. For temperature intervals that do not contain $T = 298.15$ K, the fit is constrained to give the same functional values at the common temperature point for any contiguous intervals. When phase transitions occur, the fit is constrained so that the difference in Gibbs energy is zero between the phases at the transition point.

Chapter 5
Thermal Transport Property Data

The CEA program provides an option for calculating mixture viscosities and thermal conductivities. The formulas for these mixture properties are given in section 5.2. Viscosity and thermal conductivity data for individual gaseous species, which are required for the mixture calculations, are included with the current program. Thermal transport properties for condensed species are not included inasmuch as there is no feasible method for calculating thermal transport properties for a multi-phase mixture. The thermal transport data were taken from Svehla (1995).

5.1 Data for Individual Species

The thermal transport property data provided with the CEA program are in the form of least-squares coefficients. The data for each species were fitted to the following form, which is also used in Gordon et al. (1984):

$$\begin{rcases} \ln \eta \\ \ln \lambda \end{rcases} = A \ln T + \frac{B}{T} + \frac{C}{T^2} + D \qquad (5.1)$$

where η is viscosity and λ is thermal conductivity. A binary interaction parameter η_{ij} is also included for some pairs of species in the same form as equation (5.1).

The coefficients in equation (5.1) were generated to give viscosity in units of micropoise (μP) and thermal conductivity in units of microwatts per centimeter-kelvin ($\mu W/cm$-K). The order and format of the transport data coefficients are given in part II of this report.

5.2 Mixture Property Data

Thermal conductivity and specific heat of a mixture each consists of two parts, the so-called "frozen" and "reaction" contributions. This was discussed for specific heat in section 2.5. Equation (2.49a) shows specific heat as the sum of these two parts. Analogously, thermal conductivity can be written as

$$\lambda_{eq} = \lambda_{fr} + \lambda_{re} \qquad (5.2)$$

where λ_{eq}, λ_{fr}, and λ_{re} are the equilibrium, frozen, and reaction thermal conductivities of the mixture, respectively. The mixture viscosity, on the other hand, has only one term.

5.2.1 Viscosity and Frozen Thermal Conductivity

As pointed out in Gordon et al. (1984), most approximate mixture methods have the following form for mixture viscosities and frozen thermal conductivities (also the form used in the CEA program):

$$\eta_{mix} = \sum_{i=1}^{NM} \frac{x_i \eta_i}{x_i + \sum_{\substack{j=1 \\ j \neq i}}^{NM} x_j \phi_{ij}} \qquad (5.3)$$

and

$$\lambda_{fr} = \sum_{i=1}^{NM} \frac{x_i \lambda_i}{x_i + \sum_{\substack{j=1 \\ j \neq i}}^{NM} x_j \psi_{ij}} \qquad (5.4)$$

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where NM is the number of gaseous species for thermal transport property calculations (NM ≤ 50), x_i is the mole fraction of species i relative to the NM gaseous species used for thermal transport property calculations, η_i is the viscosity of species i, η_{mix} is the viscosity of the mixture, λ_i is the thermal conductivity of species i, ϕ_{ij} is the viscosity interaction coefficient between species i and j in equation (5.3) ($\phi_{ij} \neq \phi_{ji}$), and ψ_{ij} is the interaction coefficient between species i and j in equation (5.4) ($\psi_{ij} \neq \psi_{ji}$).

Several forms for the interaction coefficients ϕ_{ij} and ψ_{ij} available in the literature are compared in Gordon et al. (1984), and the following were used:

$$\phi_{ij} = \frac{1}{4}\left[1 + \left(\frac{\eta_i}{\eta_j}\right)^{1/2}\left(\frac{M_j}{M_i}\right)^{1/4}\right]^2\left(\frac{2M_j}{M_i + M_j}\right)^{1/2} \quad (5.5)$$

and

$$\psi_{ij} = \phi_{ij}\left[1 + \frac{2.41(M_i - M_j)(M_i - 0.142M_j)}{(M_i + M_j)^2}\right] \quad (5.6)$$

For some pairs of species an interaction parameter η_{ij} is available from the literature. As discussed in section 5.1, these values have been least squared and are included in the transport property data file. When this parameter is available, ϕ_{ij} is obtained from the following equation rather than from equation (5.5):

$$\phi_{ij} = \frac{\eta_i}{\eta_{ij}}\frac{2M_j}{M_i + M_j} \quad (5.7)$$

The interaction parameter η_{ij} also appears in the expression for the reaction contribution to thermal conductivity. The same values of ϕ_{ij} that are obtained from equations (5.5) or (5.7) are also used in equation (5.6).

5.2.2 Reaction Thermal Conductivity

The reaction contribution to thermal conductivity is obtained in the same manner as discussed by Butler and Brokaw (1957) and Brokaw (1960) and as used by Svehla and McBride (1973). The following equation is used, which is applicable when local equilibrium exists in a mixture of reacting or ionizing gases:

$$\lambda_{re} = R \sum_{i=1}^{NR} \frac{\Delta_r H_i^o}{RT} \lambda_{r,i} \quad (5.8)$$

where NR is the total number of chemical reactions of gaseous species and $\Delta_r H_i^o$ is the heat of reaction for reaction i at temperature T expressed as

$$\Delta_r H_i^o(T) = \sum_{k=1}^{NM} \alpha_{ik}H_k^o \quad (i = 1,2,...,NR) \quad (5.9)$$

where α_{ik} are the stoichiometric coefficients written for the chemical reactions involving species A_k as follows:

$$\sum_{k=1}^{NM} \alpha_{ik}A_k = 0 \quad (i = 1,2,...,NR) \quad (5.10)$$

Equations (5.8) to (5.10) are also applicable to ionizing gases. In this case the heat of reaction is replaced by the ionization potential, and ions and electrons are species.

Note that the stoichiometric coefficients α_{ik} discussed here are defined differently from the stoichiometric coefficients a_{ij} discussed in chapter 2. In the coefficients α_{ik} the subscripts refer to species k in reaction i, and the coefficient may be positive or negative. In the coefficients a_{ij} the subscripts refer to chemical element i in species j, and the coefficient is always positive.

The $\lambda_{r,i}$ required in equation (5.8) are found by solving the following set of linear equations:

$$\sum_{j=1}^{NR} g_{ij}\lambda_{r,j} = \frac{\Delta_r H_i^o(T)}{RT} \quad (i = 1,2,...,NR) \quad (5.11)$$

where the g_{ij} are given by

$$g_{ij} = \sum_{k=1}^{NM-1} \sum_{\ell=k+1}^{NM} \left(\frac{RT}{PD_{k\ell}}x_k x_\ell\right)\left(\frac{\alpha_{ik}}{x_k} - \frac{\alpha_{i\ell}}{x_\ell}\right)\left(\frac{\alpha_{jk}}{x_k} - \frac{\alpha_{j\ell}}{x_\ell}\right) \quad (5.12)$$

and where

$$\frac{RT}{PD_{k\ell}} = \frac{5M_k M_\ell}{3A_{k\ell}^*\eta_{k\ell}(M_k + M_\ell)} \quad (5.13)$$

The $A_{k\ell}^*$ factor in the previous equation is a collision cross-section ratio that is used in Svehla and McBride (1973) but is not used in this report. In its place we have substituted the value of 1.1, which, as may be seen in Hirschfelder et al. (1954) (table I–N for the Lennard-Jones potential and table VII–E for the modified

Buckingham 6-exp potential), is a typical value (to two figures) for this parameter. The parameter $\eta_{k\ell}$ in equation (5.13) was briefly discussed in section 5.2.1 and is available for some pairs of species with the transport properties of individual species. For most pairs of species, however, it is calculated from equation (5.7) where $\phi_{k\ell}$ is defined, with appropriate subscripts, by equation (5.5). The thermal conductivity of the gas mixture as given by equation (5.2) is then obtained by adding the results of equations (5.4) and (5.8).

5.2.3 Specific Heat for Gases Only

Some functions, such as Prandtl number, involve a number of other parameters (e.g., specific heat, viscosity, and thermal conductivity). In this event, for consistency, the parameters involved should be based on similar assumptions. Inasmuch as viscosity and thermal conductivity are calculated for a maximum of 50 gases (with no condensed species permitted), specific heat, when used with these properties, should also be based on the same gases. The following equation, which is similar to equation (2.49a) but with different subscripts, is used to express specific heat for transport property calculations:

$$c_{p,\text{eq}} = c_{p,\text{fr}} + c_{p,\text{re}} \quad (5.14)$$

When no condensed species are present and the same gaseous species are included in the transport property calculations as in the thermodynamic property calculations, equations (2.49a) and (5.14) will produce the same numerical results. Otherwise, they may yield different results.

The equation for $c_{p,\text{fr}}$ is similar to equation (2.49b) except for being restricted to gases and having a different limit for the number of gases involved; that is,

$$c_{p,\text{fr}} = \frac{\sum\limits_{i=1}^{NM} x_i C_{p,i}^\circ}{\sum\limits_{i=1}^{NM} x_i M_i} \quad (5.15)$$

An alternative method of calculating the reaction contribution to specific heat is given in Svehla and Brokaw (1966) that differs from but is equivalent to equation (2.49c) or the reaction part of equation (2.59). It is analogous to the method for obtaining the reaction contribution to thermal conductivity (eq. (5.8)), namely

$$c_{p,\text{re}} = \frac{R\sum\limits_{i=1}^{NR} \dfrac{\Delta_r H_i^\circ}{RT} X_i}{\sum\limits_{i=1}^{NM} x_i M_i} \quad (5.16)$$

Note that the upper case X_i in equation (5.16) are not the same variables as the lower case x_i. The X_i are found by solving the following set of linear equations:

$$\sum\limits_{j=1}^{NR} d_{ij} X_i = \frac{\Delta_r H_i^\circ}{RT} \quad i = 1,2,...,NR \quad (5.17)$$

where the d_{ij} are given by

$$d_{ij} = \sum\limits_{k=1}^{NM-1} \sum\limits_{\ell=k+1}^{NM} x_k x_\ell \left(\frac{\alpha_{ik}}{x_k} - \frac{\alpha_{i\ell}}{x_\ell} \right) \left(\frac{\alpha_{jk}}{x_k} - \frac{\alpha_{j\ell}}{x_\ell} \right) \quad (5.18)$$

Note that the terms in equation (5.18) are the same as those in equation (5.12) except that the $RT/PD_{k\ell}$ group is not present.

5.2.4 Prandtl Number

Prandtl numbers have application in heat transfer calculations. Frozen and equilibrium Prandtl numbers may be calculated from previously calculated properties by means of

$$\text{Pr}_{\text{fr}} = \frac{c_{p,\text{fr}} \eta_{\text{mix}}}{\lambda_{\text{fr}}} \quad (5.19a)$$

and

$$\text{Pr}_{\text{eq}} = \frac{c_{p,\text{eq}} \eta_{\text{mix}}}{\lambda_{\text{eq}}} \quad (5.19b)$$

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Chapter 6
Theoretical Rocket Performance

Before the publication of Gordon and McBride (1988), the Chemical Equilibrium Calculations (CEC) computer program described in Gordon and McBride (1976) could calculate theoretical rocket performance only for an infinite-area combustion chamber (IAC). Calculation of rocket performance for a finite-area combustor (FAC), presented in Gordon and McBride (1988), was added as an option to the Chemical Equilibrium with Transport Properties (CET) program in 1988.

Figure 6.1 presents schematic cross sections of FAC and IAC rocket engines. Various points at which calcula-

Figure 6.1.—Schematics of rocket combustion chamber cross sections. (a) Finite-area combustion chamber. (b) Infinite-area combustion chamber.

tions are made in the CEA program to obtain rocket performance are indicated in these figures. Combustion and throat parameters are always calculated first automatically. For the IAC model, only one combustion point is calculated, namely, at infinite area (inf). However, for the FAC model, two combustion points are calculated, namely, at the combustion chamber inlet (or equivalently at the injector face, inj) and at the combustor end, c. In addition to these two combustion points for the FAC, a combustion calculation for an infinite-area combustor, indicated in figure 6.1(a) by the dashed line, is also made. The results at this fictitious point are used as an aid in an iteration procedure to obtain combustor end conditions, as discussed in section 6.4. In addition, the pressure at this point is used in calculating c^* (see section 6.2.6). Throat conditions are indicated by the subscript t; other nozzle exit conditions, either subsonic or supersonic, are indicated by the subscript e. Nozzle conditions are assigned as an option and may be in the form of assigned area ratios, pressure ratios, or both.

6.1 Assumptions

The calculation of theoretical rocket performance involves a number of assumptions. For the same propellant and operating conditions theoretical performance can vary depending on which assumptions are used. For this report most of the assumptions are the same for both the IAC and FAC models. These assumptions are one-dimensional form of the continuity, energy, and momentum equations; zero velocity at the combustion chamber inlet; complete combustion; adiabatic combustion; isentropic expansion in the nozzle; homogeneous mixing; ideal-gas law; and zero temperature lags and zero velocity lags between condensed and gaseous species. The chamber in the FAC model is assumed to have a constant cross-sectional area. In this chamber
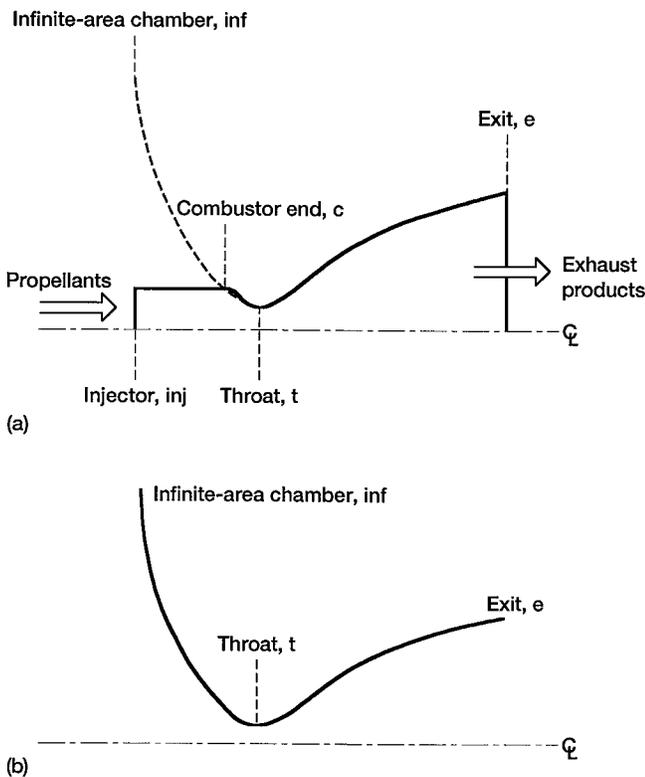
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combustion is a nonisentropic, irreversible process. During the burning process part of the energy released is used to raise the entropy, and the pressure drops. Expansion in the nozzle is assumed to be isentropic.

Combustion conditions are obtained with the assumption of chemical equilibrium of the combustion products. For the IAC model the CEA program provides the option of calculating either equilibrium or frozen theoretical rocket performance. Equilibrium performance is based on the assumption of instantaneous chemical equilibrium during expansion in the nozzle. Frozen performance is based on the assumption that composition remains frozen at the combustion composition during expansion. For the FAC model only equilibrium performance is permitted.

Assuming the same velocity (either zero or otherwise) at the combustion chamber inlet, identical thermodynamic results are obtained for the combustion inlet condition for both the IAC and FAC models.

6.2 Parameters

6.2.1 Conservation Equations

Rocket performance, as well as other fluid dynamic problems in the program, is based on the following conservation equations, which are consistent with the assumptions previously discussed:

(1) Continuity:

$$\rho_2 A_2 u_2 = \rho_1 A_1 u_1 \qquad (6.1)$$

(2) Momentum:

$$P_2 + \rho_2 u_2^2 = P_1 + \rho_1 u_1^2 \qquad (6.2)$$

(3) Energy:

$$h_2 + \frac{u_2^2}{2} = h_1 + \frac{u_1^2}{2} \qquad (6.3)$$

Equation (6.1) describes the condition of constant mass flow rate, which will be given the symbol $\dot{m}$; that is,

$$\dot{m} = \rho A u \qquad (6.4)$$

Equation (6.2) applies only for constant-area, one-dimensional flow.

6.2.2 Velocity of Flow

The combustion chamber inlet is indicated by the subscripts inf for the IAC model and inj for the FAC model. Then using these subscripts instead of 1 and using e instead of 2 in equation (6.3) and assuming the velocity at the combustion chamber inlet to be negligible relative to the exit velocity result in equation (6.3) becoming

$$u_e = \begin{cases} \sqrt{2(h_{\text{inf}} - h_e)} & \text{for IAC model} \\ \sqrt{2(h_{\text{inj}} - h_e)} & \text{for FAC model} \end{cases} \qquad (6.5)$$

where h is in units of joules per kilogram and u is in units of meters per second.

6.2.3 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 the increase in pressure forces acting on the body. For rocket applications this is expressed as

$$F = \frac{\dot{m} u_e}{g_c} + (P_e - P_a)A_e \qquad (6.6)$$

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 the International System (Goldman and Bell, 1986), $g_c = 1$. However, in the English Technical System, commonly used by engineers,

$$g_c = 32.1740 \ (\text{lbm/lbf})(\text{ft/s}^2)$$

6.2.4 Specific Impulse

Specific impulse is defined as force per unit mass flow rate. From equation (6.6)

$$I = \frac{F}{\dot{m}} = \frac{u_e}{g_c} + \frac{(P_e - P_a)A_e}{\dot{m}} \qquad (6.7)$$

In rocket literature specific impulse is often expressed in English Technical System 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}. From equation (6.7)

$$I_{sp} = \frac{u_e}{g_c} \qquad (6.8)$$

When the ambient pressure is assumed to be zero (vacuum conditions), specific impulse will be given the symbol I_{vac}. From equations (6.7) and (6.8)

$$I_{vac} = I_{sp} + \frac{P_e A_e}{\dot{m}} \qquad (6.9)$$

6.2.5 Mach Number

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

$$\mathcal{M} = \frac{u}{a} \qquad (6.10)$$

Velocity of flow is given by equation (6.5). Velocity of sound is given by equation (2.74) (or eq. (3.10)).

6.2.6 Characteristic Velocity

Characteristic velocity is given the symbol c^* and is defined as

$$c^* = \frac{P_{inf} A_t g_c}{\dot{m}} \qquad (6.11)$$

6.2.7 Area per Unit Mass Flow Rate

From equation (6.4)

$$\frac{A}{\dot{m}} = \frac{1}{\rho u_e} \qquad (6.12)$$

The terms ρ and u_e are obtained from equations (2.1b) and (6.5), respectively.

6.2.8 Coefficient of Thrust

The coefficient of thrust is defined in terms of previously defined parameters

$$C_F = \frac{u}{c^*} \qquad (6.13)$$

6.2.9 Area Ratio

The ratio of area at any exit nozzle station to area at the throat is obtained from the values of equation (6.12) at these two points

$$\frac{A_e}{A_t} = \frac{(A/\dot{m})_e}{(A/\dot{m})_t} \qquad (6.14)$$

6.3 Procedure for Obtaining Equilibrium Rocket Performance for IAC Model

The procedure for obtaining equilibrium performance differs somewhat for the IAC and FAC models. The principal difference is due to only one combustion point being required for the IAC model (point inf in fig. 6.1(b)) but two combustion points being required for the FAC model, namely, at the inlet and exit of the finite chamber (points inj and c in fig. 6.1(a)). The procedure for the IAC model is discussed first, inasmuch as it is somewhat simpler.

For the IAC model the procedure consists of first determining combustion properties and then determining exhaust properties at the throat and at other assigned stations, if any, in the nozzle exit. Combustion and throat conditions are always obtained first automatically by the CEA program. To obtain other nozzle conditions (either subsonic or supersonic), the desired points must be specified as part of the input in the form of assigned area ratios or pressure ratios.

For the FAC model the procedure involves first determining combustion properties at the combustor inlet. This station is also referred to as the "injector (inj) station." Conditions at the end of the combustor c and at the throat are then both determined by means of an iteration loop that also includes the fictitious point inf

(fig. (6.1(a)), as discussed in section 6.4. The two combustion stations inj and c and the throat are always calculated first automatically by the CEA program. As is the case for the IAC model other nozzle exit points, if desired, must be specified.

6.3.1 Combustion Conditions

For both the FAC model at station inj and the IAC model at station inf, the same 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 and other combustion properties are determined. For the IAC model the combustion entropy s_{inf} is assumed to be constant during isentropic expansion in the nozzle. However, combustion in a finite-area rocket chamber (the FAC model) is a nonisentropic process. The entropy increases during the combustion process from s_{inj} to s_c while pressure drops from P_{inj} to P_c. For the FAC model the entropy at the end of the combustion chamber s_c is held constant during isentropic expansion in the nozzle.

6.3.2 Exit Conditions

Exit conditions include the throat conditions and assigned area ratios A_e/A_t or pressure ratios P_{inf}/P_e or P_{inj}/P_e. Throat conditions are always determined automatically by the program. Other exit conditions, on the other hand, are optional and, if included, will be calculated after throat calculations are completed.

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_{inf} for IAC and s_{inj} for FAC). For throat and assigned area ratios iteration procedures are used to determine the correct pressure ratios. These procedures are described in sections 6.3.3 to 6.3.7.

After equilibrium compositions and temperature are obtained for an assigned pressure ratio or area ratio, all the rocket parameters for that point can be determined.

6.3.3 Throat Conditions

Throat conditions can be determined by locating the pressure or pressure ratio for which the area ratio is a minimum or, equivalently, for which the velocity of flow

is equal to the velocity of sound. The second procedure is used in this report. Throat pressure is determined by iteration.

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

$$\frac{P_{inf}}{P_t} = \left(\frac{\gamma_s + 1}{2}\right)^{\gamma_s/(\gamma_s-1)} \qquad (6.15)$$

Equation (6.15) is found in many references on rocket propulsion, such as Sutton and Ross (1976), but is exact only when γ_s is constant from combustion point to throat. Because the value of γ_s is not yet known at the throat, the value of γ_s from the combustion point is used by the CEA program in equation (6.15). It generally gives an excellent initial estimate.

Equilibrium properties for s_{inf} and for the value of P_t calculated from equation (6.15) are obtained as for any exit point. From these properties u_e^2 (using eq. (6.5)) and a_e^2 (using eq. (2.74)) are calculated and the following test for convergence is made:

$$\left|\frac{u_e^2 - a_e^2}{u_e^2}\right| \leq 0.4 \times 10^{-4} \qquad (6.16)$$

This criterion is equivalent to ensuring that at the throat the Mach number is within $1 \pm 0.2 \times 10^{-4}$.

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

$$P_{t,k+1} = \left(P\frac{1 + \gamma_s \mathcal{M}^2}{1 + \gamma_s}\right)_{t,k} \qquad (6.17)$$

where the subscript k indicates the kth iteration. A maximum of four iterations on throat pressure is permitted. Usually, no more than two are required.

6.3.4 Discontinuities at Throat

Gordon (1970) gives a special procedure for obtaining throat conditions when the velocity of sound is discontinuous at the throat. This type of discontinuity may occur when a transition point, such as a melting point, is being calculated at the throat. The solution of this problem requires the following equation, which

permits estimating the throat pressure at the melting point, where the solid phase just begins to appear:

$$\ln P_t = \ln P + \left(\frac{\partial \ln P}{\partial \ln T}\right)_S (\ln T_m - \ln T) \qquad (6.18)$$

where the derivative is given by equation (2.75).

6.3.5 Assigned Subsonic or Supersonic Area Ratios

An iteration process is used in the CEA program to obtain the pressure ratios corresponding to the assigned area ratios. In general, initial estimates for pressure ratios in the iteration scheme are obtained from empirical equations derived from plots of previously calculated data. However, if the current as well as the previous assigned supersonic area ratios are 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.

6.3.6 Empirical Formulas for Initial Estimates of P_{inf}/P_e

Initial estimates of pressure ratios corresponding to subsonic area ratios are obtained from the following empirical formulas:

$$\ln\frac{P_{inf}}{P_e} = \frac{\ln\frac{P_{inf}}{P_t}}{\frac{A_e}{A_t} + 10.587\left(\ln\frac{A_e}{A_t}\right)^3 + 9.454\,\ln\frac{A_e}{A_t}}$$

$$\left(\frac{A_e}{A_t} \geq 1.09\right) \qquad (6.19)$$

and

$$\ln\frac{P_{inf}}{P_e} = \frac{0.9\ln\frac{P_{inf}}{P_t}}{\frac{A_e}{A_t} + 10.587\left(\ln\frac{A_e}{A_t}\right)^3 + 9.454\ln\frac{A_e}{A_t}}$$

$$\left(1.0001 < \frac{A_e}{A_t} < 1.09\right) \qquad (6.20)$$

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:

$$\ln\frac{P_{inf}}{P_e} = \ln\frac{P_{inf}}{P_t} + \sqrt{3.294\left(\ln\frac{A_e}{A_t}\right)^2 + 1.535\,\ln\frac{A_e}{A_t}}$$

$$\left(1.0001 < \frac{A_e}{A_t} < 2\right) \qquad (6.21)$$

and

$$\ln\frac{P_{inf}}{P_e} = \gamma_s + 1.4\,\ln\frac{A_e}{A_t} \qquad \left(\frac{A_e}{A_t} \geq 2\right) \qquad (6.22)$$

In equation (6.22) the value of γ_s is that determined for throat conditions.

6.3.7 Analytic Expression for Improved Estimates of P_{inf}/P_e

The equilibrium properties obtained for the initial and each subsequently improved estimate of P_{inf}/P_e are used in equations (6.23) and (6.24) to obtain the next improved estimates. From table I of Gordon and Zeleznik (1962) the following derivative can be obtained:

$$\left(\frac{\partial \ln\frac{P_{inf}}{P_e}}{\partial \ln\frac{A_e}{A_t}}\right)_s = \frac{1}{\left(\frac{1}{\gamma_s} - \frac{nRT}{u^2}\right)_e} = \left(\frac{\gamma_s u^2}{u^2 - a^2}\right)_e \qquad (6.23)$$

This derivative is used in the following correction formula to obtain an improved estimate for P_{inf}/P_e:

$$\left(\ln\frac{P_{inf}}{P_e}\right)_{k+1} = \left(\ln\frac{P_{inf}}{P_e}\right)_k + \left[\left(\frac{\partial \ln\frac{P_{inf}}{P_e}}{\partial \ln\frac{A_e}{A_t}}\right)_s\right]_k$$

$$\times \left[\ln\frac{A_e}{A_t} - \left(\ln\frac{A_e}{A_t}\right)_k\right] \qquad (6.24)$$

where the subscript k refers to the kth estimate and where the area ratio with no iteration subscript is the assigned value. The iteration procedure is continued until

$$\left|\left(\ln\frac{P_{inf}}{P_e}\right)_{k+1} - \left(\ln\frac{P_{inf}}{P_e}\right)_k\right| \leq 0.00004 \qquad (6.25)$$

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

6.4 Procedure for Obtaining Equilibrium Rocket Performance for FAC Model

In this report the finite-area combustor is assumed to have a constant cross section. For this constant-area combustion chamber the momentum equation (6.2) can be written as

$$(P + \rho u^2)_{inj} = (P + \rho u^2)_c \qquad (6.26)$$

Substituting $\dot{m}/A = \rho u$ (from the continuity eq. (6.4)) into equation (6.26) gives

$$\left(P + \frac{\dot{m}u}{A}\right)_{inj} = \left(P + \frac{\dot{m}u}{A}\right)_c \qquad (6.27)$$

When velocity at the injector face is negligible, equations (6.26) and (6.27) reduce to

$$P_{inj} = (P + \rho u^2)_c = \left(P + \frac{\dot{m}u}{A}\right)_c \qquad (6.28)$$

An iteration procedure is required to satisfy equation (6.28). This procedure is somewhat different for each of the two possible input options available for FAC. In option 1 the contraction ratio A_c/A_t is assigned. In option 2 the mass flow rate per unit combustor area $\dot{m}/A_c$ is assigned. The iteration procedure for option 1 is simpler and therefore will be described first. Four points shown in figure 6.1 (inj, inf, c, and t) are involved in the iteration procedure. Thermodynamic parameters at the injector face are obtained by a combustion calculation. This point needs to be calculated only once. Starting with an estimated value for P_{inf}, calculations are then made for points inf, t, and c (the assigned contraction ratio) exactly as is done for the IAC model (for the infinite-area combustion point, the throat, and an assigned subsonic area ratio). A check is then made to see if equation (6.28) is satisfied to within the tolerance

$$\frac{|P_{inj} - (P + \rho u^2)_c|}{P_{inj}} \leq 2\times10^{-5} \qquad (6.29)$$

If equation (6.29) is satisfied, the calculations for the finite-area combustor are complete for points c and t. Calculations are then continued if other values of pressure ratio and/or area ratio have been specified in the input. If equation (6.29) is not satisfied, an improved estimate for P_{inf} is obtained as described in section 6.4.2, and the procedure for the points inf, t, and c is repeated until equation (6.29) is satisfied.

An iteration procedure similar to that described for option 1 is also used for option 2. However, the contraction ratio is not known for option 2. Therefore, the iteration procedure involves starting with an estimated value for A_c/A_t as well as for P_{inj} and then obtaining improved estimates for both P_{inj} and A_c/A_t. Not surprisingly, more iterations are required for option 2 than for option 1, which requires improved estimates for P_{inj} only. As for option 1 iteration is complete when equation (6.29) is satisfied.

6.4.1 Initial Estimates for P_{inf} and A_c/A_t

A curve given in figure 3–14 of Sutton and Ross (1976) relates P_{inf}/P_{inj} with A_c/A_t for an assumed value of $\gamma = 1.2$. The following empirical equation was derived by fitting three selected points read from the curve:

$$P_{inf} = P_{inj}\left(\frac{1.0257 - 1.2318\frac{A_c}{A_t}}{1 - 1.26505\frac{A_c}{A_t}}\right) \qquad (6.30)$$

Equation (6.30) is used only to obtain an initial estimate for P_{inf}.

For option 1 the assigned value of the contraction ratio A_c/A_t is used in equation (6.30). For option 2 an initial estimate of A_c/A_t is required. This initial estimate is obtained from

$$\frac{A_c}{A_t} = \frac{P_{inf}}{2350\frac{\dot{m}}{A_c}} \qquad (6.31)$$

Equation (6.31) was derived by starting with the relationship for characteristic velocity $c^* = P_{inf}A_t/\dot{m}$ (eq. (6.11) with $g_c = 1$), multiplying both sides by A_c, and using a representative but approximate value of $c^* = 2350$ m/s. When equation (6.31) is substituted into equation (6.30), a quadratic in P_{inf} is obtained. The solution of this quadratic gives the initial estimate for P_{inf}. This estimate for P_{inf}, when used in equation (6.31), gives the initial estimate for A_c/A_t. If the input value of $\dot{m}/A_c$ is so large that equation (6.31) calculates a value less than 1, the program will stop the calculations and print out the error message INPUT VALUE OF MDOT/A = (value) IS TOO LARGE. GIVES CR ESTIMATE LESS THAN 1.

6.4.2 Improved Estimates for P_{inf} and A_c/A_t

For option 1 an improved estimate for P_{inf} ($P_{inf,new}$) is obtained by assuming that the ratio of this desired $P_{inf,new}$ value to the current value of P_{inf} is equal to the ratio of the assigned value of P_{inj} ($P_{inj,a}$) to the current value of P_{inj} (obtained by means of eq. (6.28)). This assumption leads to

$$P_{inf,new} = P_{inf}\frac{P_{inj,a}}{P_{inj}} \qquad (6.32)$$

Equation (6.32) often gives such an excellent improved estimate for P_{inf} that it need be used only once to obtain convergence (eq. (6.29)). For option 2 an improved estimate for A_c/A_t is required in addition to the one for P_{inf} and is obtained from

$$\frac{A_c}{A_t} = \frac{\dfrac{\dot{m}}{A_t}}{\dfrac{\dot{m}}{A_c}} \qquad (6.33)$$

For some test cases involving hydrogen and oxygen as propellant, approximately four iterations involving equation (6.33) were required for convergence (eq. (6.29)).

6.5 Procedure for Obtaining Frozen Rocket Performance

The procedure for obtaining rocket performance assuming that composition is frozen (infinitely slow reaction rates) during expansion is simpler than that assuming equilibrium composition. The reason is that equilibrium compositions need 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.

6.5.1 Exit Conditions

Improved estimates of the exit temperature corresponding to some assigned P_{inf}/P_e are obtained by means of the following iteration formulas:

$$(\ln T_e)_{k+1} = (\ln T_e)_k + (\Delta \ln T_e)_k \qquad (6.34)$$

where

$$(\Delta \ln T_e)_k = \frac{S_{inf} - S_{e,k}}{C_{p,e,k}} \qquad (6.35)$$

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

$$|\Delta \ln T_e| < 0.5 \times 10^{-4} \qquad (6.36)$$

The maximum number of iterations permitted by the program is eight, although the convergence criterion of equation (6.36) 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 (section 6.2) can be determined.

6.5.2 Throat Conditions

Calculations for frozen throat conditions are similar to those for equilibrium conditions. That is, equation (6.15) is used to get initial estimates for P_{inf}/P_t, equation (6.17) is used to get improved estimates for P_{inf}/P_t, and equation (6.16) is used as the convergence criterion. With composition and phases frozen, there is no possibility of discontinuities at the throat, in contrast to equilibrium compositions.

6.5.3 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 Zeleznik and Gordon (1968) for further discussion). An expression for specific heat, based on frozen composition, has already been given in equation (2.49b). Some other derivatives based on frozen composition are as follows: From equations (2.50) and (2.51), respectively.

$$\left(\frac{\partial \ln V}{\partial \ln T}\right)_P = 1 \qquad (6.37)$$

$$\left(\frac{\partial \ln V}{\partial \ln P}\right)_T = -1 \qquad (6.38)$$

From equation (2.70)

$$c_v = c_{p,f} - nR \qquad (6.39)$$

From equations (2.73) and (6.38), it is clear that for frozen composition

$$\gamma_s = \gamma \qquad (6.40)$$

Chapter 7
Incident and Reflected Shocks

The solution to the conservation equations that 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 that calculates shock properties in terms of assigned velocities, and that is the scheme used in this report.

No consistent nomenclature has been found in the literature for shock parameters. For example, in Gaydon and Hurle (1963) 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 Glass and Hall (1959), however, the converse is given. We will use essentially the nomenclature of Gaydon and Hurle (1963).

Figure II.6 in Gaydon and Hurle (1963) shows the usual incident and reflected conditions in both laboratory-fixed and shock-fixed coordinates. Velocities can be expressed as

$$\vec{u} = \vec{v} - \vec{w} = \vec{v} + \vec{w} \quad \text{or} \quad \vec{u} = \vec{w} - \vec{v} \tag{7.1}$$

For incident shock waves equation (7.1) gives

$$\vec{u}_1 = \vec{w}_S - \vec{v}_1 = \vec{w}_S \tag{7.2}$$

and

$$\vec{u}_2 = \vec{w}_S - \vec{v}_2 \tag{7.3}$$

In equation (7.2) it is assumed that the test gas is at rest ($\vec{v}_1 = 0$). For reflected waves equation (7.1) gives

$$\vec{u}_2^* = \vec{v}_2 + \vec{w}_R \tag{7.4}$$

and

$$\vec{u}_5 = \vec{v}_5 + \vec{w}_R = \vec{w}_R \tag{7.5}$$

In equation (7.5) 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 (7.4) to differentiate it from $\vec{u}_2$ in equation (7.3). The gas properties are the same for condition 2, but the relative velocities are different. All quantities that appear in equations (7.2) to (7.5) are positive, and henceforth the arrows will be dropped.

7.1 Incident Shocks

For a constant-area shock the conservation equations describing incident conditions are those given by equations (6.1) to (6.3) with $A_1 = A_2$. For iterative purposes it is convenient to reduce these equations to a form similar to that given in Zeleznik and Gordon (1962b) as follows:

$$\frac{P_2}{P_1} = 1 - \frac{\rho_1 u_1^2}{P_1}\left(\frac{\rho_1}{\rho_2} - 1\right) \tag{7.6}$$

$$h_2 = h_1 + \frac{u_1^2}{2}\left[1 - \left(\frac{\rho_1}{\rho_2}\right)^2\right] \tag{7.7}$$

It is also convenient to use the symbols P^* and h^* for the right sides of equations (7.6) and (7.7), respectively. These equations then become

$$P^* - \frac{P_2}{P_1} = 0 \qquad (7.8)$$

$$h^* - h_2 = 0 \qquad (7.9)$$

In equation (7.9), h_2 is defined by means of equation (2.14).

7.1.1 Iteration Equations

Applying the Newton-Raphson method to equations (7.8) and (7.9) divided by R and using for the independent variables the logarithm of temperature ratio and pressure ratio across the shock give

$$\frac{\partial\left(P^* - \frac{P_2}{P_1}\right)}{\partial\ln\frac{P_2}{P_1}}\Delta\ln\frac{P_2}{P_1} + \frac{\partial\left(P^* - \frac{P_2}{P_1}\right)}{\partial\ln\frac{T_2}{T_1}}\Delta\ln\frac{T_2}{T_1}$$
$$= \frac{P_2}{P_1} - P^* \qquad (7.10)$$

$$\frac{\partial\left(\frac{h^* - h_2}{R}\right)}{\partial\ln\frac{P_2}{P_1}}\Delta\ln\frac{P_2}{P_1} + \frac{\partial\left(\frac{h^* - h_2}{R}\right)}{\partial\ln\frac{T_2}{T_1}}\Delta\ln\frac{T_2}{T_1}$$
$$= \frac{h_2 - h^*}{R} \qquad (7.11)$$

where

$$\left(\Delta\ln\frac{P_2}{P_1}\right)_k = \ln\left(\frac{P_2}{P_1}\right)_{k+1} - \ln\left(\frac{P_2}{P_1}\right)_k \qquad (7.12a)$$

$$\left(\Delta\ln\frac{T_2}{T_1}\right)_k = \ln\left(\frac{T_2}{T_1}\right)_{k+1} - \ln\left(\frac{T_2}{T_1}\right)_k \qquad (7.12b)$$

and the subscript k stands for the kth iteration.

The partial derivatives and right sides in equations (7.10) and (7.11) are given as follows:

$$\frac{\partial\left(P^* - \frac{P_2}{P_1}\right)}{\partial\ln\frac{P_2}{P_1}} = -\frac{\rho_1}{\rho_2}\frac{M_1 u_1^2}{RT_1}\left(\frac{\partial\ln V}{\partial\ln P}\right)_{T,2} - \frac{P_2}{P_1} \qquad (7.13)$$

$$\frac{\partial\left(P^* - \frac{P_2}{P_1}\right)}{\partial\ln\frac{T_2}{T_1}} = -\frac{\rho_1}{\rho_2}\frac{M_1 u_1^2}{RT_1}\left(\frac{\partial\ln V}{\partial\ln P}\right)_{P,2} \qquad (7.14)$$

$$\frac{P_2}{P_1} - P^* = \frac{P_2}{P_1} - 1 + \frac{M_1 u_1^2}{RT_1}\left(\frac{\rho_1}{\rho_2} - 1\right) \qquad (7.15)$$

$$\frac{\partial\left(\frac{h^* - h_2}{R}\right)}{\partial\ln\frac{P_2}{P_1}} = -\frac{u_1^2}{R}\left(\frac{\rho_1}{\rho_2}\right)^2\left(\frac{\partial\ln V}{\partial\ln P}\right)_{T,2}$$
$$+ \frac{T_2}{M_2}\left[\left(\frac{\partial\ln V}{\partial\ln T}\right)_{P,2} - 1\right] \qquad (7.16)$$

$$\frac{\partial\left(\frac{h^* - h_2}{R}\right)}{\partial\ln\frac{T_2}{T_1}} = -\frac{u_1^2}{R}\left(\frac{\rho_1}{\rho_2}\right)^2\left(\frac{\partial\ln V}{\partial\ln T}\right)_{P,2} - \frac{T_2 c_{p,2}}{R} \qquad (7.17)$$

$$\frac{h_2 - h^*}{R} = \frac{h_2 - h_1}{R} - \frac{u_1^2}{2R}\left[1 - \left(\frac{\rho_1}{\rho_2}\right)^2\right] \qquad (7.18)$$

where from equations (2.1b) and (2.3a)

$$\frac{\rho_1}{\rho_2} = \frac{P_1}{P_2}\frac{M_1}{M_2}\frac{T_2}{T_1} \qquad (7.19)$$

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7.1.2 Corrections and Convergence

An arbitrary control factor λ is applied to the corrections obtained from solution of equations (7.10) and (7.11) before using the corrections in equations (7.12) to obtain improved estimates. The purpose of the control factor is to limit the size of the corrections in order to prevent divergence. Different maximum corrections are permitted during the course of the iteration process. Depending on the iteration number this control factor permits a maximum correction of 1.5 to 0.05 times the previous estimates of P_2/P_1 and T_2/T_1. This is the same as permitting a maximum absolute correction of 0.40546511 to 0.04879016 on $\ln P_2/P_1$ and $\ln T_2/T_1$. As an illustration, the control factor λ, corresponding to the maximum correction of 0.40546511 is obtained by means of the following equations:

$$\lambda_3 = \frac{0.40546511}{\left|\Delta \ln \dfrac{P_2}{P_1}\right|} \qquad (7.20)$$

$$\lambda_4 = \frac{0.40546511}{\left|\Delta \ln \dfrac{T_2}{T_1}\right|} \qquad (7.21)$$

$$\lambda = \min(\lambda_3, \lambda_4, 1) \qquad (7.22)$$

A schedule of numerical values used in equations (7.20) and (7.21) (in addition to the value of 0.40546511) and the criteria for when they are used are discussed in part II of this report.

Improved estimates are obtained by using equation (7.22) with equation (7.12) to give

$$\ln\left(\frac{P_2}{P_1}\right)_{k+1} = \ln\left(\frac{P_2}{P_1}\right)_k + \lambda\left(\Delta \ln \frac{P_2}{P_1}\right)_k \qquad (7.23a)$$

$$\ln\left(\frac{T_2}{T_1}\right)_{k+1} = \ln\left(\frac{T_2}{T_1}\right)_k + \lambda\left(\Delta \ln \frac{T_2}{T_1}\right)_k \qquad (7.23b)$$

The iteration process is continued until corrections obtained from equations (7.10) and (7.11) meet the following criteria:

$$\left|\Delta \ln \frac{P_2}{P_1}\right| < 0.00005 \qquad (7.24a)$$

$$\left|\Delta \ln \frac{T_2}{T_1}\right| < 0.00005 \qquad (7.24b)$$

7.1.3 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, can be found in texts such as Gaydon and Hurle (1963). These formulas, slightly rearranged, are

$$\frac{P_2}{P_1} = \frac{2\gamma_1 \mathcal{M}_1^2 - \gamma_1 + 1}{\gamma_1 + 1} \qquad (7.25)$$

$$\frac{T_2}{T_1} = \frac{P_2}{P_1} \frac{\dfrac{2}{\mathcal{M}_1^2} + \gamma_1 - 1}{\gamma_1 + 1} \qquad (7.26)$$

If γ is constant over the temperature range T_1 to T_2, equations (7.25) and (7.26) give exact theoretical values for P_2/P_1 and T_2/T_1. When composition is assumed to be frozen across the shock, γ_2 does not vary greatly from γ_1, and equations (7.25) and (7.26) generally give excellent first estimates. Improved estimates are then obtained as described in sections 7.1.1 and 7.1.2. However, if equilibrium composition is assumed across the shock, equation (7.26) generally gives estimates of temperature ratio that are too high. In Gordon and McBride (1976) an empirical equation is used to lower the T_2 estimates obtained from equation (7.26). This procedure has now been replaced by a new estimating scheme that gives considerably better estimates, especially at high Mach numbers. The initial estimate for P_2 is still obtained from equation (7.25). However, the initial estimate for T_2 is obtained by carrying out a combustion calculation using the estimate for P_2 for the assigned pressure and the value obtained from the following equation for the assigned enthalpy:

$$h_0 = h_2 = h_1 + \frac{u_1^2}{2} \qquad (7.27)$$

The properties for condition 1 are for the unshocked gases.

7.2 Reflected Shocks

The reflected shock conservation equations could be written like equations (6.1) to (6.3), but it is more convenient to use the relations in equations (7.4) and (7.5), which give

$$\rho_5 w_R = \rho_2(v_2 + w_R) \qquad (7.28)$$

$$P_5 + \rho_5 w_R^2 = P_2 + \rho_2(v_2 + w_R)^2 \qquad (7.29)$$

$$h_5 + \frac{1}{2}w_R^2 = h_2 + \frac{1}{2}(v_2 + w_r)^2 \qquad (7.30)$$

For iterative purposes it is convenient to reduce equations (7.28) to (7.30) to a form similar to equations (7.6) and (7.7) as follows:

$$\frac{P_5}{P_2} = 1 + \frac{\rho_2 v_2^2}{P_2}\frac{\dfrac{\rho_5}{\rho_2}}{\dfrac{\rho_5}{\rho_2} - 1} \qquad (7.31)$$

$$h_5 = h_2 + \frac{v_2^2}{2}\left(1 + \frac{2}{\dfrac{\rho_5}{\rho_2} - 1}\right) \qquad (7.32)$$

For convenience, the right sides of equations (7.31) and (7.32) will be given the symbols P' and h'. The reflected shock parameters may now be solved by the simultaneous solutions of

$$P' - \frac{P_5}{P_2} = 0 \qquad (7.33)$$

$$h' - h_5 = 0 \qquad (7.34)$$

7.2.1 Iteration Equations

Applying the Newton-Raphson method to equations (7.33) and (7.34) divided by R and using for independent variables the logarithm of temperature ratio and pressure ratio across the shock give

$$\frac{\partial\left(P' - \dfrac{P_5}{P_2}\right)}{\partial\ln\dfrac{P_5}{P_2}}\Delta\ln\frac{P_5}{P_2} + \frac{\partial\left(P' - \dfrac{P_5}{P_2}\right)}{\partial\ln\dfrac{T_5}{T_2}}\Delta\ln\frac{T_5}{T_2} = \frac{P_5}{P_2} - P' \qquad (7.35)$$

$$\frac{\partial\left(\dfrac{h' - h_5}{R}\right)}{\partial\ln\dfrac{P_5}{P_2}}\Delta\ln\frac{P_5}{P_2} + \frac{\partial\left(\dfrac{h' - h_5}{R}\right)}{\partial\ln\dfrac{T_5}{T_2}}\Delta\ln\frac{T_5}{T_2} = \frac{h_5 - h'}{R} \qquad (7.36)$$

where

$$\left(\Delta\ln\frac{P_5}{P_2}\right)_k = \ln\left(\frac{P_5}{P_2}\right)_{k+1} - \ln\left(\frac{P_5}{P_2}\right)_k \qquad (7.37)$$

$$\left(\Delta\ln\frac{T_5}{T_2}\right)_k = \ln\left(\frac{T_5}{T_2}\right)_{k+1} - \ln\left(\frac{T_5}{T_2}\right)_k \qquad (7.38)$$

The partial derivatives and right sides for equations (7.35) and (7.36) are as follows:

$$\frac{\partial\left(P' - \dfrac{P_5}{P_2}\right)}{\partial\ln\dfrac{P_5}{P_2}} = \frac{M_2 v_2^2}{RT_2}\frac{\dfrac{\rho_5}{\rho_2}}{\left(\dfrac{\rho_5}{\rho_2} - 1\right)^2}\left(\frac{\partial\ln V}{\partial\ln P}\right)_{T,5} - \frac{P_5}{P_2} \qquad (7.39)$$

$$\frac{\partial\left(P' - \dfrac{P_5}{P_2}\right)}{\partial\ln\dfrac{T_5}{T_2}} = \frac{M_2 v_2^2}{RT_2}\frac{\dfrac{\rho_5}{\rho_2}}{\left(\dfrac{\rho_5}{\rho_2} - 1\right)^2}\left(\frac{\partial\ln V}{\partial\ln T}\right)_{P,5} \qquad (7.40)$$

$$\frac{P_5}{P_2} - P' = \frac{P_5}{P_2} - 1 - \frac{M_2 v_2^2}{RT_2}\left(\frac{\dfrac{\rho_5}{\rho_2}}{\dfrac{\rho_5}{\rho_2} - 1}\right) \qquad (7.41)$$

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$$\frac{\partial\left(\dfrac{h'-h_5}{R}\right)}{\partial\ln\dfrac{P_5}{P_2}} = \frac{v_2^2}{R}\frac{\dfrac{\rho_5}{\rho_2}}{\left(\dfrac{\rho_5}{\rho_2}-1\right)^2}\left(\frac{\partial\ln V}{\partial\ln P}\right)_{T,5}$$

$$+ \frac{T_5}{M_5}\left[\left(\frac{\partial\ln V}{\partial\ln T}\right)_{P,5} - 1\right] \qquad (7.42)$$

$$\frac{\partial\left(\dfrac{h'-h_5}{R}\right)}{\partial\ln\dfrac{T_5}{T_2}} = \frac{v_2^2}{R}\frac{\dfrac{\rho_5}{\rho_2}}{\left(\dfrac{\rho_5}{\rho_2}-1\right)^2}\left(\frac{\partial\ln V}{\partial\ln T}\right)_{P,5} - \frac{T_5 c_{p,5}}{R} \qquad (7.43)$$

$$\frac{h_5 - h'}{R} = \frac{h_5 - h_2}{R} - \frac{v_2^2}{2R}\frac{\dfrac{\rho_5}{\rho_2}+1}{\dfrac{\rho_5}{\rho_2}-1} \qquad (7.44)$$

7.2.2 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. (7.20) to (7.24)) are applicable for $\ln P_5/P_2$ and $\ln T_5/T_2$.

7.2.3 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 can be obtained by inverting equation (2.36) in Gaydon and Hurle (1963). For $T_5/T_2 = 2$ this gives

$$\left(\frac{P_5}{P_2}\right)^2 - \left(\frac{\gamma_s+1}{\gamma_s-1}\right)\frac{P_5}{P_2} - 2 = 0 \qquad (7.45)$$

Only one solution of equation (7.45) is positive.

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Chapter 8
Chapman-Jouguet Detonations

The method used for obtaining Chapman-Jouguet detonation parameters is described in Zeleznik and Gordon (1962b). There are three steps in the calculation procedure. First, an initial estimate of the detonation pressure and temperature is made. Second, the estimate of these parameters is improved by using a recursion formula. Third, the correct values are obtained by means of a Newton-Raphson iteration procedure. The required equations are derived in Zeleznik and Gordon (1962b) and are summarized herein for convenience in slightly modified form.

The same conservation equations (6.1) to (6.3) 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 two:

$$\frac{P_1}{P_2} = 1 - \gamma_{s,2}\left(\frac{\rho_2}{\rho_1} - 1\right) \tag{8.1}$$

$$h_2 = h_1 + \frac{R\gamma_{s,2}T_2}{2M_2}\left[\left(\frac{\rho_2}{\rho_1}\right)^2 - 1\right] \tag{8.2}$$

The pressure ratio in equation (8.1) is the reciprocal of the pressure ratio in equation (7.6) because, as pointed out in Zeleznik and Gordon (1962b), the Newton-Raphson iteration encounters fewer problems in the form of equation (8.1).

For convenience in writing the iteration equations the symbols P'' and h'' are used to represent the right sides of equations (8.1) and (8.2), respectively. These equations then become

$$P'' - \frac{P_1}{P_2} = 0 \tag{8.3}$$

$$h'' - h_2 = 0 \tag{8.4}$$

8.1 Iteration Equations

Applying the Newton-Raphson method to equations (8.3) and (8.4), dividing by R, and using for independent variables the logarithm of temperature ratio and pressure ratio across the detonation give

$$\frac{\partial\left(P'' - \frac{P_1}{P_2}\right)}{\partial\ln\frac{P_2}{P_1}}\Delta\ln\frac{P_2}{P_1} + \frac{\partial\left(P'' - \frac{P_1}{P_2}\right)}{\partial\ln\frac{T_2}{T_1}}\Delta\ln\frac{T_2}{T_1} = \frac{P_1}{P_2} - P'' \tag{8.5}$$

$$\frac{\partial\left(\frac{h'' - h_2}{R}\right)}{\partial\ln\frac{P_2}{P_1}}\Delta\ln\frac{P_2}{P_1} + \frac{\partial\left(\frac{h'' - h_2}{R}\right)}{\partial\ln\frac{T_2}{T_1}}\Delta\ln\frac{T_2}{T_1} = \frac{h_2 - h''}{R} \tag{8.6}$$

where $\Delta\ln P_2/P_1$ and $\Delta\ln T_2/T_1$ are defined by equation (7.12).

The partial derivatives appearing in equations (8.5) and (8.6) can be evaluated if γ_s is taken to be independent of temperature and pressure. This assumption is reasonable for moderate ranges of temperatures and pressures. To within the accuracy of this assumption the partial derivatives and right sides of equations (8.5) and (8.6) are

$$\frac{\partial\left(P'' - \dfrac{P_1}{P_2}\right)}{\partial\ln\dfrac{P_2}{P_1}} = \frac{P_1}{P_2} + \gamma_{S,2}\frac{\rho_2}{\rho_1}\left(\frac{\partial\ln V}{\partial\ln P}\right)_{T,2} \qquad (8.7)$$

$$\frac{\partial\left(P'' - \dfrac{P_1}{P_2}\right)}{\partial\ln\dfrac{T_2}{T_1}} = \gamma_{S,2}\frac{\rho_2}{\rho_1}\left(\frac{\partial\ln V}{\partial\ln T}\right)_{P,2} \qquad (8.8)$$

$$\frac{P_1}{P_2} - P'' = \frac{P_1}{P_2} - 1 + \gamma_{S,2}\left(\frac{\rho_2}{\rho_1} - 1\right) \qquad (8.9)$$

$$\frac{\partial\left(\dfrac{h'' - h_2}{R}\right)}{\partial\ln\dfrac{P_2}{P_1}} = \frac{\gamma_{S,2}T_2}{2M_2}\left\{\left(\frac{\rho_2}{\rho_1}\right)^2 - 1 - \left(\frac{\partial\ln V}{\partial\ln P}\right)_{T,2}\left[1 + \left(\frac{\rho_2}{\rho_1}\right)^2\right]\right\}$$
$$+ \frac{T_2}{M_2}\left[\left(\frac{\partial\ln V}{\partial\ln T}\right)_{P,2} - 1\right] \qquad (8.10)$$

$$\frac{\partial\left(\dfrac{h'' - h_2}{R}\right)}{\partial\ln\dfrac{T_2}{T_1}} = -\frac{\gamma_{S,2}T_2}{2M_2}\left[\left(\frac{\rho_2}{\rho_1}\right)^2 + 1\right]\left(\frac{\partial\ln V}{\partial\ln T}\right)_{P,2} - \frac{T_2 c_{p,2}}{R} \qquad (8.11)$$

$$\frac{h_2 - h''}{R} = \frac{h_2 - h_1}{R} - \frac{\gamma_{S,2}T_2}{2M_2}\left[\left(\frac{\rho_2}{\rho_1}\right)^2 - 1\right] \qquad (8.12)$$

8.2 Corrections and Convergence

The discussion of convergence controls and corrections for shock calculations applies equally well for Chapman-Jouguet detonations. Equations (7.20) to (7.22) give the control factor λ; equation (7.23) gives the new estimates for P_2/P_1 and T_2/T_1; and equation (7.24) is the test for convergence.

8.3 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 $(P_2/P_1)_0 = 15$ has been found to be satisfactory. An initial estimate for temperature ratio is found by calculating the flame temperature T_2 corresponding to the enthalpy

$$h_2 = h_1 + \frac{3}{4}\frac{RT_1}{M_1}\left(\frac{P_2}{P_1}\right)_0 \qquad (8.13)$$

Improved initial estimates for the assumed value of $(P_2/P_1)_0$ and the estimated value of $(T_2/T_1)_0$ corresponding to h_2 in equation (8.13) can be obtained by using the recursion formulas

$$\left(\frac{P_2}{P_1}\right)_{k+1} = \frac{1 + \gamma_{S,2}}{2\gamma_{S,2}\alpha_k}\left\{1 + \left[1 - \frac{4\gamma_{S,2}\alpha_k}{(1 + \gamma_{S,2})^2}\right]^{1/2}\right\} \qquad (8.14)$$

$$\left(\frac{T_2}{T_1}\right)_{k+1} = \left(\frac{T_2}{T_1}\right)_0 - \frac{3}{4}\frac{R}{M_1 c_{p,2}}\left(\frac{P_2}{P_1}\right)_0$$
$$+ \frac{R\gamma_{S,2}}{2M_1 c_{p,2}}\frac{r_{k+1}^2 - 1}{r_{k+1}}\left(\frac{P_2}{P_1}\right)_{k+1} \qquad (8.15)$$

where

$$\alpha_k = \left(\frac{T_1}{T_2}\right)_k\frac{M_2}{M_1} \qquad (8.16)$$

$$r_{k+1} = \alpha_k\left(\frac{P_2}{P_1}\right)_{k+1} \qquad (8.17)$$

The quantities M_2, $\gamma_{S,2}$, and $c_{p,2}$ in equations (8.14) to (8.16) are the equilibrium values for $(P_2/P_1)_0$ and $(T_2/T_1)_0$. Repeating the use of equations (8.14) to (8.17) three times in the program generally provides excellent initial estimates for the Newton-Raphson iteration.

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Chapter 9
Input Calculations

A number of options are provided in the program for specifying input, and these options are discussed in detail in part II. Part of the input concerns reactants. The total reactant may be composed of a number of reactants, each of which 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, the fuels 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°, enthalpy h_0, internal energy u_0', molecular weight M_0, density ρ_0, positive and negative oxidation states V^+ and V^-, specific heat c_0, and entropy s_0) 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.

To obtain assigned properties for the total reactant, each reactant j may be specified as either a fuel or an oxidant even though a reactant may ordinarily be thought of as inert (e.g., N_2). If reactants are not divided into fuels and oxidants, they are treated like fuels with $o/f = 0$. Letting the superscript k equal 1 for oxidant (provided that there is an oxidant) and 2 for fuel, the kilogram-atoms of the ith element per kilogram of total oxidant or total fuel is

$$b_i^{(k)} = \sum_{j=1}^{NREAC} a_{ij}^{(k)} n_j^{(k)} \qquad (i = 1,...,\ell;\ k = 1,2) \qquad (9.1)$$

where NREAC is the total number of reactants and $n_j^{(k)}$ 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, $n_j^{(k)}$ is obtained by

$$n_j^{(k)} = \frac{W_j^{(k)}}{M_j^{(k)} \sum_{j=1}^{NREAC} W_j^{(k)}} \qquad (j = 1,...,NREAC;\ k = 1,2)$$

$$(9.2)$$

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 $N_j^{(k)}$,

$$n_j^{(k)} = \frac{N_j^{(k)}}{\sum_{j=1}^{NREAC} N_j^{(k)} M_j^{(k)}} \qquad (j = 1,...,NREAC;\ k = 1,2)$$

$$(9.3)$$

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

$$M_j^{(k)} = \sum_{i=1}^{\ell} a_{ij}^{(k)} M_i \qquad (j = 1,...,NREAC;\ k = 1,2) \qquad (9.4)$$

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

$$b_i^{\circ} = \frac{b_i^{(2)} + \left(\dfrac{o}{f}\right) b_i^{(1)}}{1 + \dfrac{o}{f}} \qquad (i = 1,...,\ell) \qquad (9.5)$$

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

Formulas analogous to equations (9.1) and (9.5) can be used to obtain other properties of the total oxidant, total fuel, and total reactant (such as enthalpies, internal

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energies, molecular weights, and densities). The energies given in the next four equations are in the form in which they appear in the matrix arrays (tables 2.1 to 2.3).

(1) Specific enthalpy of total oxidant ($k = 1$) or total fuel ($k = 2$) $h^{(k)}$ divided by RT, (kg-mole/kg)$^{(k)}$:

$$\frac{h^{(k)}}{RT} = \sum_{j=1}^{NREAC} \frac{\left(H_j^o\right)^{(k)} n_j^{(k)}}{RT} \qquad (k = 1,2) \qquad (9.6)$$

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

(2) Specific enthalpy of total reactant h_0 divided by RT, kg-mole/kg:

$$\frac{h_0}{RT} = \frac{\dfrac{h^{(2)}}{RT} + \left(\dfrac{o}{f}\right)\dfrac{h^{(1)}}{RT}}{1 + \dfrac{o}{f}} \qquad (k = 1,2) \qquad (9.7)$$

(3) Specific internal energy of total oxidant ($k = 1$) or total fuel ($k = 2$) $(u')^{(k)}$ divided by RT, (kg-mole/kg)$^{(k)}$:

$$\frac{(u')^{(k)}}{RT} = \sum_{j=1}^{NREAC} \frac{\left(U_j^o\right)^{(k)} n_j^{(k)}}{RT} \qquad (k = 1,2) \qquad (9.8)$$

where $\left(U_j^o\right)^{(k)}$ is the molar internal energy of the jth reactant, (J/kg-mole)$_j^{(k)}$.

(4) Specific internal energy of total reactant u_0' divided by RT, kg-mole/kg:

$$\frac{u_0'}{RT} = \frac{\dfrac{(u')^{(2)}}{RT} + \left(\dfrac{o}{f}\right)\dfrac{(u')^{(1)}}{RT}}{1 + \dfrac{o}{f}} \qquad (9.9)$$

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

$$M^{(k)} = \frac{1}{\sum\limits_{j=1}^{NREAC} n_j^{(k)}} \qquad (k = 1,2) \qquad (9.10)$$

(6) Molecular weight of total reactant, kg/kg-mole:

$$M_0 = \frac{\left[\dfrac{o}{f} + 1\right] M^{(1)} M^{(2)}}{M^{(1)} + \left(\dfrac{o}{f}\right) M^{(2)}} \qquad (9.11)$$

(If $M^{(1)} = 0$, $M_0 = M^{(2)}$; and if $M^{(2)} = 0$, $M_0 = M^{(1)}$.)

(7) Density of total oxidant or fuel:

$$\rho^{(k)} = \frac{1}{\sum\limits_{j=1}^{NREAC} \dfrac{n_j^{(k)} M_j^{(k)}}{\rho_j^{(k)}}} \qquad (k = 1,2) \qquad (9.12)$$

(8) Density of total reactant:

$$\rho_0 = \frac{\left[\dfrac{o}{f} + 1\right] \rho^{(1)} \rho^{(2)}}{\rho^{(1)} + \left(\dfrac{o}{f}\right) \rho^{(2)}} \qquad (9.13)$$

In the main program of CEA several alternative expressions are given for specifying the relative amounts of total oxidant to total fuel and for relating them to o/f. Two expressions are given for equivalence ratio—a chemical equivalence ratio r and a fuel-to-air (or fuel-to-oxidant) equivalence ratio ϕ. If the chemical 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

$$V^{+(k)} = \sum_{i=1}^{\ell} V_i^+ b_i^{(k)} \qquad (k = 1,2) \qquad (9.14)$$

$$V^{-(k)} = \sum_{i=1}^{\ell} V_i^- b_i^{(k)} \qquad (k = 1,2) \qquad (9.15)$$

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

$$V^+ = \frac{V^{+(2)} + \left(\frac{o}{f}\right) V^{+(1)}}{1 + \frac{o}{f}} \qquad (9.16)$$

$$V^- = \frac{V^{-(2)} + \left(\frac{o}{f}\right) V^{-(1)}}{1 + \frac{o}{f}} \qquad (9.17)$$

The chemical equivalence ratio is now defined as

$$r \equiv -\frac{V^+}{V^-} \qquad (9.18)$$

The equivalence ratio ϕ, commonly used in engineering practice, is defined as

$$\phi = \frac{\frac{f}{a}}{\left(\frac{f}{a}\right)_{stoich}} \qquad (9.19)$$

where f/a is the fuel-to-air weight ratio. As Gordon (1982) points out, the two equivalence ratios r and ϕ are always identical for the stoichiometric condition. In addition, they are always identical when all the positive valence atoms are in the fuel and all the negative valence atoms are in the oxidizer (eg., $CH_4 + O_2$). However, if some negative valence atoms are in the fuel (e.g., CH_3OH) or if some positive valence atoms are in the

oxidizer (e.g., H_2O_2), then for off-stoichiometric conditions r and ϕ differ for the same reaction. For example, for $CH_3OH + 1/2\ O_2$, $r = 2$ and $\phi = 3$.

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

$$m_j = \left(\frac{o}{f}\right) \frac{n_j^{(k)}}{1 + \frac{o}{f}} \qquad \text{for } k = 1$$

$$= \frac{n_j^{(k)}}{1 + \frac{o}{f}} \qquad \text{for } k = 2$$

$$(j = 1,...,NREAC) \qquad (9.20)$$

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

Specific heat and entropy for the total reactant in kilogram-moles per kilogram can be calculated by using the m_j, $C_{p,j}^o$, and S_j of the j reactants:

$$\frac{c_0}{R} = \sum_{j=1}^{NREAC} m_j \frac{C_{p,j}^o}{R} \qquad (9.21)$$

$$\frac{s_0}{R} = \sum_{j=1}^{NREAC} m_j \left(\frac{S_j}{R}\right) \qquad (9.22)$$

Appendix—Symbols

A,B,C,D transport property coefficients, eq. (5.1)

A area, m^2

A_e/A_t ratio of nozzle exit area to throat area, eq. (6.14)

$A_{k\ell}^*$ collision cross-section ratio, eq. (5.13)

A_k chemical formula of species k, dimensionless, eq. (5.10)

a velocity of sound, m/s, eqs. (2.67) and (2.74)

$a_i(i = 1...9)$ least-squares coefficients, eqs. (4.6) to (4.11)

a_{ij} stoichiometric coefficients, kilogram-atoms of element i per kilogram-mole of species j, (kg-atom)$_i$/(kg-mole)$_j$, eq. (2.7a)

$a_{ij}^{(k)}$ stoichiometric coefficients, kilogram-atoms of element i per kilogram-mole of reactant j (oxidant if $k = 1$, fuel if $k = 2$), (kg-atom)$_i^{(k)}$/(kg-mole)$_j^{(k)}$, eq. (9.1)

$a_{S,T}$ velocity of sound, m/s, defined by eq. (3.10)

b_i kilogram-atoms of element i per kilogram of mixture, (kg-atom)$_i$/kg, eq. (2.7c)

$b_i^{(k)}$ assigned kilogram-atoms of element i per kilogram of total oxidant ($k = 1$) or total fuel ($k = 2$), (kg-atom)$_i^{(k)}$/kg$_{(k)}$, eq. (9.1)

b_i° assigned kilogram-atoms of element i per kilogram of total reactant, (kg-atom)$_i$/kg, eq. (9.5)

C_F coefficient of thrust, eq. (6.13)

$C_{p,j}^\circ$ molar heat capacity at constant pressure for standard state for species or reactant j, J/(kg-mole)$_j$(K)

$C_{v,j}^\circ$ molar heat capacity at constant volume for standard state for species j, J/(kg-mole)$_j$(K)

c_0 specific heat at constant pressure of total reactant, J/kg-K, eq. (9.21)

c_p specific heat at constant pressure of mixture, equilibrium or frozen, J/kg-K

$c_{p,e}$ equilibrium specific heat at constant pressure, J/kg-K, eq. (2.49a)

$c_{p,eq}$ equilibrium specific heat at constant pressure for transport properties, J/kg-K, eq. (5.14)

$c_{p,f}$ frozen specific heat at constant pressure, J/kg-K, eq. (2.49b)

$c_{p,fr}$ frozen specific heat at constant pressure for transport properties, J/kg-K, eq. (5.15)

$c_{p,r}$ reaction specific heat at constant pressure, J/kg-K, eq. (2.49c)

$c_{p,re}$ reaction specific heat at constant pressure for transport properties, J/kg-K, eq. (5.16)

c_v specific heat at constant volume of mixture, equilibrium or frozen, J/kg-K, eq. (2.70) or (6.39)

c^* characteristic velocity, m/s, eq. (6.11)

$D_{k\ell}$ binary diffusion coefficient, m^2/s, eq. (5.13)

d_{ij} matrix coefficient in eq. (5.17)

F	Helmholtz energy of mixture with constraints, defined by eq. (2.33), J/kg; or force, N, eq. (6.6)	M_j	molecular weight of species j, eqs. (2.3b) and (2.4)
$\%F$	percent of total fuel in total reactant by weight or mass	M_0	molecular weight of total reactant, kg/kg-mole, eq. (9.11)
f	Helmholtz energy of mixture, J/kg, eqs. (2.30) and (2.31)	$M^{(k)}$	molecular weight of total oxidant ($k = 1$) or total fuel ($k = 2$), (kg/kg-mole)$^{(k)}$, eq. (9.10)
G	Gibbs energy of mixture with constraints, J/kg, defined by eq. (2.8)	$M_j^{(k)}$	molecular weight of reactant j (oxidant if $k = 1$; fuel if $k = 2$, (kg/kg-mole)$_j^{(k)}$, eqs. (9.4)
g	Gibbs energy of mixture, J/kg, eq. (2.5)		
g_c	conversion factor, eqs. (6.6) to (6.8)	MW	molecular weight of mixture, kg/kg-mole, eqs. (2.4)
H_j°	molar standard-state enthalpy for species j, J/(kg-mole)$_j$	$\mathcal{M}$	Mach number, eq. (6.10)
$(H_j^\circ)^{(k)}$	molar enthalpy of reactant j ($k = 1$ for oxidant, $k = 2$ for fuel), J/(kg-mole)$_j^{(k)}$, eq. (9.6)	m_j	kilogram-moles of reactant j per kilogram of total reactant, (kg-mole)$_j$/kg, eq. (9.20)
$\Delta_f H^\circ(T)$	heat of formation at temperature T, J/kg-mole, eq. (4.2)	$\dot{m}$	mass flow rate, kg/s, eq. (6.4)
$\Delta_r H^\circ(T)$	heat of reaction at temperature T, J/(kg-mole), eq. (5.9)	$N_j^{(k)}$	kilogram-moles of reactant j (oxidant if $k = 1$; fuel if $k = 2$), (kg-mole)$_j^{(k)}$
h	specific enthalpy of mixture, J/kg, eq. (2.14)	n	kilogram-moles of mixture per unit mass, kg-mole/kg, eq. (2.2)
$h^{(k)}$	specific enthalpy of total oxidant ($k = 1$) or total fuel ($k = 2$), (J/kg)$^{(k)}$, eq. (9.6)	n_j	kilogram-moles of species j per kilogram of mixture, (kg-mole)$_j$/kg, eq. (2.2)
h_0	specific enthalpy of total reactants, J/kg, eq. (9.7)	$n_j^{(k)}$	kilogram-mole per kilogram of reactant j (oxidant if $k = 1$; fuel if $k = 2$), (kg-mole)$_j^{(k)}$/kg$^{(k)}$, eq. (9.2) or (9.3)
h'	term defined by right side of eq. (7.32)	o/f	oxidant-to-fuel weight (or mass) ratio
h''	term defined by right side of eq. (8.2)	P	pressure, N/m^2
h^*	term defined by right side of eq. (7.7)	P_{inf}/P_e	ratio of combustion pressure to exit pressure for IAC model
I	specific impulse, N/(kg/s) or m/s, eq. (6.7)	P_0	assigned or initial pressure, N/m^2
I_{sp}	specific impulse with exit and ambient pressures equal, N/(kg/s) or m/s, eq. (6.8)	P'	term defined by right side of eq. (7.31)
		P''	term defined by right side of eq. (8.1)
I_{vac}	vacuum specific impulse, N/(kg/s) or m/s, eq. (6.9)	P^*	term defined by right side of eq. (7.6)
		Pr	Prandtl number, eqs. (5.19)
M	molecular weight of mixture, kg/kg-mole, eqs. (2.3)	R	universal gas constant, 8314.51 J/(kg-mole)(K)
M_i	atomic weight of chemical element i, (kg/kg-atom)$_i$, eq. (9.4)	r	equivalence ratio based on oxidation states, eq. (9.18)

Symbol	Definition
S_j	molar entropy of species j, J/(kg-mole)$_j$(K), eq. (2.17)
S_j°	molar standard-state entropy for species j, J/(kg-mole)$_j$(K)
s	specific entropy of mixture, J/kg-K, eq. (2.16)
s_0	specific entropy of total reactants, J/kg-K, eq. (9.22)
T	temperature, K
U_j°	molar standard-state internal energy for species j, J/kg-mole, eq. (2.38)
$(U_j^\circ)^{(k)}$	molar internal energy of reactant j (oxidant if $k = 1$; fuel if $k = 2$), (J/kg-mole)$_j^{(k)}$, eq. (9.8)
u	velocity (in shock problems, velocity relative to incident or reflected shock front), m/s, eqs. (6.5) and (7.1)
u'	specific internal energy of mixture, J/kg, eq. (2.38)
$u'^{(k)}$	specific internal energy of total oxidant ($k = 1$) or total fuel ($k = 2$), (J/kg)$^{(k)}$, eq. (9.8)
u_0'	specific internal energy of total reactant, J/kg, eq. (9.9)
V	specific volume, m^3/kg, eq. (2.1a)
V^+	positive oxidation state of total reactant, eq. (9.16)
V^-	negative oxidation state of total reactant, eq. (9.17)
$V^{+(k)}$	positive oxidation state of total oxidant ($k = 1$) or total fuel ($k = 2$), eq. (9.14)
$V^{-(k)}$	negative oxidation state of total oxidant ($k = 1$) or total fuel ($k = 2$), eq. (9.15)
v	actual velocity of gases in shock tube, m/s, eq. (7.1)
$W_j^{(k)}$	weight of jth reactant (oxidant if $k = 1$; fuel if $k = 2$), kg$_j^{(k)}$, eq. (9.2)
w	shock front velocity, m/s, eq. (7.1)
w_R	reflected shock front velocity, m/s, eq. (7.4)
w_S	incident shock front velocity, m/s, eq. (7.2)
X_i	unknowns in eq. (5.16)
x_i	mole fraction of species i relative to all species (gaseous and condensed) in eq. (2.4a) and relative to NM gaseous species used for thermal transport property calculations in eqs. (5.3), (5.4), (5.12), (5.15), (5.16), and (5.18)
α_{ik}	stoichiometric coefficients of species k in reaction i for transport property calculations, eq. (5.10)
α_k	parameter defined by equation (8.16)
γ	specific heat ratio, eq. (2.72)
γ_s	isentropic exponent, eqs. (2.71) and (2.73)
η_i	viscosity of species i, μP, eq. (5.3)
η_{ij}	viscosity interaction parameter, μP, eq. (5.7)
η_{mix}	viscosity of mixture, μP, eq. (5.3)
λ	control factor, eqs. (3.3) and (7.22); thermal conductivity, eq. (5.1)
λ_i	Lagrangian multipliers, eqs. (2.8) and (2.33); thermal conductivity of species i, μW/cm-K, eq. (5.4)
$\lambda_1, \lambda_2, \lambda_3, \lambda_4$	control factors, eqs. (3.1), (3.2), (7.20), and (7.21)
λ_{eq}	equilibrium thermal conductivity of mixture, μW/cm-K, eq. (5.2)
λ_{fr}	frozen thermal conductivity of mixture, μW/cm-K, eq. (5.4)
$\lambda_{r,i}$	variables in eqs. (5.8) and (5.11)
λ_{re}	reaction thermal conductivity of mixture, μW/cm-K, eq. (5.8)
μ_j	chemical potential of species j, J/(kg-mole)$_j$, eqs. (2.11) and (2.35)
μ_j°	standard-state chemical potential of species j, J/(kg-mole)$_j$, eq. (2.11)
π_e	Lagrangian multiplier for ions divided by RT

π_i	Lagrangian multiplier for element i divided by RT, eqs. (2.18), (2.19), (2.40), and (2.41)	P	pressure
		s	entropy
ρ	density of mixture, kg/m^3, eq. (2.1b)	stoich	stoichiometric
ρ_0	density of total reactant, kg/m^3, eq. (9.13)	T	temperature
$\rho^{(k)}$	density of total oxidant ($k = 1$) or total fuel ($k = 2$), (kg/m^3)$^{(k)}$, eq. (9.12)	t	throat
		0	total reactant; zeroth iteration
$\rho_j^{(k)}$	density of reactant j (oxidant if $k = 1$; fuel if $k = 2$), (kg/m^3)$_j^{(k)}$, eq. (9.12)	1,2,5	stations

Superscripts:

ψ_{ij}	frozen thermal conductivity interaction coefficient between species i and j, eqs. (5.4) and (5.6)	$\circ$	symbol for standard state; an assigned or initial condition
ϕ	equivalence ratio based on f/a ratios, eq. (9.19)	k	1 if oxidant, 2 if fuel

Indices:

ϕ_{ij}	viscosity interaction coefficient between species i and j, eqs. (5.5) and (5.7)

Subscripts:

		ℓ	number of chemical elements (if ions are considered, number of chemical elements plus one)
a	ambient; assigned		
c	end of combustion chamber; condensed	NG	number of gaseous species in thermodynamic data for current chemical system
e	exit; electrons		
g	gas	NM	number of gaseous species for transport property calculations
inf	combustor station assuming infinite chamber area	NR	number of reactions for transport property calculations
inj	combustor inlet or injector station for finite-area combustor	NREAC	number of reactants
k	iteration k	NS	number of species, gaseous and condensed, in thermodynamic data for current chemical system
m	melting		

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TABLE 2.1—ITERATION EQUATIONS TO DETERMINE EQUILIBRIUM COMPOSITIONS FOR EITHER ASSIGNED TEMPERATURE AND PRESSURE, ENTHALPY AND PRESSURE, OR ENTROPY AND PRESSURE

Equation	Variable									Right side
	π_1	π_2	$\cdots$	π_ℓ	Δn_{NG+1}	$\cdots$	Δn_{NS}	$\Delta \ln n$	$\Delta \ln T$ (a)	
(2.24)	$\sum_{j=1}^{NG} a_{1j}a_{1j}n_j$	$\sum_{j=1}^{NG} a_{1j}a_{2j}n_j$	$\cdots$	$\sum_{j=1}^{NG} a_{1j}a_{\ell j}n_j$	$a_{1,NG+1}$	$\cdots$	a_{1NS}	$\sum_{j=1}^{NG} a_{1j}n_j$	$\sum_{j=1}^{NG} a_{1j}n_j \frac{H_j^\circ}{RT}$	$(b_1^\circ - b_1) + \sum_{j=1}^{NG} a_{1j}n_j \frac{\mu_j}{RT}$
	$\sum_{j=1}^{NG} a_{2j}a_{1j}n_j$	$\sum_{j=1}^{NG} a_{2j}a_{2j}n_j$	$\cdots$	$\sum_{j=1}^{NG} a_{2j}a_{\ell j}n_j$	$a_{2,NG+1}$	$\cdots$	a_{2NS}	$\sum_{j=1}^{NG} a_{2j}n_j$	$\sum_{j=1}^{NG} a_{2j}n_j \frac{H_j^\circ}{RT}$	$(b_2^\circ - b_2) + \sum_{j=1}^{NG} a_{2j}n_j \frac{\mu_j}{RT}$
	$\cdots$	$\cdots$	$\cdots$	$\cdots$	$\cdots$	$\cdots$	$\cdots$	$\cdots$	$\cdots$	$\cdots$
	$\sum_{j=1}^{NG} a_{\ell j}a_{1j}n_j$	$\sum_{j=1}^{NG} a_{\ell j}a_{2j}n_j$	$\cdots$	$\sum_{j=1}^{NG} a_{\ell j}a_{\ell j}n_j$	$a_{\ell,NG+1}$	$\cdots$	$a_{\ell NS}$	$\sum_{j=1}^{NG} a_{\ell j}n_j$	$\sum_{j=1}^{NG} a_{\ell j}n_j \frac{H_j^\circ}{RT}$	$(b_\ell^\circ - b_\ell) + \sum_{j=1}^{NG} a_{\ell j}n_j \frac{\mu_j}{RT}$
(2.25)	$a_{1,NG+1}$	$a_{2,NG+1}$	$\cdots$	$a_{\ell,NG+1}$	0	$\cdots$	0	0	$\frac{H_{NG+1}^\circ}{RT}$	$\frac{\mu_{NG+1}}{RT}$
	$\cdots$	$\cdots$		$\cdots$	$\cdots$		$\cdots$	$\cdots$	$\cdots$	$\cdots$
	a_{1NS}	a_{2NS}	$\cdots$	$a_{\ell NS}$	0	$\cdots$	0	0	$\frac{H_{NS}^\circ}{RT}$	$\frac{\mu_{NS}}{RT}$
(2.26)	$\sum_{j=1}^{NG} a_{1j}n_j$	$\sum_{j=1}^{NG} a_{2j}n_j$	$\cdots$	$\sum_{j=1}^{NG} a_{\ell j}n_j$	0	$\cdots$	0	$\sum_{j=1}^{NG} n_j - n$	$\sum_{j=1}^{NG} n_j \frac{H_j^\circ}{RT}$	$n - \sum_{j=1}^{NG} n_j + \sum_{j=1}^{NG} n_j \frac{\mu_j}{RT}$
[b] (2.27)	$\sum_{j=1}^{NG} a_{1j}n_j \frac{H_j^\circ}{RT}$	$\sum_{j=1}^{NG} a_{2j}n_j \frac{H_j^\circ}{RT}$	$\cdots$	$\sum_{j=1}^{NG} a_{\ell j}n_j \frac{H_j^\circ}{RT}$	$\frac{H_{NG+1}^\circ}{RT}$	$\cdots$	$\frac{H_{NS}^\circ}{RT}$	$\sum_{j=1}^{NG} n_j \frac{H_j^\circ}{RT}$	$\sum_{j=1}^{NS} n_j \frac{C_{pj}^\circ}{R} + \sum_{j=1}^{NG} n_j \frac{H_j^\circ}{RT}\frac{H_j^\circ}{RT}$	$\frac{h_0}{RT} - \frac{h}{RT} + \sum_{j=1}^{NG} n_j \frac{H_j^\circ}{RT}\frac{\mu_j}{RT}$
[c] (2.28)	$\sum_{j=1}^{NG} a_{1j}n_j \frac{S_j}{R}$	$\sum_{j=1}^{NG} a_{2j}n_j \frac{S_j}{R}$	$\cdots$	$\sum_{j=1}^{NG} a_{\ell j}n_j \frac{S_j}{R}$	$\frac{S_{NG+1}}{R}$	$\cdots$	$\frac{S_{NS}}{R}$	$\sum_{j=1}^{NG} n_j \frac{S_j}{R}$	$\sum_{j=1}^{NS} n_j \frac{C_{pj}^\circ}{R} + \sum_{j=1}^{NG} n_j \frac{H_j^\circ}{RT}\frac{S_j}{R}$	$\frac{s_0}{R} - \frac{s}{R} + n - \sum_{j=1}^{NG} n_j + \sum_{j=1}^{NG} n_j \frac{S_j}{R}\frac{\mu_j}{RT}$

[a] Column not used for assigned temperature and volume.
[b] Row used only for assigned enthalpy and pressure.
[c] Row used only for assigned entropy and pressure.

TABLE 2.2—ITERATION EQUATIONS TO DETERMINE EQUILIBRIUM COMPOSITIONS FOR EITHER ASSIGNED TEMPERATURE AND VOLUME, INTERNAL ENERGY AND VOLUME, OR ENTROPY AND VOLUME

Equation	Variable								$\Delta \ln T$ (a)	Right side
	π_1	π_2	$\cdots$	π_ℓ	$\cdots$	Δn_{NG+1}	$\cdots$	Δn_{NS}		
(2.45)	$\sum_{j=1}^{NG} a_{1j}a_{1j}n_j$	$\sum_{j=1}^{NG} a_{1j}a_{2j}n_j$	$\cdots$	$\sum_{j=1}^{NG} a_{1j}a_{\ell j}n_j$	$\cdots$	$a_{1,NG+1}$	$\cdots$	a_{1NS}	$\sum_{j=1}^{NG} a_{1j}n_j \frac{U_j^o}{RT}$	$(b_1^o - b_1) + \sum_{j=1}^{NG} a_{1j}n_j \frac{\mu_j}{RT}$
	$\sum_{j=1}^{NG} a_{2j}a_{1j}n_j$	$\sum_{j=1}^{NG} a_{2j}a_{2j}n_j$	$\cdots$	$\sum_{j=1}^{NG} a_{2j}a_{\ell j}n_j$	$\cdots$	$a_{2,NG+1}$	$\cdots$	a_{2NS}	$\sum_{j=1}^{NG} a_{2j}n_j \frac{U_j^o}{RT}$	$(b_2^o - b_2) + \sum_{j=1}^{NG} a_{2j}n_j \frac{\mu_j}{RT}$
	$\cdots$	$\cdots$		$\cdots$		$\cdots$		$\cdots$	$\cdots$	$\cdots$
	$\sum_{j=1}^{NG} a_{\ell j}a_{1j}n_j$	$\sum_{j=1}^{NG} a_{\ell j}a_{2j}n_j$	$\cdots$	$\sum_{j=1}^{NG} a_{\ell j}a_{\ell j}n_j$	$\cdots$	$a_{\ell,NG+1}$	$\cdots$	$a_{\ell NS}$	$\sum_{j=1}^{NG} a_{\ell j}n_j \frac{U_j^o}{RT}$	$(b_\ell^o - b_\ell) + \sum_{j=1}^{NG} a_{\ell j}n_j \frac{\mu_j}{RT}$
(2.46)	$a_{1,NG+1}$	$a_{2,NG+1}$	$\cdots$	$a_{\ell,NG+1}$	$\cdots$	0	$\cdots$	0	$\frac{U_{NG+1}^o}{RT}$	$\frac{\mu_{NG+1}}{RT}$
	$\cdots$	$\cdots$		$\cdots$		$\cdots$		$\cdots$	$\cdots$	$\cdots$
	a_{1NS}	a_{2NS}	$\cdots$	$a_{\ell NS}$	$\cdots$	0	$\cdots$	0	$\frac{U_{NS}^o}{RT}$	$\frac{\mu_{NS}}{RT}$
[b](2.47)	$\sum_{j=1}^{NG} a_{1j}n_j \frac{U_j^o}{RT}$	$\sum_{j=1}^{NG} a_{2j}n_j \frac{U_j^o}{RT}$	$\cdots$	$\sum_{j=1}^{NG} a_{\ell j}n_j \frac{U_j^o}{RT}$	$\cdots$	$\frac{U_{NG+1}^o}{RT}$	$\cdots$	$\frac{U_{NS}^o}{RT}$	$\sum_{j=1}^{NS} n_j \frac{C_{Vj}^o}{R} + \sum_{j=1}^{NG} n_j \frac{U_j^o}{RT}\frac{U_j^o}{RT}$	$\frac{u_0'}{RT} - \frac{u'}{RT} + \sum_{j=1}^{NG} n_j \frac{U_j^o}{RT}\frac{\mu_j}{RT}$
[c](2.48)	$\sum_{j=1}^{NG} a_{1j}n_j \left(\frac{S_j}{R} - 1\right)$	$\sum_{j=1}^{NG} a_{2j}n_j \left(\frac{S_j}{R} - 1\right)$	$\cdots$	$\sum_{j=1}^{NG} a_{\ell j}n_j \left(\frac{S_j}{R} - 1\right)$	$\cdots$	$\frac{S_{NG+1}}{R}$	$\cdots$	$\frac{S_{NS}}{R}$	$\sum_{j=1}^{NS} n_j \frac{C_{Vj}^o}{R} + \sum_{j=1}^{NG} n_j \frac{U_j^o}{RT}\left(\frac{S_j}{R} - 1\right)$	$\frac{s_0}{R} - \frac{s}{R} + \sum_{j=1}^{NG} n_j \left(\frac{S_j}{R} - 1\right)\frac{\mu_j}{RT}$

[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 2.3—EQUATIONS FOR EVALUATING DERIVATIVES WITH RESPECT TO

LOGARITHM OF TEMPERATURE AT CONSTANT PRESSURE

Equation	Variable								Right side
	$\dfrac{\partial \pi_1}{\partial \ln T}$	$\dfrac{\partial \pi_2}{\partial \ln T}$	$\cdots$	$\dfrac{\partial \pi_\ell}{\partial \ln T}$	$\dfrac{\partial n_{NG+1}}{\partial \ln T}$	$\cdots$	$\dfrac{\partial n_{NS}}{\partial \ln T}$	$\dfrac{\partial \ln n}{\partial \ln T}$	
(2.56)	$\sum\limits_{j=1}^{NG} a_{1j}a_{1j}n_j$	$\sum\limits_{j=1}^{NG} a_{1j}a_{2j}n_j$	$\cdots$	$\sum\limits_{j=1}^{NG} a_{1j}a_{\ell j}n_j$	$a_{1,NG+1}$	$\cdots$	a_{1NS}	$\sum\limits_{j=1}^{NG} a_{1j}n_j$	$-\sum\limits_{j=1}^{NG} a_{1j}n_j \dfrac{H_j^\circ}{RT}$
	$\sum\limits_{j=1}^{NG} a_{2j}a_{1j}n_j$	$\sum\limits_{j=1}^{NG} a_{2j}a_{2j}n_j$	$\cdots$	$\sum\limits_{j=1}^{NG} a_{2j}a_{\ell j}n_j$	$a_{2,NG+1}$	$\cdots$	a_{2NS}	$\sum\limits_{j=1}^{NG} a_{2j}n_j$	$-\sum\limits_{j=1}^{NG} a_{2j}n_j \dfrac{H_j^\circ}{RT}$
	$\cdots$	$\cdots$	$\cdots$	$\cdots$			$\cdots$	$\cdots$	$\cdots$
	$\sum\limits_{j=1}^{NG} a_{\ell j}a_{1j}n_j$	$\sum\limits_{j=1}^{NG} a_{\ell j}a_{2j}n_j$	$\cdots$	$\sum\limits_{j=1}^{NG} a_{\ell j}a_{\ell j}n_j$	$a_{\ell,NG+1}$	$\cdots$	$a_{\ell NS}$	$\sum\limits_{j=1}^{NG} a_{\ell j}n_j$	$-\sum\limits_{j=1}^{NG} a_{\ell j}n_j \dfrac{H_j^\circ}{RT}$
(2.57)	$a_{1,NG+1}$	$a_{2,NG+1}$	$\cdots$	$a_{\ell,NG+1}$	0	$\cdots$	0	0	$-\dfrac{H_{NG+1}^\circ}{RT}$
	$\cdots$			$\cdots$			$\cdots$	$\cdots$	$\cdots$
	a_{1NS}	a_{2NS}	$\cdots$	$a_{\ell NS}$	0	$\cdots$	0	0	$-\dfrac{H_{NS}^\circ}{RT}$
(2.58)	$\sum\limits_{j=1}^{NG} a_{1j}n_j$	$\sum\limits_{j=1}^{NG} a_{2j}n_j$	$\cdots$	$\sum\limits_{j=1}^{NG} a_{\ell j}n_j$	0	$\cdots$	0	0	$-\sum\limits_{j=1}^{NG} n_j \dfrac{H_j^\circ}{RT}$

TABLE 2.4—EQUATIONS FOR EVALUATING DERIVATIVES WITH RESPECT TO

LOGARITHM OF PRESSURE AT CONSTANT TEMPERATURE

Equation	Variable									
	$\dfrac{\partial \pi_1}{\partial \ln P}$	$\dfrac{\partial \pi_2}{\partial \ln P}$	$\cdots$	$\dfrac{\partial \pi_\ell}{\partial \ln P}$	$\cdots$	$\dfrac{\partial n_{NG+1}}{\partial \ln P}$	$\cdots$	$\dfrac{\partial n_{NS}}{\partial \ln P}$	$\dfrac{\partial \ln n}{\partial \ln P}$	Right side
(2.64)	$\sum_{j=1}^{NG} a_{1j}a_{1j}n_j$	$\sum_{j=1}^{NG} a_{1j}a_{2j}n_j$	$\cdots$	$\sum_{j=1}^{NG} a_{1j}a_{\ell j}n_j$	$\cdots$	$a_{1,NG+1}$	$\cdots$	a_{1NS}	$\sum_{j=1}^{NG} a_{1j}n_j$	$\sum_{j=1}^{NG} a_{1j}n_j$
	$\sum_{j=1}^{NG} a_{2j}a_{1j}n_j$	$\sum_{j=1}^{NG} a_{2j}a_{2j}n_j$	$\cdots$	$\sum_{j=1}^{NG} a_{2j}a_{\ell j}n_j$	$\cdots$	$a_{2,NG+1}$	$\cdots$	a_{2NS}	$\sum_{j=1}^{NG} a_{2j}n_j$	$\sum_{j=1}^{NG} a_{2j}n_j$
	$\cdots$	$\cdots$		$\cdots$		$\cdots$		$\cdots$	$\cdots$	$\cdots$
	$\sum_{j=1}^{NG} a_{\ell j}a_{1j}n_j$	$\sum_{j=1}^{NG} a_{\ell j}a_{2j}n_j$	$\cdots$	$\sum_{j=1}^{NG} a_{\ell j}a_{\ell j}n_j$	$\cdots$	$a_{\ell,NG+1}$	$\cdots$	$a_{\ell NS}$	$\sum_{j=1}^{NG} a_{\ell j}n_j$	$\sum_{j=1}^{NG} a_{\ell j}n_j$
(2.65)	$a_{1,NG+1}$	$a_{2,NG+1}$	$\cdots$	$a_{\ell,NG+1}$		0	$\cdots$	0	0	0
	$\cdots$	$\cdots$		$\cdots$		$\cdots$		$\cdots$	$\cdots$	$\cdots$
	a_{1NS}	a_{2NS}	$\cdots$	$a_{\ell NS}$		0	$\cdots$	0	0	0
(2.66)	$\sum_{j=1}^{NG} a_{1j}n_j$	$\sum_{j=1}^{NG} a_{2j}n_j$	$\cdots$	$\sum_{j=1}^{NG} a_{\ell j}n_j$		0	$\cdots$	0	0	$\sum_{j=1}^{NG} n_j$

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13. ABSTRACT *(Maximum 200 words)*

This report presents the latest in a number of versions of chemical equilibrium and applications programs developed at the NASA Lewis Research Center over more than 40 years. These programs have changed over the years to include additional features and improved calculation techniques and to take advantage of constantly improving computer capabilities. The minimization-of-free-energy approach to chemical equilibrium calculations has been used in all versions of the program since 1967. The two principal purposes of this report are presented in two parts. The first purpose, which is accomplished here in part I, is to present in detail a number of topics of general interest in complex equilibrium calculations. These topics include mathematical analyses and techniques for obtaining chemical equilibrium; formulas for obtaining thermodynamic and transport mixture properties and thermodynamic derivatives; criteria for inclusion of condensed phases; calculations at a triple point; inclusion of ionized species; and various applications, such as constant-pressure or constant-volume combustion, rocket performance based on either a finite- or infinite-chamber-area model, shock wave calculations, and Chapman-Jouguet detonations. The second purpose of this report, to facilitate the use of the computer code, is accomplished in part II, entitled "Users Manual and Program Description." Various aspects of the computer code are discussed, and a number of examples are given to illustrate its versatility.

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